

State of California
AIR RESOURCES BOARD

Staff Report: Initial Statement of Reasons
for Proposed Rulemaking

Public Hearing to Consider the Adoption of a Regulatory
Amendment Identifying Hexavalent Chromium as a
Toxic Air Contaminant

Agenda Item No.: 86-1-3
Scheduled for Consideration: January 23, 1986
Release Date: December 9, 1985

(This report has been reviewed by the staffs of the California Air Resources Board and the California Department of Health Services and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board or the Department of Health Services, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.)

OVERVIEW AND RECOMMENDATION

I. INTRODUCTION

The Air Resources Board ("ARB" or "Board") identified toxic air contaminants and develops regulations for the control of their emissions according to the requirements of state law. A toxic air contaminant (TAC) is an air pollutant that the Board or the Department of Food and Agriculture* finds "may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."** This report recommends that the Board find hexavalent chromium chromium(VI) to be a toxic air contaminant.

Section II of this Overview to the report presents the regulatory background and reviews the procedures by which the Board considers substances for the TAC designation. The Overview also summarizes the technical and toxicological information that supports the staff's recommendation. Section IIIA is a summary of Part A, which presents data on the uses of chromium, its emissions, and the public's exposure to chromium via the ambient air. Section IIIB summarizes the Department of Health Services' (DHS) analysis in Part B of the health effects of chromium. Section IV of this Overview discusses potential environmental effects of the recommended action, and Section V contains the staff's recommendation to the Board.

II. REGULATORY BACKGROUND AND PROCEDURES

Health and Safety Code (HSC) Section 39650 et seq. and Food and Agriculture Section 14021 et seq. set forth the procedure for identifying

* See Section II.

** Health and Safety Code Section 39655; all statutory references are to the Health and Safety Code, except as otherwise stated.

and controlling toxic air contaminants in California. (These provisions were enacted in September 1983 as Assembly Bill 1807; Stats 1983 ch 1047.) The Department of Food and Agriculture is responsible for identifying and controlling TACs in their pesticial uses. The ARB has authority over TACs in all their other uses.

HSC Section 39650 sets forth the Legislature's findings about substances which may be TACs. The Legislature has declared:

"That public health, safety, and welfare may be endangered by the emission into the ambient air of substances which are determined to be carcinogenic, teratogenic, mutagenic, or otherwise toxic or injurious to humans" (HSC Section 39650(a).)

The findings also include directives on the consideration of scientific evidence and the basis for regulatory action. With respect to the control of TACs, the Legislature has declared:

"That it is the public policy of this state that emissions of toxic air contaminants should be controlled to levels which prevent harm to the public health," (HSC Section 39650(b).)

The Legislature has further declared:

"That, while absolute and undisputed scientific evidence may not be available to determine the exact nature and extent of risk from toxic air contaminants, it is necessary to take action to protect public health," (HSC Section 39650(e).)

In the evaluation of substances, the Legislature has declared that the best available scientific evidence, gathered from both public agencies and private sources including industry, should be used. The Legislature has also determined that this information should be reviewed by a scientific review panel, created pursuant to HSC Section 39670, and by the public.

The Board's determination of whether or not a substance is a toxic air contaminant includes several steps specified in the HSC. First, we request the DHS to evaluate the health effects of a substance (HSC Section 39660). The evaluation includes a comprehensive review of all available scientific data. Upon receipt of a report on health effects from DHS and in consideration of their recommendations, we prepare and submit a report to the Scientific Review Panel (SRP) for its review (HSC Section 39661(a)). The report consists of the DHS report (Part B), material prepared by the ARB staff on the use, emissions and ambient concentrations of the substance (Part A), and public comments on the draft Report and responses (Part C). It serves as the basis for future regulatory action by the Board. The report is also made available to the public, which may submit comments on the report to the SRP (HSC Section 39661(b)).

After receiving the SRP's written findings on the report, the Board issues a public hearing notice and a proposed regulation which includes a proposed determination as to whether or not the substance is a toxic air contaminant (HSC Section 39662(a)). If, after a public hearing and other procedures to comply with Government Code Section 11340 et seq., the Board determines that a substance is a toxic air contaminant, its findings must be set forth in a regulation (Section 39662). The HSC also sets forth procedures for developing and adopting control measures for substances identified as TACs (Sections 39665-39667); such measures are not proposed during this proceeding.

III. EVALUATION OF CHROMIUM

Consistent with the provisions of state law, the ARB and the DHS prioritize candidate substances for evaluation and regulation as "toxic air contaminants" pursuant to HSC Section 39660(f). Briefly, the selection of a substance for the Board's evaluation and consideration as a toxic air contaminant is to be based on the risk to the public from exposure to the substance, amount or potential amount of emissions from use of the substance,

manner of usage in California, atmospheric persistence, and concentration in the ambient air. After consulting with the Department of Health Services (DHS), chromium and its compounds were among candidate substances selected for consideration as a TAC.

Chromium was chosen for evaluation because it was identified by the International Agency for Research on Cancer (IARC) as a human and animal carcinogen, because chromium was found to be emitted from many sources throughout the state (both directly from processes using chromium or chromium compounds, and as a product of the combustion of coal, oil, and other chromium-containing fuels), and because its presence in the atmosphere was documented.

A. EMISSIONS, PERSISTENCE IN THE ATMOSPHERE, AND AMBIENT CONCENTRATIONS OF CHROMIUM

Data in the revised Part A are summarized in Table I.

Industrial sources of chromium may emit chromium in the hexavalent state (chromium(VI)) or the trivalent state (chromium(III)), or a mixture of the two. Chrome plating and the use of hexavalent chromium as a corrosion inhibitor in cooling towers accounted for most of the known hexavalent chromium emissions in California. Refractory (firebrick) production is a source of trivalent chromium emissions.

Combustion of oil, coal, municipal waste, and sewage sludge is a source of chromium emissions. Because historical data for these source categories refer to total chromium, rather than to one form or the other, the oxidation state of chromium emitted from these sources is not known. Available information suggests that combustion-related emissions are trivalent chromium.

Total chromium has been measured in the air at sites in many populated areas of California. Estimates of population exposure to total and hexavalent chromium are summarized in Table 1. Limited preliminary data on ambient concentrations of hexavalent chromium indicate that hexavalent chromium comprised between 3 and 8 percent of ambient total chromium. Efforts are under way to validate the analytical method and to gather more data on ambient concentrations.

Evaluation of concentrations of chromium near sources of chromium(VI) suggest that significant population exposure may occur close to sources.

The atmospheric persistence of chromium(VI) is not known. It has been suggested that chromium(VI) reacts in the atmosphere with available organic matter; however, there is no information available on the atmospheric reactions of chromium(VI) or chromium(III). Chromium is removed from the atmosphere by physical deposition processes. Measurements have shown that most chromium deposition occurs through wet deposition.

The draft of Part A was released for public review and comment. Comments and our responses are presented in Part C.

B. HEALTH EFFECTS AND RISK ASSESSMENT

Pursuant to Health and Safety Code Section 39660, we requested that the Department of Health Services conduct a health effects evaluation of chromium. The DHS evaluation was conducted in accordance with the provisions of that section, which requires that the DHS consider all available scientific data, including, but not limited to, relevant data provided by the ARB, the Department of Industrial Relations, international and federal health agencies, private industry, academic researchers, and public health and environmental

TABLE I
SUMMARY OF DATA IN PART A

Emissions

	<u>Inventory Year</u>	<u>Chromium Measured</u>	<u>Estimated Statewide Emissions, tons</u>
Stationary Sources			
Chrome plating	1983	Hexavalent	0.77-16.
Cooling towers	1979/81	Hexavalent	0.23-9.2
Oil combuston	1983	Total	13.2-28.1
Coal combustion	1981	Total	0.02
Cement production	1981	Total	0.9
Waste incineration	1981	Total	0.02-0.16
Refractory Production	1984	Hexavalent	< 0.01

Fate in the atmopshere: The half-life and reactions of chromium(VI) are unknown; chromium particulate is removed from the atmosphere through physical processes, mainly by wet deposition.

Ambient Concentrations

<u>Location (year)</u>	<u>Form</u>	<u>Concentration nanogram/cubic meter (ng/m³)</u>
San Francisco Bay Area Air Basin (partial)(1977)	Total chromium, annual average	10.8
South Coast Air Basin (1977)	Total chromium, annual average	16.9
Fresno Area (1977)	Total chromium, annual average	12.3
San Diego Area (1977)	Total chromium, annual average	11.7
San Jose Area (1977)	Total chromium, annual average	14.3
El Monte (1985) ¹	Total chromium (average of four samples)	13.2
El Monte (1985) ¹	Hexavalent chromium (average of four samples)	0.5

¹Samples taken during the last week of August, 1985.

organizations. To facilitate the identification of all available data, we sent, prior to formally requesting the DHS evaluation, a letter to potential sources of chromium compounds in California and other interested members of the public requesting that they submit any information they considered pertinent to the DHS evaluation. We also conducted a reference search on the health effects of chromium and its compounds using the MEDLARS II and DIALOG Information Services and included a bibliography from that search in our request for information. The data compiled in the search were also provided to the DHS.

The DHS' draft report (Part B) was released to the public for comment. The comments received and responses are included in Part C. A revised Part B is presented to the Scientific Review Panel for review.

In meeting the requirements of Section 39666 for DHS' evaluation, the DHS addresses these issues in Part B: 1) Is chromium or its compounds, or both, a human and/or animal carcinogen? 2) Does chromium have a carcinogenic threshold? 3) Are health effects other than cancer expected to occur at current ambient levels?, and 4) What is the range of added lifetime cancer risk for populations continuously exposed to the ambient concentrations of chromium measured in California? In response to these issues, the DHS concludes that: 1) hexavalent chromium is a human and animal carcinogen and insufficient information exists to decide whether chromium(III) is a potential human carcinogen; 2) hexavalent chromium should be treated as a substance without a carcinogenic threshold; 3) health effects other than cancer are not expected to occur at current ambient levels with the possible exception of adverse reproductive effects, where experimental data are inadequate to assess potential human reproductive risks; and, 4) the theoretical added

lifetime cancer risk from a continuous 70-year exposure to atmospheric hexavalent chromium (chromiumVI) exposure ranges from 12 to 146 cases per million people per nanogram per cubic meter (ng/m^3).

The DHS has found in its report that: 1) many epidemiologic studies show a strong high association between hexavalent chromium exposure in the work place and respiratory cancer; and 2) all short-term assays reported show that hexavalent chromium compounds possess genotoxic capabilities, while tests of chromium(III) compounds are generally negative or generate positive results at much higher doses than those used in chromium(VI) tests. The DHS agrees with the findings of IARC that there is sufficient evidence to demonstrate the carcinogenicity of chromium in both animals and humans. The DHS believes there are inadequate data available at this time to confirm or refute the carcinogenic potential of trivalent chromium.

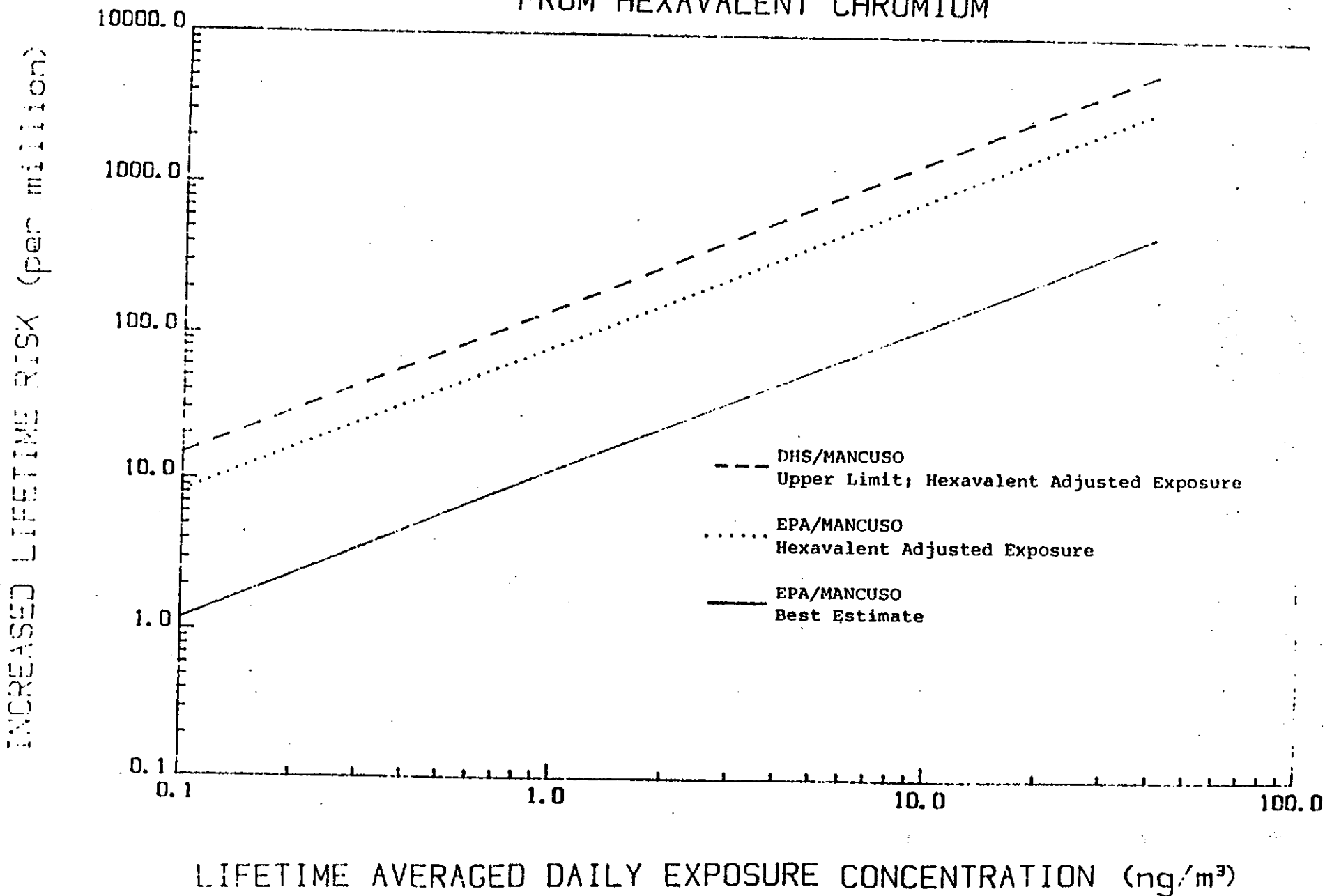
To determine that a substance has a carcinogenic threshold, the DHS requires strong positive evidence that the substance acts only through mechanisms which ought to have a threshold. The DHS found that no positive evidence exists for this position with respect to chromium.

The staff of DHS recommends adopting the risk assessment performed by the Environmental Protection Agency (EPA), in which a linear nonthreshold model was applied to the epidemiologic study (Mancuso, 1975) judged to be most methodologically sound and to contain the best exposure data to derive dose-response curves for hexavalent chromium. Data from animal studies were judged to be inadequate for quantitative risk assessment by the staff of DHS.

Making certain assumptions, the DHS described dose-response curves for hexavalent chromium. Based on the results derived from application of the

Figure A

CANCER RISK FROM HEXAVALENT CHROMIUM



linear nonthreshold model and the Mancuso data, the staff of DHS recommends that the Air Resources Board consider the increased lifetime carcinogenic risk from a continuous lifetime exposure to hexavalent chromium as falling in the range of 12 to 146 cancer cases per nanogram hexavalent chromium per cubic meter of air per million people exposed (12-146 cancers/ng/m³/million). This range is illustrated in Figure A, where the solid line represents the curve based on the EPA assessment using total chromium as the exposure, the dotted line is based on the EPA assessment adjusting for the hexavalent chromium fraction of the exposure, and the dashed line was generated by taking the upper limit of the 95% confidence interval for carcinogenic risk due to chromium and adjusting for the hexavalent fraction of the workplace exposure. There are not, however, sufficient data from this or other epidemiologic studies to estimate the risk of specific hexavalent compounds for airborne exposures.

There is very limited information on levels of ambient hexavalent chromium in California. Preliminary data on ambient concentrations of hexavalent and total chromium at a site in the South Coast Air Basin during August 1985 indicate that 3 to 8 percent of total ambient chromium is in the hexavalent state. Although it is not known whether this ratio is representative of other sites, it is the best information available at this time.

There is a need to better characterize the concentration of chromium(VI) in the ambient air of California; we are working with the air pollution control districts and air quality management districts to gather such data. We are also carrying out emission testing of chromium sources to determine the oxidation state and magnitude of chromium emissions. Such information will be an important part of any control effort for hexavalent chromium.

III. ENVIRONMENTAL IMPACTS

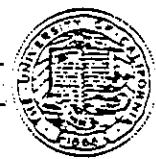
The identification of hexavalent chromium as a toxic air contaminant is not in itself expected to result in any environmental effects. The identification of hexavalent chromium as a toxic air contaminant by the Board may require that the Board and air pollution control districts adopt toxic control measures in accordance with the provisions of state law. Any such toxic control measures may result in reduced emissions of hexavalent chromium to the atmosphere, resulting in reduced ambient concentrations, concurrently reducing the health risk due to hexavalent chromium. Therefore, the identification of hexavalent chromium as a toxic air contaminant may ultimately result in environmental benefits. Environmental impacts identified with respect to specific control measures will be included in the consideration of such control measures pursuant to Health and Safety Code Sections 39665 and 39666.

IV. RECOMMENDATION

Because hexavalent chromium is a known human and animal carcinogen, and is known to be emitted in California, the ARB staff recommends the listing of hexavalent chromium as a toxic air contaminant. In making this recommendation, we note that there is not sufficient available scientific evidence to support the identification of an exposure level below which carcinogenic effects would not occur.

NOV 25 1985

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DAVID PIERPONT GARDNER
President of the University

UNIVERSITY HOUSE
DAVIS, CALIFORNIA 95616

EMIL M. MRAK
Chancellor Emeritus

November 21, 1985

Mr. James D. Boyd, Executive Officer
State Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Dear Mr. Boyd:

The Scientific Review Panel on Toxic Air Contaminants has reviewed the Report to the Scientific Review Panel on Chromium, and has formulated its findings regarding the report. With this letter, I am formally submitting the Scientific Review Panel's written findings to the Air Resources Board.

Kindest personal regards,

Emil M. Mrak

Enclosure

cc: Scientific Review Panel
Dr. John Holmes
Mr. Richard Bode

Findings of the Scientific Review Panel

Regarding the Report on Chromium

In accordance with the provisions of the Health and Safety Code Section 39661, the Scientific Review Panel (SRP) has reviewed the September 1985 Report to the Scientific Review Panel on Chromium, and has reviewed the public comments received regarding this report. The SRP finds the Report on Chromium to be adequate and sufficient.

Specifically, the SRP finds each of the following propositions to be prudent interpretations of the available evidence:

1. In epidemiologic studies, where the oxidation state of chromium was unknown (either in the hexavalent [Cr(VI)] or trivalent [Cr(III)] state, chromium was shown to be a human carcinogen.
2. In other studies conducted in laboratory animals, chromium in the hexavalent state [Cr(VI)] was shown to be carcinogenic. Accordingly, the SRP finds that hexavalent chromium [Cr(VI)] should be considered a potential carcinogen in humans.
3. An exposure level below which no significant adverse health effects are anticipated could not be identified. Based on our knowledge of the pharmacokinetics, metabolism, and mode of action of chemical carcinogens like chromium, there is no scientific basis for determining an exposure level below which carcinogenic effects would not have some probability of occurring.
4. Adverse health effects other than cancer are not anticipated at current ambient chromium exposure levels.

For these reasons, we agree that hexavalent chromium [Cr(VI)] should be listed by the Air Resources Board as a toxic air contaminant, but we are unable to recommend an exposure level below which carcinogenic effects would not have some probability of occurring.

COMMENTS

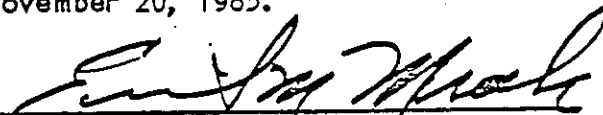
Using extrapolation procedures recommended by the EPA and Interagency advisory groups, DHS has estimated that the added lifetime cancer risk from a 70-year exposure to 1 nanogram per cubic meter (ng/m^3) of atmospheric hexavalent chromium ranges from .12 to 146 cases per million people exposed. The SRP concurs with DHS's evaluation, but wishes to clarify several points:

1. The range of risk presented (12 to 146 cases) was derived using conservative estimation procedures.
2. Chromium may exist in several chemical states, predominately at the trivalent [Cr(III)] and hexavalent [Cr(VI)] states. The health effects impact of these states are not equal. Hexavalent chromium [Cr(VI)] has been shown in animal tests to be carcinogenic. On the other hand, there are inadequate data to indicate any association between trivalent chromium [Cr(III)] exposure and cancer induction in animal tests. However, trivalent chromium [Cr(III)] is an essen-

tial element. Chromium, as a mixture of oxidation states, has been shown to be a human carcinogen.

3. Whereas there is uncertainty associated with the absolute value of the risk estimated, the range of 12 to 146 cases is useful in comparing risk from exposure to chromium to other environmental carcinogens in ambient air.

I certify that the above is a true and correct copy of the findings adopted by the Scientific Review Panel on November 20, 1985.



Dr. Emil M. Mrak, Chairman
Scientific Review Panel

11/21/85

Date

STATE OF CALIFORNIA
AIR RESOURCES BOARD

TECHNICAL SUPPORT DOCUMENT

PUBLIC HEARING TO CONSIDER THE ADOPTION OF A REGULATORY
AMENDMENT IDENTIFYING HEXAVALENT CHROMIUM AS A
TOXIC AIR CONTAMINANT

Agenda Item No.: 86-
Scheduled for consideration: January 24, 1986
Release Date: December 9, 1985

TABLE OF CONTENTS

- Part A A Review of Chromium Uses, Emissions, and Public Exposure
- Part B Health Effects of Chromium
- Part C Public Comments and Responses

PART A - A REVIEW OF CHROMIUM USES,
EMISSIONS, AND PUBLIC EXPOSURE

Prepared by the Staff of the Air Resources Board

November 1985

(This report has been reviewed by the staffs of the California Air Resources Board and the California Department of Health Services and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board or the Department of Health Services, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.)

Part A - A Review of Chromium Uses,
Emissions, and Public Exposure

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES AND FIGURES	
I. <u>CHROMIUM USAGE AND EMISSIONS</u>	
A. PRODUCTION AND USAGE	I-1
B. CURRENT AND PROJECTED STATIONARY AND MOBILE SOURCE EMISSIONS	I-3
C. NATURAL OCCURRENCE	I-7
II. <u>PERSISTENCE IN THE ATMOSPHERE</u>	
A. PHYSICAL AND CHEMICAL PROPERTIES	II-1
B. FORMATION AND FATE IN THE ATMOSPHERE	II-3
III. <u>AMBIENT CONCENTRATIONS IN THE COMMUNITY</u>	
A. AMBIENT AIR DATA	III-1
B. ESTIMATE OF AMBIENT CHROMIUM EXPOSURE	III-8
C. CONCENTRATIONS CLOSE TO SOURCES	III-31
D. EXPOSURE BY ROUTES OTHER THAN AMBIENT AIR	III-39
APPENDIX A - INFORMATION REQUEST LETTER WITH ATTACHMENTS AND RESPONSES	
APPENDIX B - HEALTH EFFECTS REQUEST TO DHS AND LETTER OF RESPONSE	
APPENDIX C - DISCUSSION OF EMISSION ESTIMATES	
APPENDIX D - ARB ANALYTICAL METHODS FOR SAMPLING AND ANALYSIS OF ATMOSPHERIC TOTAL CHROMIUM AND ATMOSPHERIC HEXAVALENT CHROMIUM	

LIST OF TABLES AND FIGURES

TABLES

- I-1 Estimated Chromium Emissions in California
- II-2 Physical Properties of Chromium
- III-1 Peak-to-Mean Ratios for Chromium - 1977-1981
- III-2 Summary of Average Chromium Concentrations from ARB Dichotomous Samplers
- III-3 Peak-to-Mean Ratios for Total (Fine + Coarse) Dichotomous Chromium
- III-4 Peak-to-Mean Ratios for Coarse Fraction Dichotomous Chromium
- III-5 Peak to Mean Ratios for Fine Fraction Dichotomous Chromium
- III-6 Summary of Location Characteristics and Dominating Influences Surrounding Sampling Sites Used in Exposure Analysis
- III-7 Summary of 1977 Chromium Data from the EPA National Aerometric Data Bank
- III-8 Annual Chromium Exposure for Specific Urban Census Tracts
- III-9 Comparison of Population exposures to Chromium During 1977 using Three Approaches
- III-10 Summary of ARB Chromium Data Sampled January through June 1985
- III-11 Comparison of 1977 EPA Chromium Data with 1985 ARB Chromium Data
- III-12 Population Exposure to Chromium from a Plating Facility
- III-13 Population Exposure to Chromium from a Bank of Industrial Cooling Towers
- III-14 Intake of Chromium by Exposure Routes Other Than Ambient Air

LIST OF FIGURES

- III-1 Location of Modeling Areas and Stations Used to Interpolate Chromium in the South Coast Air Basin
- III-2 SoCAB 1977 Total Chromium in 5 km cells
- III-3 SoCAB 1980 Population Density for 5 km cells
- III-4 1977 Chromium Exposure for SoCAB Annual Average Concentrations
- III-5 1977 Chromium Exposure for SoCAB Annual Average Concentrations
- III-6 Location of Modeling Areas and Stations Used to Interpolate Chromium in the San Francisco Bay Area
- III-7 San Francisco Bay Area 1977 Total Chromium in 5 km Cells
- III-8 San Francisco Bay Area 1980 Population Density in 5 km Cells
- III-9 1977 Chromium Exposure for San Francisco Bay Area Annual Average Concentrations
- III-10 1977 Chromium Exposure for San Francisco Bay Area Annual Average Concentrations
- III-11 Population Exposure to Chromium from a Chromium Plating Facility
- III-12 Cumulative Population Exposure to Chromium from a Chromium Plating Facility
- III-13 Population Exposure to Chromium from a Bank of Industrial Cooling Towers
- III-14 Cumulative Population Exposure to Chromium from a Bank of Industrial Cooling Towers

I. USAGE AND EMISSIONS

A. PRODUCTION AND USAGE

Chromium occurs in nature primarily as chromite (chrome iron ore). This mineral is best represented as $(\text{Fe},\text{Mg})\text{O}(\text{Cr},\text{Fe},\text{Al})_2\text{O}_3$.^{1/} Chromite ore is not mined commercially in the United States; countries in Africa and Europe are the main sources of United States imports^{2/}. The ore is used to produce chromium metal and alloys, refractory materials, and chromium chemicals.

The metallurgical industry used 49 percent of the chromite ore consumed in the United States in 1982, mostly in the production of stainless steels.^{2/}

There are no primary steel production facilities currently operating in California. However, there are a number of melting and recasting facilities; hence, chromium use in the California steel industry would be limited to that present in scrap metal or feedstock.

Production of refractory brick accounted nationally in 1982 for 15 percent of the chromite ore consumption.^{2/} Kaiser Refractories is the major facility in California manufacturing chromium containing refractory products.^{3/} Production furnaces in the cement, glass, and nonferrous metal industries use chromium-containing refractory materials.

The chemical industry used 36 percent of the chromite ore consumed in the United States in 1982 in the manufacture of various chromium chemicals.^{2/} These chemicals find diverse use in metal finishing and plating, in leather tanning, in wood preserving and textile finishing, and as corrosion inhibitors in water treatment.

There are no plants in California which produce chromic acid, sodium chromate, or sodium dichromate chemicals, which are used to make a wide range

of other chromium chemicals. These or other chromium chemicals are used in the State in metal finishing and plating, in the manufacture of certain green container glass, and in formulation of corrosion inhibitors for water treatment. Nationwide use of sodium dichromate in 1982 was 150,000 tons, of which 42,000 tons (28%) was used to produce chromic acid^{4/} for metal plating. The largest supplier of chromic acid in the United States estimated that 1,500 tons of chromic acid were sold in California in 1984 for chrome plating usage.^{18/} It has been estimated that there are 9,750 chromium plating shops in the United States.^{5/} It has been estimated that between 1,500 and 1,800 electroplaters operate in California.^{6/} An ARB survey of chrome platers in Northern California which are known to discharge to publicly-owned treatment works accounted for 150 facilities. There are 168 chrome platers listed in the South Coast Air Quality Management District inventory of potentially toxic compound emissions.^{7/} Based on this information, it is estimated that about 400 chrome platers operate in California.

Chromium pigments are used in inks, plastics, industrial coatings, some truck original equipment manufacture finishes, and traffic paints. One industry estimate of chromium pigment usage in California in 1983 was 2,500 tons.^{8/} Calculation of California chromium pigment consumption as a fraction of the 1982 national total^{9/} yields an estimate of 3,600 tons. Formulators of chromium paint pigments have been identified in Southern California. In the 1983 South Coast AQMD emission inventory of potentially toxic/hazardous air contaminants^{7/}, approximately 90 tons of chromium pigments were reported used in the formulation of paints and coatings in the South Coast air basin.

There are six container glass manufacturers in California that use chromium compounds as colorants to produce green glass. Trivalent chromium (as iron chromite) or hexavalent chromium (as sodium or potassium dichromate) may be used as colorants in green glass formulations.^{10/}

Also, chromium(VI) compounds are used in cooling towers as corrosion inhibitors by some industrial and commercial facilities.

Five facilities listed in the ARB's emissions data system (EDS) use chromium in wood preservation or fire retardant formulations, and sixteen other wood products facilities appear in the EDS which may also be users of chromium compounds.^{11/}

B. CURRENT AND PROJECTED STATIONARY AND MOBILE SOURCE EMISSIONS

Chromium emissions in California were estimated using data from local air pollution control districts, the Air Resources Board (ARB), the Environmental Protection Agency (EPA), and industry.

Stationary sources contribute most of the known chromium emissions which occur in California. Chromium is emitted both directly in the use and production of chromium compounds, and secondarily (or inadvertently) through the combustion of chromium-containing fuels, or as a result of other processes.

Direct sources of hexavalent chromium emissions in California include chromium plating facilities, cooling towers using hexavalent chromium-containing water treatments, and green glass plants which use chromium(VI) colorants. Steel recasting and melting facilities, and refractory (fire-brick) plants are direct sources of chromium(III). Secondary sources of chromium emissions include combustion of coal and oil, cement production,

sewage sludge and other waste incineration, and wear from furnaces with chromite refractory; available evidence suggests that chromium emitted from secondary sources is principally in the trivalent state.

Motor vehicles may contribute to chromium emissions in California. Limited information available on trace metal emissions from diesel-fueled passenger cars indicates that these cars may be a source of chromium.^{12,13/}

Table I-1 summarizes estimates of chromium emissions in California. Some emission sources of chromium are not listed, because insufficient data are available at this time to make emission estimates.

Table I-1
Estimated Chromium Emissions in California

Source	Chromium Measured	Source Type	Emissions (tons/year)	Inventory Year	Refs.
Chromium plating	Hexavalent	Point	0.77-16	1983	7,17
Cooling towers	Hexavalent	Point	0.23-9.2	1979, 1981	5,35
Oil combustion	Total	Point			
Residual oil			5.1-20	1983	22,39
Distillate oil			7.2	1983	22,39
Waste Oil			0.91	1983	23,24,25
Refractory Production	Hexavalent	Point	< 0.01	1984	36
Cement Production	Total	Point	0.9	1981	26,27
Coal combustion	Total	Point	0.02	1981	26,37
Waste Incineration	Total	Point	0.02-0.16	1981	28,29,30, 31,32

Stationary Source Total 15-54

1. Stationary Emission Sources

Chrome plating is one of the largest known sources of chromium(VI) emissions in the State. Both hard chrome (used to provide a durable coating), and decorative chrome electroplating operations are conducted in baths containing chromic acid. During the plating process, bubbles of gas are emitted through the surface of the bath; these bubbles carry entrained chromium(VI) into the air, which is usually vented to the atmosphere. Estimated emission factors from these uncontrolled operations range from 1.5×10^{-4} to 6.2×10^{-2} pounds per hour per square foot of bath surface.^{14,15,16/} Higher estimates, of up to 6.5 pounds per hour per square foot, have been obtained for large bath hard chrome operations.^{16/} A recent well documented report on plating operations at the Long Beach Naval Shipyard^{17/} yielded an emission factor of 6.4×10^{-4} pounds per hour per square foot of bath surface for uncontrolled hard chrome plating. Although there is considerable evidence for variability, two studies^{16,17/} indicate that the emission factor for decorative chrome plating is about 40 percent as much as for hard chrome plating.

Surveys have indicated that approximately 400 chrome platers operate in California. Roughly three-fourths of national chromic acid use for chrome plating is for hard chrome, while one-fourth is for decorative^{18/}, based on one industry estimate. California usage patterns are similar, according to an industry association estimate.

This information, in conjunction with the emission factor derived from the Long Beach Naval Shipyard report, and certain assumptions (see Appendix C) yields a emissions estimate of 0.77-15.6 tons of chromium(VI) per year for

chrome plating in California. This estimate reflects the fact that both hard and decorative chrome plating are done in California. The lower value represents a theoretical minimum emission estimate, based on technically achievable control (92% removal efficiency by wet scrubber) of emissions from all platers statewide. The higher value assumes that no emissions controls are used.

Although there are no air pollution control regulations which pertain specifically to chromium(VI) emissions from chrome plating operations, emission controls have been required on some chrome plating operations. These controls are usually required on the basis of nuisance law, to control chromic acid mist emissions causing property damages or nuisance. The extent to which emission controls are required, and the efficiency of any such controls, are not well known.

Insufficient evidence is available to determine whether green container glass manufacture is a source of chromium(VI) emissions. Iron chromite, or sodium dichromate, or both, have been used as colorants in green glass manufacture.^{10/} ARB tests indicate that a large green container glass manufacturer which used chromium(VI) colorants emitted 2.5 tons a year of chromium, mostly in the hexavalent form^{19/}; a recent change in the type of chromium colorant [to chromium(III)] used by this manufacturer may result in reduced hexavalent chromium emissions. Another test of this source has been conducted to measure chromium(VI) emissions subsequent to the change in formulation; results are not available at this time. Five other green glass manufacturing facilities, generally with smaller production commitments to produce green container glass, are located in California. Industry sources

indicate that only chromium(III) colorants are presently used in the California green-container glass industry.

Although an EPA-sponsored study reported chromium emissions (0.22 percent of particle emissions) from clear soda-lime glass melting furnaces to which no chromium colorants were added, a recent ARB test of a flint container glass manufacturer showed much lower (0.001 percent of particle emissions) chromium(VI) emissions. These emissions may be due to chromium loss from the chromium-containing firebrick lining of the glass furnace.^{20,21/} Additional tests are planned to measure chromium(VI) emissions from clear glass plants. Until additional data are available on chromium(VI) emissions from green-glass manufacturers which use chromium(III) colorants, and from clear glass manufacturers, it is not possible to develop a representative emission estimate for these source categories.

Oil combustion is estimated to be responsible for 13.2-28.1 tons per year of chromium emissions. Chromium occurs naturally as a trace component of most oils, and the concentrations of chromium found in residual and distillate oils have been measured.^{22,23/} Also, chromium is found in waste oil as a contaminant.^{25/} When these oils are burned, chromium is emitted. Available information suggests that the chromium is emitted in the trivalent state.

Emissions of chromium from refractory production have been shown to be in the trivalent state.^{36/} An estimate of maximum chromium(VI) emissions from this source type is based on the detection limit for chromium(VI) for the test method used; no chromium(VI) was detected in the source test on which the estimate was based.

Chromium emissions from cement production have been estimated based on the chromium content of emitted particulate matter. The chromium content in emitted particulate matter has been estimated at 0.03 percent (weight).^{26/} Emissions of chromium from the combustion of chromium-containing fuels in cement production have been included in statewide fuel combustion estimates. There are 13 cement plants in California with a total of 43 kilns. The statewide annual production of clinker was about 8 million pounds in 1980.^{27/}

Sewage sludge and municipal waste incinerators are known sources of chromium emissions.^{30,31/} Chromium present in the sludge or refuse is emitted when the fuel is burned. There are 11 facilities in California listed in the ARB's emission data system (EDS) which incinerate sewage sludge or municipal waste.^{32/} Emissions of chromium from these sources are estimated to total 0.02 to 0.16 ton per year.

C. NATURAL OCCURRENCE

Chromium(III) is a component of most soils. In areas of serpentine and peridotite rocks, chromite (chrome ore) is the predominant chromium mineral. Deposits of 5-10 percent chromite have been found in beach sands and stream placers in several California counties.^{33/} Also, chromium has been found in non-serpentine areas in the state at concentrations ranging from a trace to 500 ppm.^{34/}

Soil chromium is generally in an insoluble, biologically unavailable form, mainly as the weathered form of the parent chromite or as the chromium (III) oxide hydrate. Weathering and wind action can transport soil chromium to the atmosphere; generally, such mechanical weathering processes generate

particles greater than 10 um diameter, which have significant settling velocities. The extent to which natural sources of chromium contribute to measured ambient chromium levels in California is not known. Ambient chromium derived from soil is expected to exist as chromium(III).^{38/}

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II. PERSISTENCE IN THE ATMOSPHERE

A. PHYSICAL AND CHEMICAL PROPERTIES

Chromium (Cr) is a hard, colorless, and lustrous metal, with a melting point above 1800°C. It is extremely resistant to corrosive agents. Selected physical properties are presented in Table II-1. Chromium metal is not found in nature, but is produced principally from the mineral chromite. Chromite contains chromium in the +3 oxidation state, or Cr(III). Chromium combines with various other elements to give compounds, the most common of which contain either Cr(III), which is trivalent chromium (the +3 oxidation state) or Cr(VI), which is hexavalent chromium (the +6 oxidation state).^{1/}

Thousands of Cr(III) compounds exist, exhibiting a wide range of colors, structures, and chemical properties.^{2/} Cr(VI) compounds are produced industrially by heating Cr(III) compounds in the presence of mineral bases (such as soda ash) and atmospheric oxygen. Most Cr(VI) compounds contain oxygen, and are highly soluble in water. Cr(VI) solutions are powerful oxidizing agents under acidic conditions, but much less oxidizing under basic conditions. Depending on the concentration and acidity, Cr(VI) can exist as either chromate ion ($\text{CrO}_4^{=}$), or as dichromate ion ($\text{Cr}_2\text{O}_7^{=}$). Because dilute chromate solutions passivate metal surfaces, they are widely used to inhibit corrosion in recirculating water systems such as cooling towers.

Table II-1
Physical Properties of Chromium^{1/}

Property	Value
atomic weight	51.996
isotopes, %	
50	4.31
52	83.76
53	9.55
54	2.38
crystal structure	body centered cube
density at 20°C, g/cm ³	7.19
melting point, °C	1875
boiling point, °C	2680
vapor pressure, 130 Pa ^{a/} , °C	1610
heat of fusion, kJ/mol ^{b/}	13.4-14.6
latent heat of vaporization at bp kJ/mol ^{b/}	320.6
specific heat at 25°C, kJ/(mol-K) ^{b/}	23.9 (0.46 kJ/kg-K)
linear coefficient of thermal expansion at 20°C	6.2 x 10 ⁻⁶
thermal conductivity at 20°C, W/(m-K)	91
electrical resistivity at 20°C, microhm-m	0.129
specific magnetic susceptibility at 20°C	3.6 x 10 ⁻⁶
total emissivity at 100°C nonoxidizing atm	0.08
reflectivity, R	
lambda, nm	300 500 1000 4000
%	67 70 63 88
refractive index	
alpha	1.64-3.28
lambda	2,570-6,080
standard electrode potential, valence 0 to 3+, V	0.71
ionization potential, V	
1st	6.74
2nd	16.6
half-life of ⁵¹ Cr isotope, days	27.8
thermal neutron scattering cross section, m ²	6.1 x 10 ⁻²⁸
elastic modulus, GPa ^{c/}	250
compressibility ^{a,d/} at 10-60 TPa	70 x 10 ⁻³

- ^{a/} To convert Pa to mm Hg, multiply by 0.0075.
^{b/} To convert J to cal, divide by 4.184.
^{c/} To convert GPa to psi, multiply by 145,000.
^{d/} 99% Cr; to convert TPa to megabars, multiply by 10.

B. FORMATION AND FATE IN THE ATMOSPHERE

There is very little information available on the reactivity of chromium compounds in the atmosphere.

Atmospheric reactions of chromium compounds have not been characterized. The persistence of chromium(VI) in the atmosphere has not been determined. It has been postulated that chromium metal and chromium (III) would be stable in the atmosphere, based on their low reactivity.^{3/} The assertion has been made that chromium(VI) would eventually react with dust or other pollutants to form chromium (III).^{4/} The rate at which chromium (VI) reacts in the atmosphere may depend on the presence and nature of oxidizable species, relative humidity, or the pH of atmospheric water, or a combination of these factors.

Physical removal of chromium from the atmosphere occurs both by atmospheric fallout (dry deposition) and by washout and rainout (wet deposition). Measurements have shown that most chromium deposition occurs through wet deposition.^{3/} Chromium particles of less than 5 um (aerodynamic equivalent) diameter may remain airborne for extended periods of time, allowing long distance transport by wind currents.^{5,6/} Because of this, meteorological conditions can play a significant role in the dispersion of chromium emitted from some sources.

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III. AMBIENT CONCENTRATIONS IN THE COMMUNITY

A. AMBIENT AIR DATA

Chromium databases compiled by both the Environmental Protection Agency (EPA) and the California Air Resources Board (ARB) were used in this analysis. The EPA data are included in the National Aerometric Data Bank and contain total chromium concentrations sampled from 1960 through 1968 and from 1977 through 1981 throughout California by various public agencies (federal, state, and local). All data were collected using high-volume samplers and were subsequently analyzed for chromium. The accuracy of data contained in the EPA database is not documented.

However, certain procedures have been undertaken to ensure reliable data. Although the chromium data were originally sampled and analyzed by a number of different agencies, the agencies presumably applied acceptable quality assurance practices during the collection and analysis phases. Additionally, after the data were received by EPA, edit and validation checks were used to further screen the data before they were included in the NADB. The purpose of the checks is to assure the accuracy and completeness of data contained in the NADB system (EPA, 1976).

Although data are available for 1960 through 1981, data from only the five most recent years (1977-1981) were used in our analysis. These data as reported in the NADB comprise total chromium concentrations greater than zero as well as values equal to zero, for a single analysis method. It should be noted that a concentration reported as zero does not necessarily indicate the absence of chromium but rather that the chromium concentration sampled was

below the limit of the analytical techniques. For the work presented in this section, zero values were replaced with a concentration equal to one-half the lowest non-zero concentration measured during the particular year of concern.

In addition to total chromium data, the EPA NADB database contains corresponding measurements of total suspended particulate matter. The Statistical Analysis System (SAS) software package was used to determine what, if any, relationship exists between chromium and total suspended particulate matter (TSP) (SAS, 1982). This analysis was used to determine whether total chromium concentrations could be predicted using TSP concentrations. Data collected at twenty sites from January 1977 through December 1981 were analyzed. No site had complete data for the entire period.

The ratio of mean chromium to mean TSP, the corresponding standard deviation, the coefficient of variation (SD/Mean), and the correlation coefficient between chromium and TSP were evaluated for each site included in the analysis. The results show a wide range of individual mean ratios, and large standard deviations around the mean ratios. No spatial or temporal patterns were apparent in the results. Correlation coefficients between chromium and TSP are relatively low (less than 0.64), indicating no significant relationship between the two variables. Based on these results, no usable relationship was found.

In addition to the statistics already discussed, peak-to-mean ratios for total chromium were also calculated to give general insights as to the nature of chromium emissions. These results are given in Table III-1. A small peak-to-mean ratio (less than 4.0) indicates relatively constant chromium concentrations and therefore, a relatively constant and homogeneous source

TABLE III-1
 PEAK-TO-MEAN RATIOS FOR CHROMIUM -- 1977-1981
 (units are ng/m³)

<u>Site Name</u>	<u>EPA Site Number</u>	<u>Peak Chromium</u>	<u>Mean Chromium</u>	<u>Peak: Mean Ratio</u>	<u>n</u>
Anaheim-Harbor	0230001	28.3	7.1	3.99	106
Bakersfield	0520003	22.5	9.4	2.39	28
Berkeley-Berkeley Wy	0740001	72.9	7.5	9.72	61
Burbank-W. Palm	0900002	23.6	10.5	2.25	30
Fresno-S. Cedar	2800002	32.4	9.5	3.41	58
Long Beach-Pine	4100001	41.0	17.9	2.29	27
Los Angeles-S. San Pedro	4180001	66.6	15.5	4.30	93
Los Angeles-Downtown	4180103	35.2	17.3	2.03	25
Oakland-Fifth St	5300001	60.3	19.0	3.17	29
Ontario-Airport	5380001	50.5	15.6	3.24	137
Oxnard	5560001	15.0	6.0	2.50	26
Pasadena	5760002	32.8	13.5	2.43	29
San Bernardino-W. 3rd	6680001	280.8	23.6	11.90	99
San Diego-Island	6800004	40.8	9.1	4.48	94
San Francisco-Grove	6860001	14.8	5.8	2.55	30
San Francisco	6860004	21.8	9.3	2.34	23
San Jose-N. 4th	6980004	36.3	12.2	2.98	99
Santa Ana-Ross	7180001	24.4	9.1	2.68	64
Torrance-Carson	8260001	315.3	30.5	10.34	29

area. A large peak-to-mean ratio (greater than or equal to 4.0) is indicative of variable chromium concentrations and either intermittent or heterogeneous emission sources.

Peak-to-mean ratios calculated for EPA data are generally low. Ratios less than 4.0 were calculated for fifteen of the twenty sites; conversely, ratios equal to or greater than 4.0 were calculated for one-fourth of the sites. The sites with the highest peak-to-mean ratios, San Bernardino-West 3rd and Torrance-Carson, also showed the highest peak concentrations and the highest mean concentrations. Results of the peak-to-mean analysis suggest that while chromium concentrations surrounding the majority of sites analyzed reflect homogeneous source areas, twenty-five percent of the sites analyzed are impacted by spatially non-uniform or intermittent sources.

The second chromium database, the ARB database, was collected from December 1982 through June 1984 using dichotomous (di-chot) samplers. The dichot samplers collect only those particles which are less than or equal to ten microns aerodynamic diameter. Particles are further subdivided into a coarse (2.5 microns to 10.0 microns diameter) and a fine (less than 2.5 microns diameter) fraction. All di-chot data used in this analysis reflect use of a percentage factor to correct for error in the sampling apparatus. Because of the nature of the dichotomous sampling apparatus, most of the fine fraction particles (approximately ninety percent) are captured in the fine fraction; however, a small percentage (approximately ten percent), are deposited in the coarse fraction. Consequently, fine and coarse fraction concentrations must be adjusted to reflect this sampling error. The accuracy of the di-chot data is approximately +50 percent.

Chromium data from the di-chot samplers (PM_{10} chromium) are summarized in Table III-2. Averages of total chromium range from 1.6 ng/m^3 to 11.4 ng/m^3 with most values in the 3 to 4 ng/m^3 range. The coarse fraction generally contained about twice as much PM_{10} chromium as the fine fraction. Long Beach showed the highest peak and the highest mean concentrations.

In addition to total chromium, the database contains corresponding measurements for particulate matter less than or equal to ten microns aerodynamic diameter (PM_{10}), and also for total suspended particulate matter (TSP). The SAS software package was used to assess the di-chot data to determine the relationship between total chromium and particulate matter. Total PM_{10} chromium, coarse fraction PM_{10} chromium, and fine fraction PM_{10} chromium, as related to PM_{10} particulate matter and TSP, were evaluated. Results showed a wide range of mean ratios and large standard deviations around the mean ratios. Correlation coefficients are all less than 0.61, indicating no statistically significant relationship between PM_{10} chromium, and PM_{10} particulate matter or TSP.

In addition, peak-to-mean ratios for PM_{10} chromium were calculated. Ratios were calculated for total (fine + coarse) chromium as well as for the coarse and fine fractions individually. Results are shown in Tables III-3, III-4, and III-5. Ratios calculated for total PM_{10} chromium (Table III-3) suggest that chromium source areas tend to be homogeneous; ratios are low at all but one of the nine sites. Results for the coarse and fine fractions individually (Tables III-4 and III-5) are more specific, and suggest impact from either intermittent or heterogeneous emission sources at one-third of the

TABLE III-2

SUMMARY OF AVERAGE CHROMIUM CONCENTRATIONS FROM ARB DICHOTOMOUS SAMPLES
(units are ng/m³)

Site Name	ARB Site Number	Coarse Fraction	Fine Fraction	Total Chromium	Total Samples
Bakersfield	1500203	2.91	1.09	4.00	56
Chico	0400628	2.75	0.85	3.60	34
China Lake	1500211	0.89	0.67	1.56	53
Fresno	1000234	2.21	1.57	3.78	41
Glendora	7000591	1.84	1.84	3.69	68
Lancaster	7000593	2.13	0.88	3.01	72
Long Beach	7000072	8.21	3.18	11.39	36
Riverside	3300146	2.06	1.61	3.67	72
Yuba City	5100895	2.49	1.35	3.84	51

TABLE III-3

PEAK TO MEAN RATIOS FOR TOTAL (FINE + COARSE) DICHOTOMOUS CHROMIUM
(units are ng/m³)

Site Name	ARB Site Number	Peak Chromium ^A	Mean Chromium ^A	P:M Ratios	Total Samples
Bakersfield	1500203	10.0	4.00	2.50	56
Chico	0400628	10.0	3.60	2.78	34
China Lake	1500211	3.0	1.56	1.92	53
Fresno	1000234	8.0	3.78	2.12	41
Glendora	7000591	10.0	3.69	2.71	68
Lancaster	7000593	16.0	3.01	5.32	72
Long Beach	7000072	39.0	11.39	3.42	36
Riverside	3300146	10.0	3.67	2.72	72
Yuba City	5100895	14.0	3.84	3.65	51

^A Total (hexavalent and trivalent) chromium

TABLE III-4

PEAK-TO-MEAN RATIOS FOR COARSE FRACTION DICHOTOMOUS CHROMIUM
(units are ng/m³)

<u>Site Name</u>	<u>ARB Site Number</u>	<u>Peak Chromium^A</u>	<u>Mean Chromium^A</u>	<u>P:M Ratio</u>	<u>Total Samples</u>
Bakersfield	1500203	6.89	2.91	2.37	56
Chico	0400628	7.78	2.75	2.83	34
China Lake	1500211	2.00	0.89	2.25	53
Fresno	1000234	5.78	2.21	2.62	41
Glendora	7000591	5.56	1.84	3.02	68
Lancaster	7000593	16.00	2.13	7.51	72
Long Beach	7000072	34.56	8.21	4.21	36
Riverside	3300146	6.78	2.06	3.29	72
Yuba City	5100895	11.78	2.49	4.73	51

TABLE III-5

PEAK-TO-MEAN RATIOS FOR FINE FRACTION DICHOTOMOUS CHROMIUM
(units are ng/m³)

<u>Site Name</u>	<u>ARB Site Number</u>	<u>Peak Chromium^A</u>	<u>Mean Chromium^A</u>	<u>P:M Ratio</u>	<u>Total Samples</u>
Bakersfield	1500203	5.55	1.09	5.09	56
Chico	0400628	2.22	0.85	2.61	34
China Lake	1500211	2.22	0.67	3.31	53
Fresno	1000234	3.33	1.57	2.12	41
Glendora	7000591	5.55	1.84	3.02	68
Lancaster	7000593	3.33	0.88	3.78	72
Long Beach	7000072	8.88	3.18	2.79	36
Riverside	3300146	7.24	1.61	4.50	72
Yuba City	5100895	13.32	1.35	9.87	51

A Total (hexavalent and trivalent) chromium

sites evaluated for each individual size fraction. Although results indicate that source areas are in more cases homogeneous, it is apparent from the data that intermittent or heterogeneous sources do impact resulting chromium concentrations at some sites and that the size distribution of particles involved is just as likely to be in the fine fraction as in the coarse fraction.

The purpose of the analyses discussed above was both to determine whether particulate matter measurements could be used to estimate total chromium concentrations, and to determine the characteristics of chromium emissions. Results show that neither TSP or PM_{10} mass measurements provide adequate information for estimating corresponding chromium concentrations. No significant correlations were found using either dataset. Peak-to-mean ratios suggest that homogeneous source areas for chromium are present at many of the locations evaluated, while other sites show impact by local intermittent or heterogeneous sources or both, and that chromium from these sources is contained both within the fine fraction and coarse fraction particulate.

Work is being carried out to characterize the concentrations of total chromium and chromium(VI) in ambient air. Recent evaluation of ARB Method 106 indicates that chromium(VI) is unstable once collected, and that substances may be present in the samples which reduce the specificity of the method to chromium(VI). Because of these problems with Method 106, the validity of data produced by the method is uncertain. Until these questions of recovery and specificity for Method 106 can be resolved, data collected using Method 106 cannot be considered reliable, and will not be used in our analyses.

An alternative method to ARB Method 106 for the determination of chromium(VI) in ambient air is being developed. A copy of draft Method

ADDL006, Method for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels, is attached.

During August 1985, four samples were collected in El Monte and analyzed for chromium(VI) using draft Method ADDL006. The four 24-hour samples showed chromium(VI) concentrations between 0.4 and 0.7 ng/m³, with an average of 0.5 ng/m³. These values are close to the estimated limit of detection (0.21 ng/m³) derived from laboratory evaluation of the method. Comparison of the limited information on chromium(VI) concentrations with total chromium concentrations in El Monte indicates that hexavalent chromium comprises between 3 and 8 percent of total atmospheric chromium. These estimates are based on preliminary chromium(VI) concentration measurements developed, using draft Method ADD1006. A validated method for sampling and analysis of chromium(VI) and additional information on chromium(VI) exposure will be prerequisite to the development of any control measures for chromium(VI).

B. ESTIMATES OF ANNUAL AMBIENT CHROMIUM EXPOSURE TO TOTAL CHROMIUM
Limitations to Analysis

Estimates of annual total chromium exposure were made for several areas in California. Because of the nature of the data used in making these estimates several important assumptions had to be made which impose certain limitations on the interpretation and use of the resulting data. The most important aspects of these limitations are summarized below:

- 1) The EPA data used to estimate annual population exposures for chromium were originally obtained from a number of different sources. It is probable that different collection and analysis methods and standards were employed by the various sources. Because

the accuracy of the chromium measurements is undocumented, the accuracy of the analyses presented here is unknown.

- 2) Data used to estimate annual population exposures for chromium are from a limited number of sites and based on a limited number of observations at those sites. Because of this, the true variability and magnitude of chromium concentrations may be more or less than those presented here. Also, because the spatial representativeness of each station is unknown, it is uncertain how differences in spatial representation between stations would affect the results presented.
- 3) Data used in these analyses are all representative of ambient outdoor concentrations; no consideration is given to indoor or workplace exposure. The exposure estimates presented here are based on the assumption that an individual's exposure was from the outdoor ambient air concentrations measured or calculated for the area in which the individual resides.
- 4) Chromium samples collected during 1977 and population data collected during 1980 have been used to make an estimate of annual population exposure to total chromium. These data were used because they allow estimation of annual average concentrations of total chromium. Changes may have occurred since these data were compiled; current total chromium concentrations and population exposures may be different. More recent data have become available which suggest that concentrations are lower, although these data are not adequate to estimate annual exposure.
- 5) Stationary sources of chromium are not explicitly considered in estimation of annual population exposure; they are considered

indirectly as a function of their contribution to chromium measured at the sampling sites. Exposures in receptor areas near large stationary sources of chromium are discussed separately.

- 6) Data presented here represent concentrations of total chromium. Limited preliminary data suggest that from 3 to 8 percent of total chromium may be chromium(VI) in areas not directly affected by chromium(VI) emissions.
- 7) Data from 1977 used for assessment of population exposure represent chromium particulate matter less than 50 micrometer (aerodynamic equivalent) diameter. Data on atmospheric concentrations of chromium particulate matter of respirable size (less than 10 micrometer diameter), gathered during 1982-1983, are presented in summary form in Table III-2 (page III-6).

Annual ambient population exposures were estimated using data from the EPA NADB database. As stated previously, the EPA comprise 24-hour total chromium concentrations collected with high-volume particulate samplers. All data were analyzed using the neutron activation analysis method. Although data are available for the years 1977 through 1981, much of the data for individual years are incomplete. Data for the year 1977 are the most suitable for use in evaluating annual total chromium exposures. The 1977 data were collected at sixteen stations. Although the sampling sites reflect a variety of land use parameters, all sites were established to provide data reflecting population oriented total chromium concentrations (EPA, 1984). Site-specific location and influence criteria are summarized in Table III-6.

Total chromium data collected at the sixteen sites during 1977 are summarized in Table III-7. Approximately two to three samples were collected at each site during each month of the year. Zero values comprised from three to seventy-seven percent of values reported at a given site; for all sites

TABLE III-6

Summary of Location Characteristics and Dominating Influences
Surrounding Sampling Sites Used in Exposure Analysis

Site Name	EPA Site Number	Location Characteristics	Dominating Influence
<u>SoCAB Sites:</u>			
Anaheim-Harbor Blvd.	0230001	Suburban	Commercial
Burbank-West Palm Ave.	0900002	Center City	Commercial
Long Beach-Pine Ave.	4100001	Center City	Commercial
Los Angeles- So. San Pedro	4180001	Center City	Commercial
Ontario Airport	5380001	Rural	Commercial
Pasadena-Cal Tech	5760002	Center City	Residential
San Bernardino-West 3rd Street	6680001	Center City	Commercial
Santa Ana-Ross Street	7180001	Center City	commercial
Torrance-Carson Street	8260001	Center City	Residential
<u>SFBAAB Sites:</u>			
Berkeley-Berkeley Way	0740001	Center City	Residential
Oakland-Fifth Street	5300001	Center City	Industrial
San Francisco- Grove Street	6860001	Center City	Commercial
<u>Other Sites:</u>			
Fresno-South Cedar Ave.	2800002	Center City	Commercial
Sacramento-Stockton Blvd.	6580001	Center City	Commercial
San Diego-Island Ave.	6800004	Center City	Commercial
San Jose- North 4th St.	6980004	Center City	Commercial

Table III-7

Summary of 1977 Chromium Data from the EPA
National Aerometric Data Bank
(units are ng/m³)

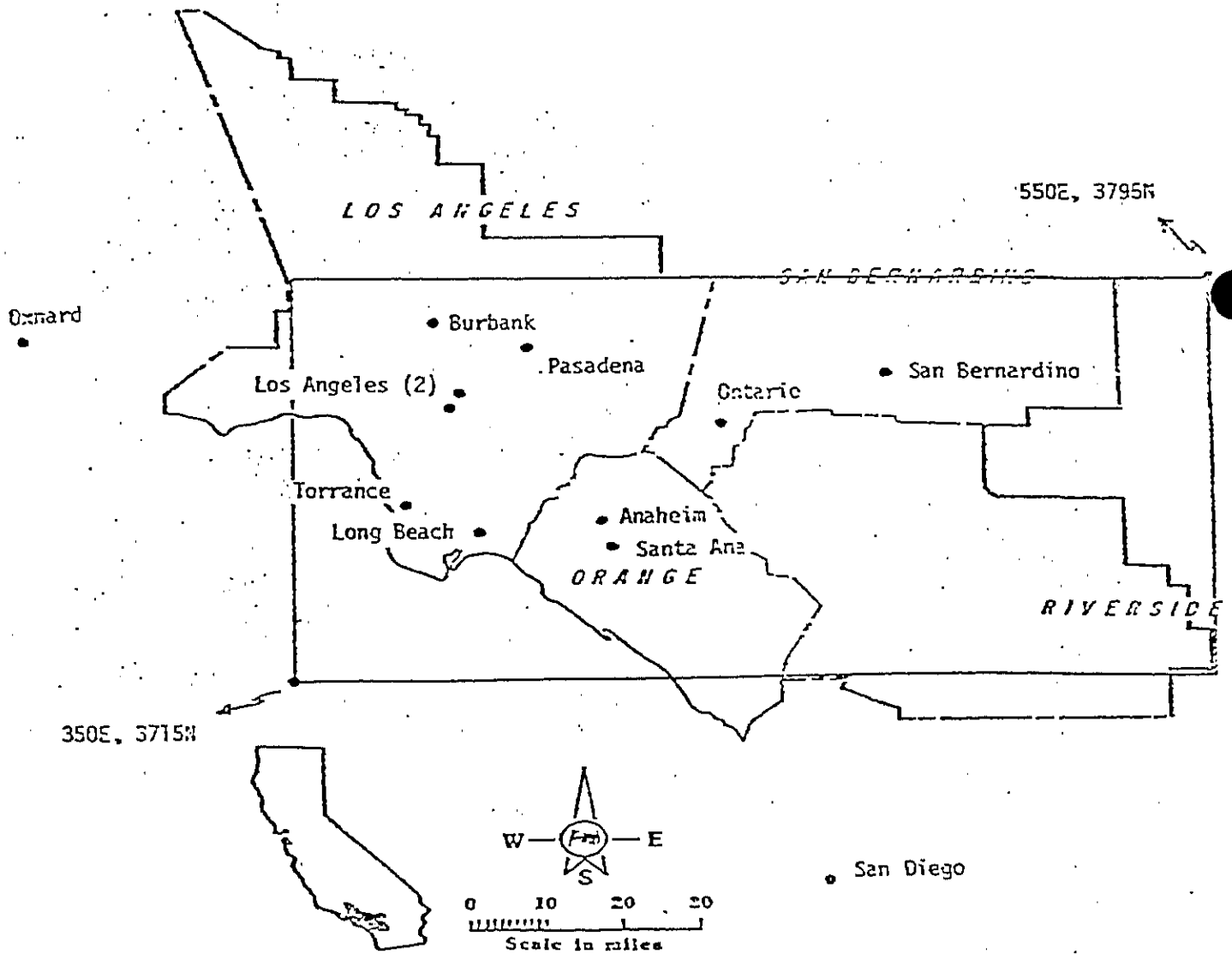
Site Name	EPA Site Number	Maximum Chromium	Average Chromium	Standard Deviation	Number of Samples: Total	Zero
SoCAB Sites:						
Anaheim- Harbor Blvd	0230001	28.3	6.4	5.2	30	23
Burbank- West Palm Ave	0900002	23.6	10.7	6.2	30	10
Long Beach- Pine Avenue	4100001	41.0	17.9	9.9	27	2
Los Angeles So. San Pedro	4180001	66.6	19.1	12.2	30	1
Ontario-Airport	5380001	34.2	18.5	6.7	30	1
Pasadena-Cal Tech	5760002	32.8	13.7	8.0	29	7
San Bernardino- West 3rd St.	6680001	103.3	33.3	24.1	29	2
Santa Ana- Ross Street	7180001	20.9	10.8	5.3	29	7
Torrance- Carson Street	8260001	315.2	30.6	56.2	29	5
SFBAAB Sites:						
Berkeley- Berkeley Way	0740001	72.9	9.0	13.7	30	19
Oakland-Fifth St.	5300001	60.3	19.0	10.1	29	1
San Francisco- Grove Street	6860001	14.8	6.2	3.6	30	21
Other Sites:						
Fresno-So. Cedar Avenue	2800002	32.4	12.3	8.3	30	10
Sacramento- Stockton Blvd.	6580001	23.6	10.8	5.7	30	7
San Diego- Island Avenue	6800004	23.6	11.7	6.3	30	7
San Jose- North 4th Street	6980004	29.1	14.3	7.6	30	5

N.B.- The minimum concentration reported at each site during 1977 was zero. The minimum non-zero value reported at any site was 8 ng/m³.

* These numbers represent the total number of samples included in the analysis and the number of samples for which a zero value was reported.

FIGURE III-1

LOCATION OF MODELING AREAS AND STATIONS, THE DATA FROM WHICH WERE USED TO INTERPOLATE CHROMIUM IN THE SOUTH COAST AIR BASIN



combined, twenty-seven percent of values were reported as zero. The number of zero values reported at each site is summarized in Table III-7. As stated previously, a reported zero concentration does not necessarily indicate an absence of chromium but rather that the chromium concentration was below the limit of the analytical techniques. There are several ways to treat zero values when calculating annual averages. Reported zero values can be assumed equal to zero, assumed equal to the lower limit of analysis, or assumed equal to one-half the lower limit of analysis. Including zero concentrations as zero results in estimates the lowest averages; assuming zero values equal the lower limit of analysis results in the highest averages. These two extremes likely bracket the possible range of concentration averages. Assuming zero concentrations equal one-half the lower limit of analysis provides a third estimate of concentrations.

In the following discussion, zero values were replaced with a concentration of one-half the lowest non-zero concentration sampled at any site during 1977, 4.0 nanograms per cubic meter. Alternatives to this approach are presented later in this section. We assume the lowest non-zero value reported during 1977 equals the lower limit of the analytical techniques used. Of the sixteen sites used in this analysis, three had more than fifty percent of all values reported as zero; nine sites had more than twenty percent of all values reported as zero. The occurrence of many zero values at a number of sites and the assumptions made in replacing them with a single concentration (4.0 ng/m^3) necessarily limits the confidence that can be placed in the results presented here.

Maximum twenty-four hour total chromium concentrations at each site range from 14.8 ng/m^3 to 315.5 ng/m^3 , while annual average chromium concentrations range from 6.2 ng/m^3 to 33.3 ng/m^3 . The highest twenty-four-hour average concentration and annual average concentration both occurred at stations located in the South Coast Air Basin.

As seen in Table III-7, the majority of sites for which chromium data are available are located in the South Coast (SoCAB) and San Francisco Bay Area (SFBAAB) air basins. Other stations are located in Fresno and San Diego. Using the appropriate annual average concentrations given in Table III-7, annual chromium concentrations were interpolated to 1980 census tract centroids for the SoCAB and SFBAAB using the McRae inverse distance-squared interpolation routine (McRae, 1982).

Total chromium concentrations in the SoCAB were interpolated for an area of 200 by 80 kilometers. The limits of the modeling area and the relative locations of stations used for interpolation are shown in Figure III-1. Barriers to interpolation, such as mountain ranges, were included as appropriate. Based on 1980 census data, total population in the SoCAB is approximately 11 million. Census tracts within the modeling area have a total population of just over 10 million. Figure III-2 is a graphic illustration of annual chromium concentrations interpolated to the modeling area. The plot indicates that annual concentrations during 1977 were highest in the eastern portion of the grid (San Bernardino station) with a secondary peak to the southwest (Torrance station). Areas with zero concentrations do not necessarily reflect an absence of chromium but rather, the influence of barriers to interpolation. Overall, annual average concentrations calculated for the modeling area are between 6.4 ng/m^3 and 33.3 ng/m^3 . A corresponding plot of population within the study area is shown in Figure III-3. Comparison of the two figures show the highest population density near the secondary peak at the Torrance-Carson site.

FIGURE III-2

SOCAB 1977 Total Chromium in 5 KM Cells

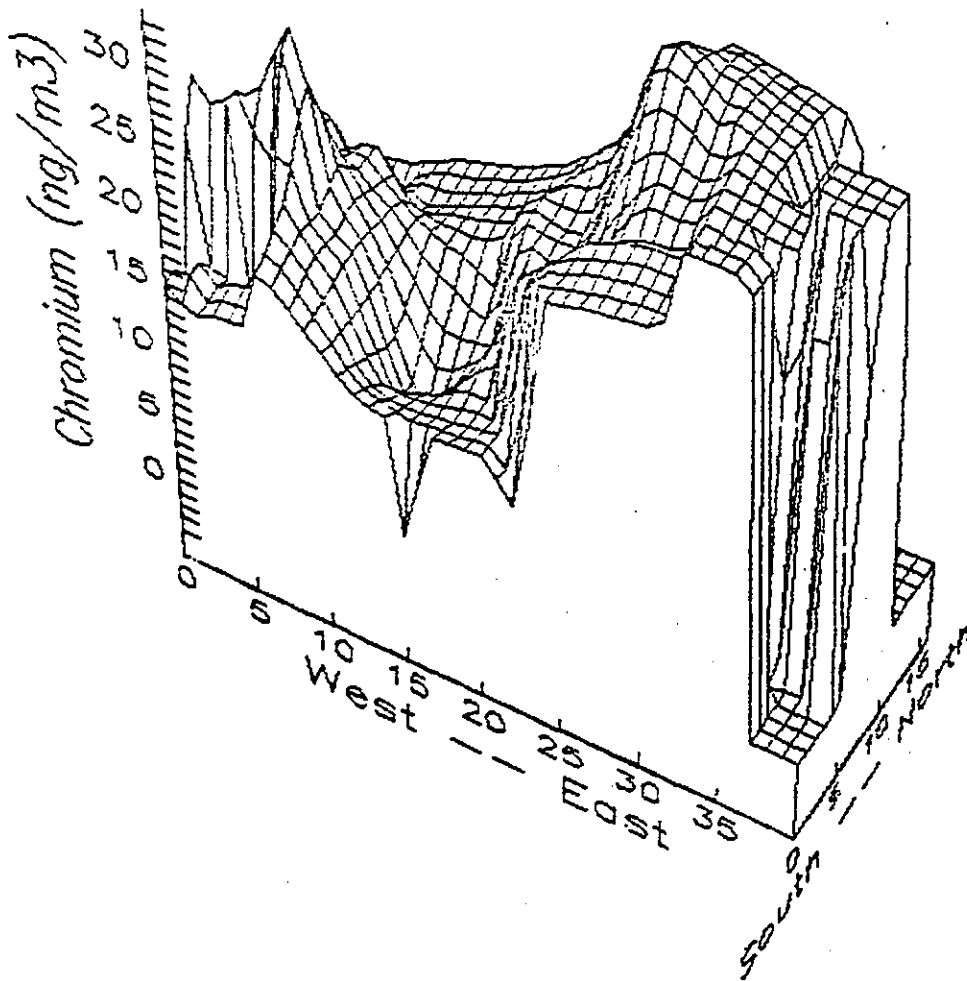


FIGURE III-3

SOCAB 1980 Population Density for 5 KM Cells

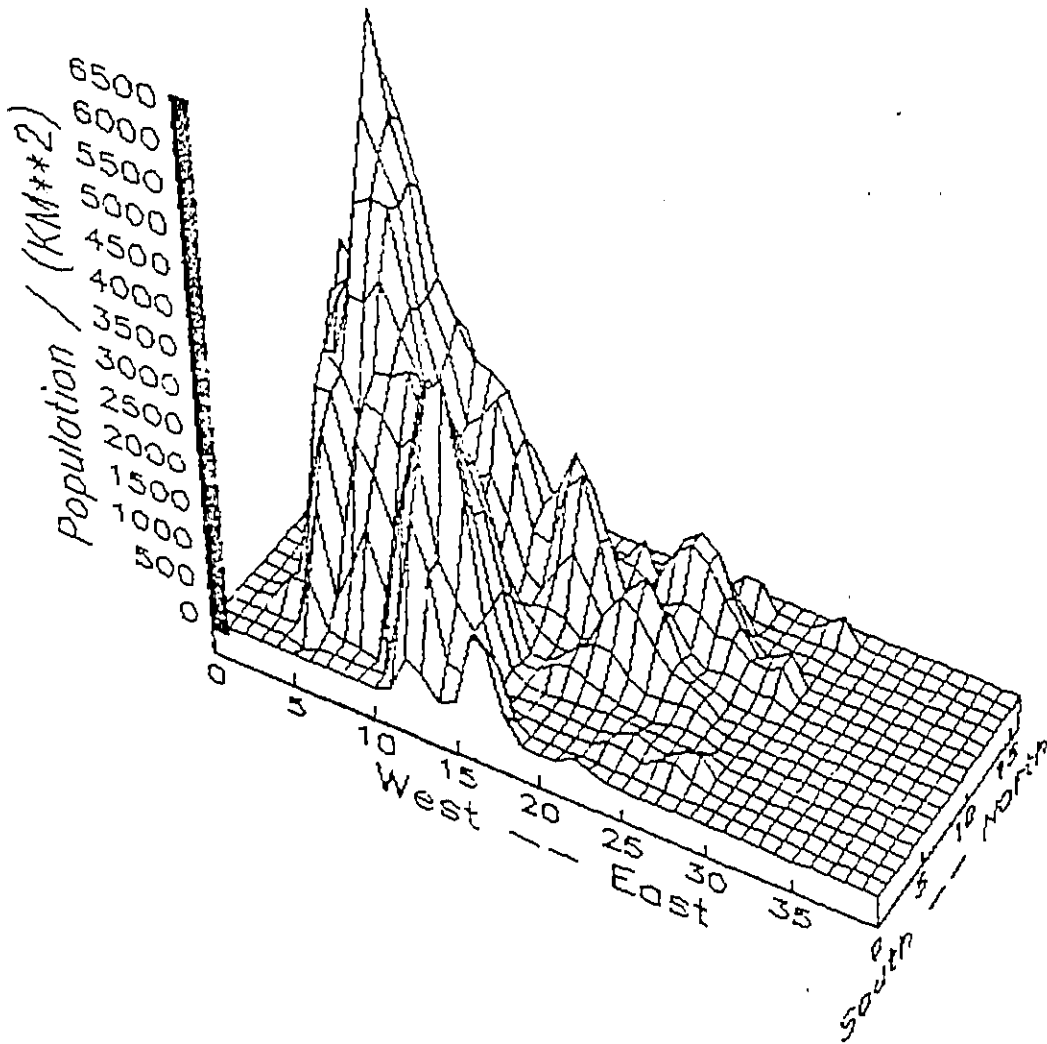


Figure III-4 shows the population exposed to various annual average chromium concentrations in the SoCAB. The majority of people were exposed to between 11.0 and 21.0 ng/m³ total chromium. The population-weighted average exposure in the SoCAB is 16.9 ng/m³ while the geographic average is 16.6 ng/m³. Figure III-5 shows the same data plotted in Figure III-4, but plotted as cumulative population versus annual average chromium. According to this figure, more than 2 million people were exposed to at least 20.0 ng/m³ total chromium in 1977.

Because the data available for the San Francisco Bay Area Air Basin lacked good spatial coverage, estimates of exposure could be estimated for only a forty by twenty-five kilometer area. The limits of the modeling area and the relative locations of stations used for interpolation are shown in Figure III-6. Barriers to interpolation were included as appropriate. Although there are approximately five million people in the SFBAAB, the total population in the modeling area is only about 1.5 million. A graphic illustration of annual chromium concentrations interpolated to the SFBAAB modeling area is shown in Figure III-7. Annual concentrations are greatest in the eastern portion of the grid (Oakland station). Areas with zero concentration reflect the influence of barriers to interpolation. A plot of population density in the study area is shown in Figure III-8. Comparison of Figures III-7 and III-8 show that the peak population density occurs to the west of the peak chromium concentrations; a secondary peak of population density occurs very near the point of peak concentration. Figure III-9 shows population exposures to total chromium in the SFBAAB modeling region. Almost 800,000 of the 1.5 million people in the study area were exposed to 9.0

FIGURE III-4

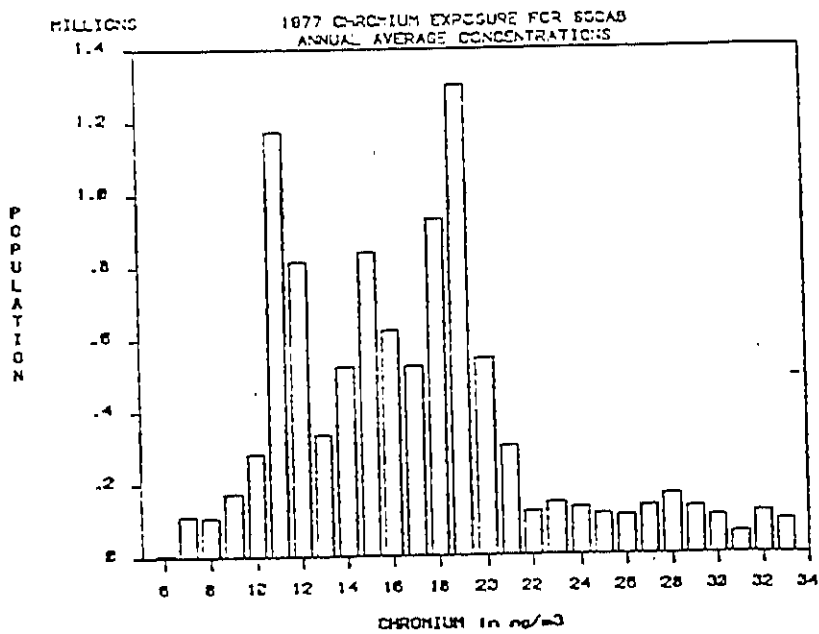


FIGURE III-5

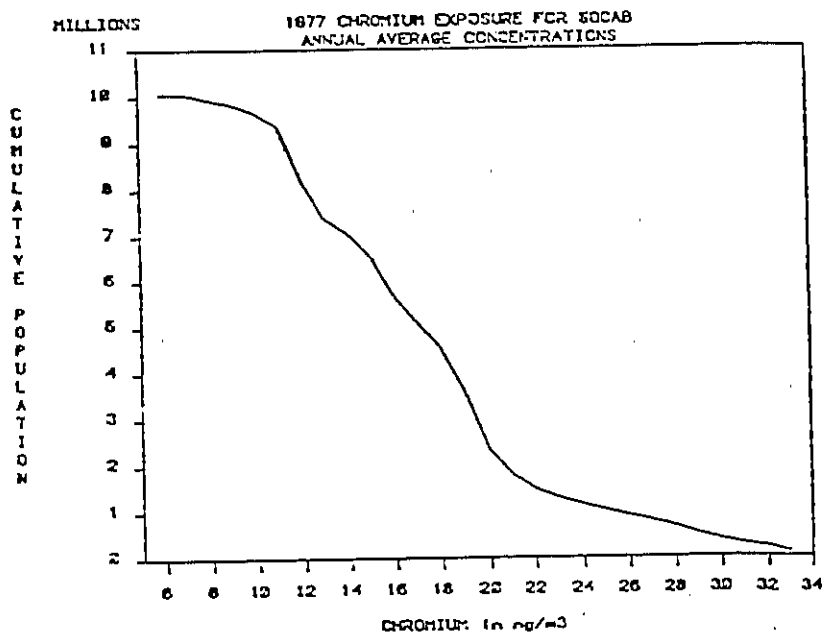


FIGURE III-6

LOCATION OF MODELING AREAS AND STATIONS USED, THE DATA FROM WHICH WERE USED TO INTERPOLATE CHROMIUM IN THE SAN FRANCISCO BAY AREA

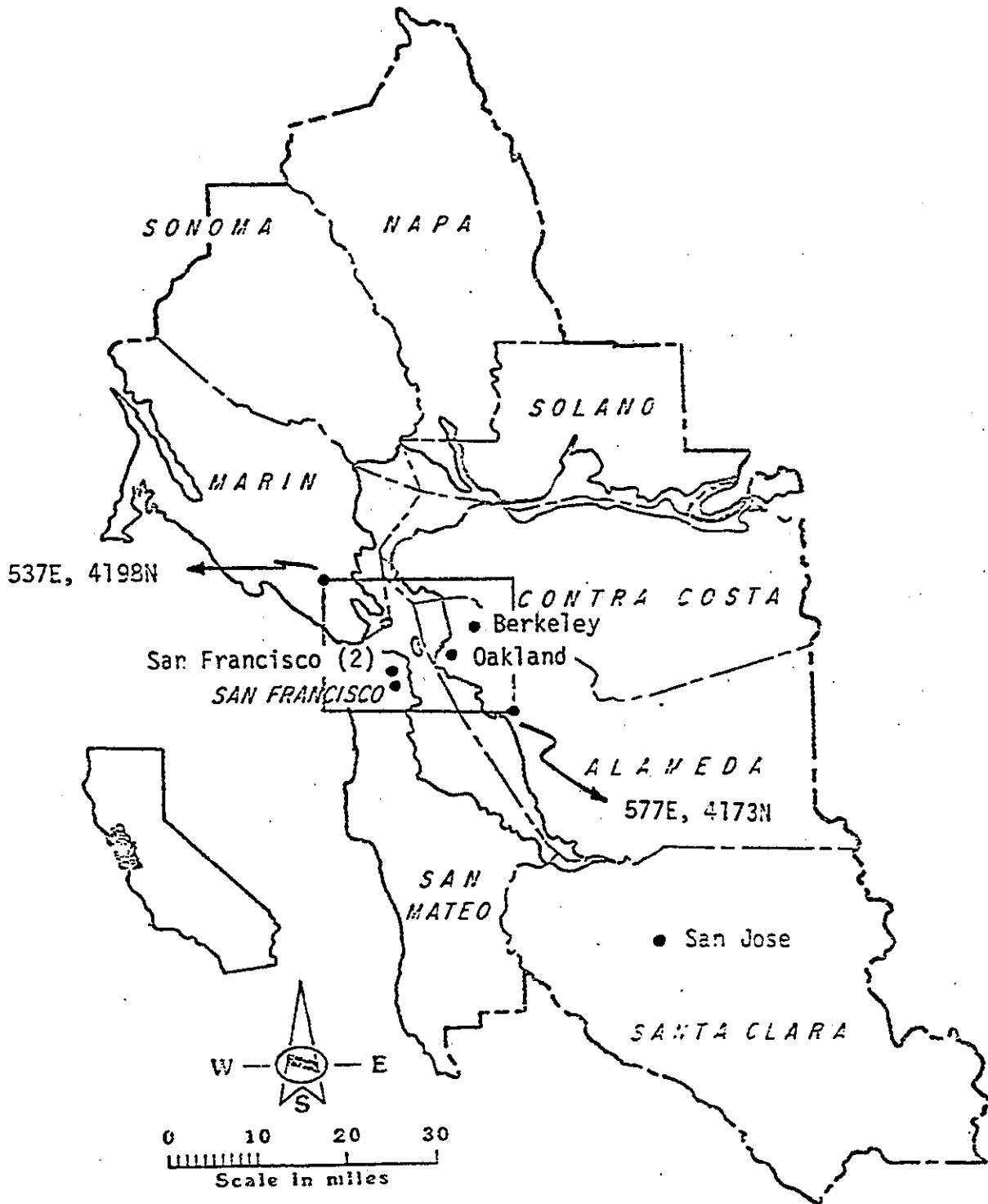


FIGURE III-7

SF Bay Area 1977 Total Chromium in 5 KM Cells

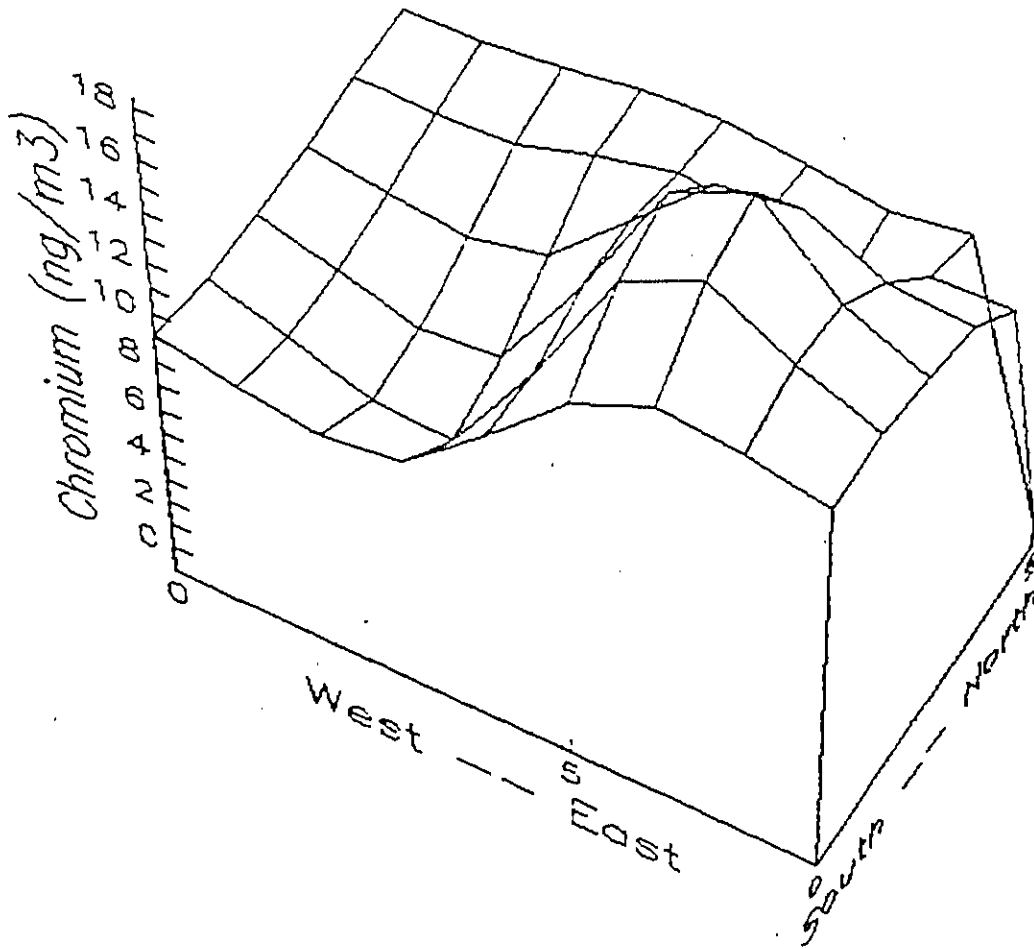


FIGURE III-8

S.F. Bay Area 1980 Population Density for 5 KM Cells

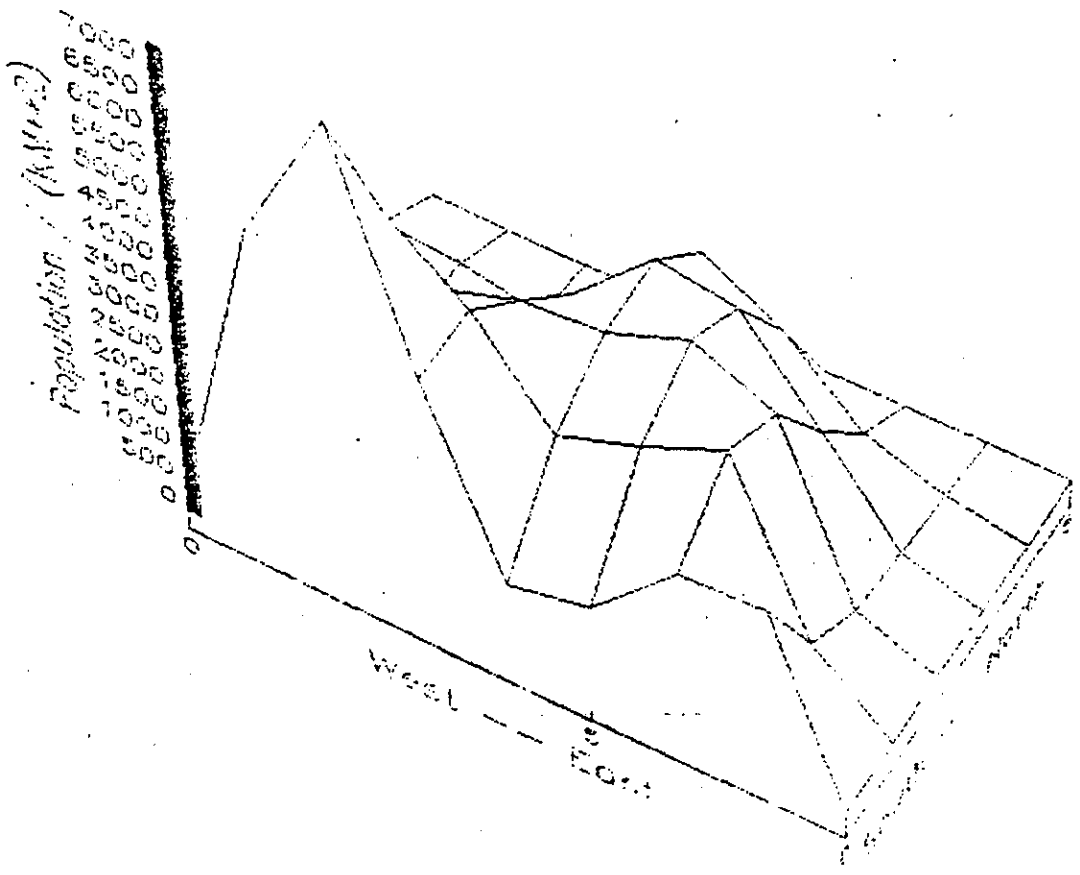
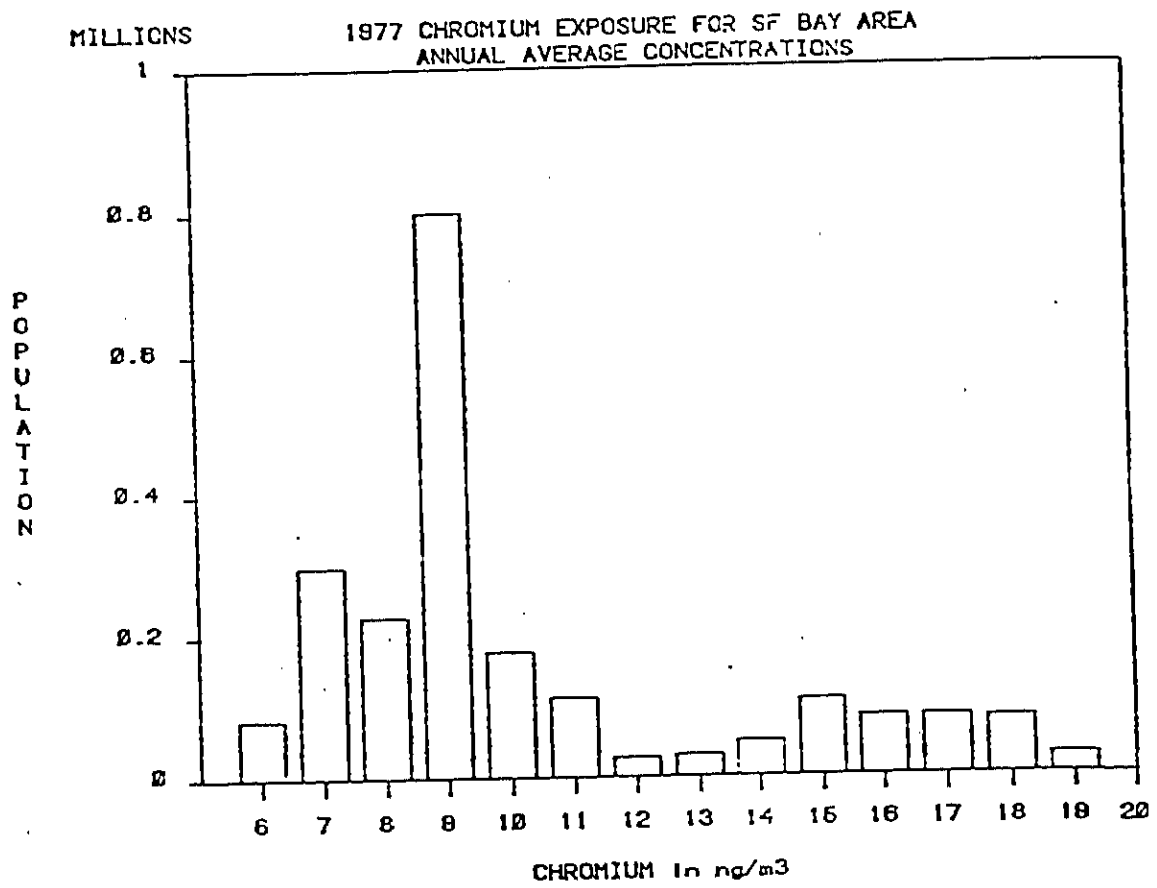


FIGURE III-9



ng/m³ or more of total chromium during 1977. Cumulative exposures are shown in Figure III-10. In the SFBAAB, the population-weighted chromium concentration for 1977 was 10.8 ng/m³. The geographic mean was 11.3 ng/m³.

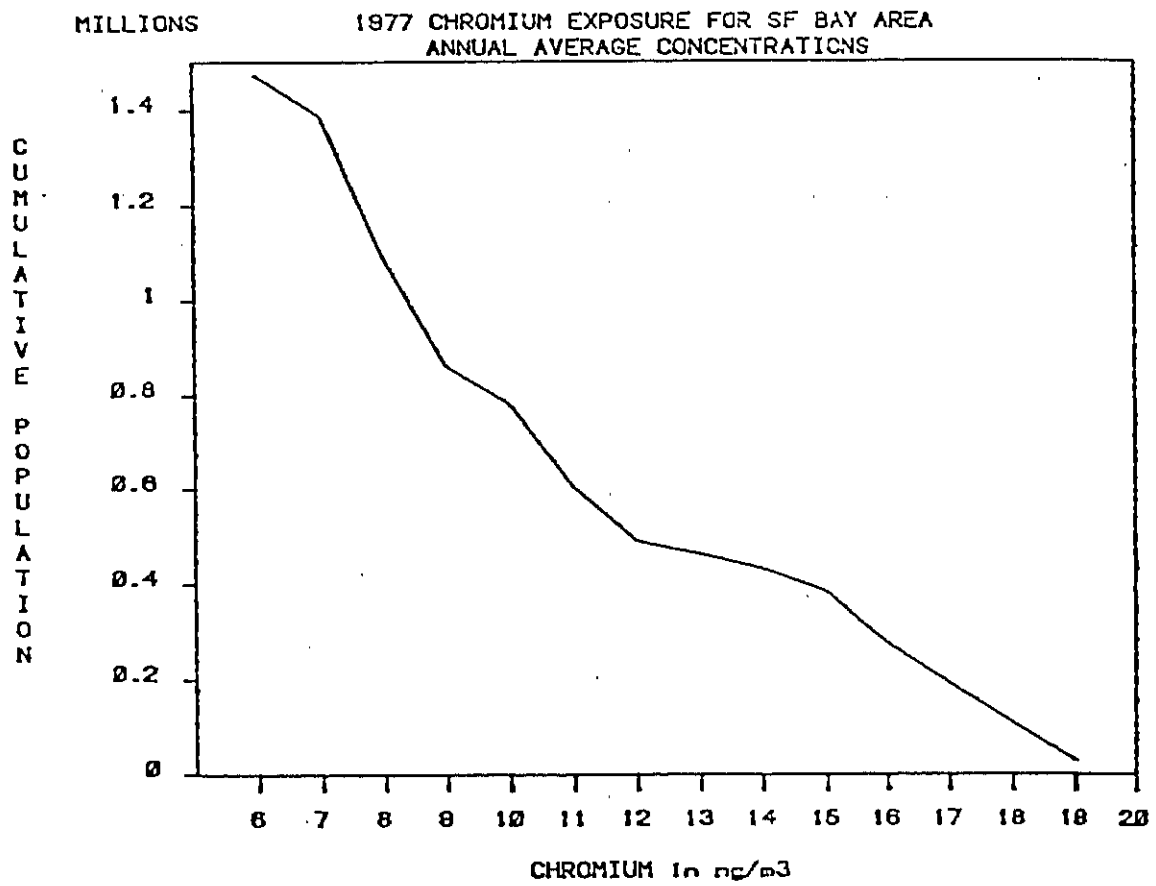
Annual total chromium exposure estimates for the other areas in the state were calculated somewhat differently from those for the South Coast and San Francisco Bay Area Air Basins. Data were available for only one site in each of four cities: Fresno, Sacramento, San Diego, and San Jose. For these cities, we assumed that the annual total chromium concentration at each site was representative of the exposure experienced by the population living in those census tracts with centroids not more than ten kilometers from the sampling site. The annual concentration at the sampling sites and the population exposed to that concentration are summarized in Table III-8. As shown in this table, annual population exposures to total chromium in these areas ranged from 10.6 ng/m³ to 14.3 ng/m³.

TABLE III-8

ANNUAL CHROMIUM EXPOSURE FOR SPECIFIC CENSUS TRACTS

<u>Site Name</u>	<u>EPA Site Number</u>	<u>Population Within 10 Kilometers</u>	<u>Annual Average Chromium (ng/m³)</u>
Fresno-South Cedar Avenue	2800002	250,612	12.3
Sacramento-Stockton Blvd.	6580001	376,283	10.6
San Diego-Island Avenue	6800004	477,482	11.7
San Jose-North 4th St.	6980004	608,945	14.3

FIGURE III-10



In addition to the approach discussed above, population exposures were determined using two alternative approaches to provide a range of possible values. The alternative approaches differ only in their treatment of zero concentrations. The first alternative approach assumes zero values in the database are actually zero concentrations. This approach provides a lower-bound estimate of population exposure. The second alternative approach assumes zero values in the database equal the lowest non-zero concentration reported during 1977 (7.9 ng/m³). This approach provides an upper bound estimate of population exposure. The effect of these alternative approaches on resulting concentrations is directly related to the number of zero concentrations reported at each individual site (refer to Table III-8). The greater the percentage of reported zero concentrations, the greater the variation in concentrations of one approach versus the other.

Exposure estimates based on these alternative approaches are summarized in Table III-9. Results based on the first approach show geographic averages ranging from 9.4 ng/m³ to 15.7 ng/m³ and population-weighted concentrations ranging from 8.9 ng/m³ to 16.1 ng/m³. Geographic average concentrations based on the second approach range from 11.7 ng/m³ to 17.5 ng/m³ while population-weighted averages range from 11.7 ng/m³ to 17.8 ng/m³.

Limited data on current ambient total chromium concentrations have recently become available as a result of the Air Resources Board's ongoing effort to document ambient levels of potentially toxic compounds. Data are available for nineteen locations for varying periods of time during January through June of 1985. These data represent twenty-four hour samples collected using either high volume or low volume particulate samplers and subsequently

analyzed for total chromium using atomic absorption or X-ray fluorescence, respectively.

The data are summarized in Table III-10. Minimum concentrations reported during the six months range from below the quantitation limit (1.0 ng/m^3) to 3.0 ng/m^3 . The maximum concentrations reported was 24.0 ng/m^3 . Averages of values at each site range from 1.9 ng/m^3 to 9.1 ng/m^3 . The average concentration for all sites combined is 4.7 ng/m^3 .

The 1985 ARB total chromium data are compared with the 1977 EPA total chromium data in Table III-11. Although all EPA sites are included in this comparison, only fourteen of the nineteen ARB sites are included. These fourteen sites are the only ARB sites located in the same areas as the EPA sampling locations. As is apparent from Table III-11, total chromium data from 1985 are different from chromium data of 1977. The 1977 data show higher concentrations. The maximum twenty-four hour concentration sampled during 1977 was 74.5 ng/m^3 whereas the maximum twenty-four hour concentration sampled during 1985 was 24.0 ng/m^3 . Average concentrations during 1977 ranged from 4.0 ng/m^3 to 34.5 ng/m^3 . This range compares with a range of 1.9 ng/m^3 to 9.1 ng/m^3 for the 1985 data. Overall concentrations reported by EPA for 1977 are approximately 1.5 to 3.5 times greater than those reported for 1985. Data summarized in Table III-11 suggest present total chromium concentrations are lower than those measured during 1977; however, several factors should be considered in comparing the data. These factors include:

1. Site locations during 1985 are not the same as those used in 1977;

TABLE III-9

Comparison of Population Exposures to Chromium During 1977

Using Three Approaches*

(units are ng/m^3)

Area Location	Approach #1	Approach #2	Approach #3
	Geog Avg/Pop-Wt Avg	Geog Avg/Pop-Wt Avg	Geog Avg/Pop-Wt Avg
SoCAB Area- (150 x 80 km)	15.7 / 16.1	16.6 / 16.9	17.5 / 17.8
BAAB Area- (40 x 20 km)	9.4 / 8.9	11.3 / 10.8	13.1 / 12.7
Fresno Area- (10 km radius)	11.0 / 11.0	12.3 / 12.3	13.6 / 13.6
Scramento Area- (10 km radius)	9.8 / 9.8	10.6 / 10.6	11.7 / 11.7
San Diego Area (10 km radius)	10.7 / 10.7	11.7 / 11.7	12.6 / 12.6
San Jose Area- (10 km radius)	13.7 / 13.7	14.3 / 14.3	15.0 / 15.0

* The three approaches used differ in the way in which zero values in the database were treated:

Approach #1: Zero values were assumed equal to zero ($0.0 \text{ ng}/\text{m}^3$).

Approach #2: Zero values were assumed equal to one-half the quantitation limit ($0.6 \text{ ng}/\text{m}^3$).

Approach #3: Zero values were assumed equal to the quantitation limit ($1.2 \text{ ng}/\text{m}^3$).

TABLE III-10

Summary of ARB Chromium Data Sampled
January through June 1985
(units are ng/m³)

Site Name	EPA Site Number	Minimum Chromium*	Maximum Chromium	Average Chromium	Number of Samples: Total	Zero
SACRAMENTO VALLEY AIR BASIN						
Citrus Heights- Sunrise Blvd	3400293	2.0	11.0	5.4	13	0
SAN DIEGO AIR BASIN						
Chula Vista- El Cajon- Redwood Avenue	8000114	0.5	6.0	2.8	14	1
8000131	1.0	4.0	3.0	8	0	
SAN FRANCISCO BAY AREA AIR BASIN						
Richmond-13th St.	0700433	2.0	5.0	3.4	14	0
Concord- 2975 Treat Blvd.	0700440	1.0	2.0	1.9	15	0
San Jose-4th St.	4300382	2.0	21.0	8.2	14	0
Fremont-Chapel Way	6000336	1.0	5.0	2.4	15	0
San Francisco- 23rd Street	9000304	2.0	6.0	3.9	15	0
SAN JOAQUIN VALLEY AIR BASIN:						
Fresno-Olive	1000234	2.0	10.0	4.3	12	0
Bakersfield- Chester Street	1500203	2.0	7.0	4.3	15	0
Stockton- Hazelton Street	3900252	3.0	6.0	4.1	12	0
Modesto- 418 14th Street	5000568	3.0	7.0	3.9	15	0
SOUTH CENTRAL COAST AIR BASIN:						
Santa Barbara- Canon Perdido	4200378	1.0	10.0	3.5	8	0
Simi Valley- SOUTH COAST AIR BASIN:	5600413	1.0	4.0	2.4	15	0
Riverside- Rubidoux	3300144	2.0	14.0	7.3	11	0
Upland	3600175	0.5	9.0	4.8	13	1
North Long Beach	7000072	2.0	11.0	6.3	12	0
Los Angeles- North Main	7000087	3.0	23.0	9.1	10	0
El Monte-ARB HSLD	7000579	3.0	24.0	8.6	50	0

* A concentration of 0.5 ng/m³ is equal to one-half the quantitation limit of 1.0 ng/m³ and was substituted for the value below the quantitation limit.

TABLE III-11

Comparison of 1977 EPA Chromium Data with 1985 ARB Chromium Data*
(units are ng/m³)

Characteristic Being Compared:	1977 EPA Chromium Data	1985 ARB Chromium Data
SAN FRANCISCO BAY AREA AIR BASIN SITES:		
Range of Minimum Concentrations	4.0 - 4.0	1.0 - 2.0
Range of Maximum Concentrations	13.9 - 28.2	2.0 - 21.0
Range of Average Concentrations (Each Site Individually)	7.2 - 16.8	1.9 - 8.2
Observations per Site	7	14 - 15
Average Concentration (All Sites Combined)	11.8	4.0
SOUTH COAST AIR BASIN SITES:		
Range of Minimum Concentrations	4.0 - 10.0	0.5 - 3.0
Range of Maximum Concentrations	4.0 - 74.5	9.0 - 24.0
Range of Average Concentrations (Each Site Individually)	4.0 - 34.5	4.8 - 9.1
Number of Observations	11 - 12	10 - 50
Average Concentration (All Sites Combined)	15.9	7.2
FRESNO AREA SITE:		
Minimum Concentration	4.0	2.0
Maximum Concentration	12.3	10.0
Average Concentration	6.8	4.3
Number of Observations	7	12
SACRAMENTO AREA SITE:		
Minimum Concentration	4.0	2.0
Maximum Concentration	17.8	11.0
Average Concentration	9.0	5.4
Number of Observations	7	13
SAN DIEGO AREA SITE:		
Minimum Concentration	4.0	0.5
Maximum Concentration	16.9	6.0
Average Concentration	10.0	2.8
Number of Observations	15	22
SAN JOSE AREA SITE:		
Minimum Concentration	4.0	0.5
Maximum Concentration	28.2	21.0
Average Concentration	16.8	8.2
Number of Observations	7	14

* Data included in this comparison are limited to samples collected from January through June of the two different years.

2. Meteorological conditions under which the 1985 data were collected may differ from those present during 1977;

3. The 1985 chromium data reflect a quantitation limit of 1.0 ng/m³. This concentration is approximately one eighth the quantitation limit for the 1977 data;

4. Chromium sampling during 1985 employed different collection and analysis methods than were used in 1977. The comparability of these various methods is not known.

Because data are available for the entire year of 1977, they were used to calculate annual exposure.

C. CONCENTRATIONS CLOSE TO SOURCES

To estimate concentrations of chromium close to sources of chromium(VI), emissions were calculated and air quality modeling done for a typical large chrome plater and for a bank of industrial cooling towers using chromate water treatment. Both sources are located in the South Coast Air Basin and are in populated areas.

After emissions from each source were calculated, an industrial source complex model (ISCST) was used to calculate annual average chromium concentrations at the points of a grid representing receptors surrounding each source. Residential population in the surrounding area was also gridded, and population exposure was estimated. The analysis encompassed an area 20 by 20 kilometers centered on the plating facility and an area 40 by 40 kilometer centered on the bank of towers. Deposition was not considered in this modeling.

The results of modeling are estimates of annual ambient concentrations based on worst case meteorology observed in the study areas. The modeled concentrations represent maximum annual average concentrations occurring outdoors. It is not known whether indoor concentrations are greater or less than those outdoors.

The concentrations and population exposures calculated from emissions from each source represent exposure above background from each source; possible additive or cumulative exposure from multiple sources is not addressed in this analysis.

Emissions of chromium from the chrome plating facility were calculated by the South Coast Air Quality Management District based on information provided by the company (Zwaicher, 1983). Chromium emissions from this source were estimated to be greater than 1,000 lbs/year. There are five chrome platers in the South Coast Air Basin which emit this or a greater amount of chromium per year. One facility was estimated to emit over 8,000 lbs/year of chromium per year. These figures reflect the assumption that 90 percent of chromium is removed by control equipment. Emissions were reported as chromium; no oxidation state was specified. Emission tests conducted by various agencies have indicated that worst-case chromium (VI) emissions from chromium platers comprise from 25 percent to 100 percent of total chromium emissions. (SCAQMD, 1985; Suzuki, 1984).

Results of modeling and population exposure assessment for the plating facility are presented in Table III-12, and shown in Figures III-11 and III-12. These numbers are estimated annual average chromium concentration above background. Because there is no information available to assess to what extent chromium(VI) reacts in the atmosphere after being emitted, the exposure is reported in terms of total chromium.

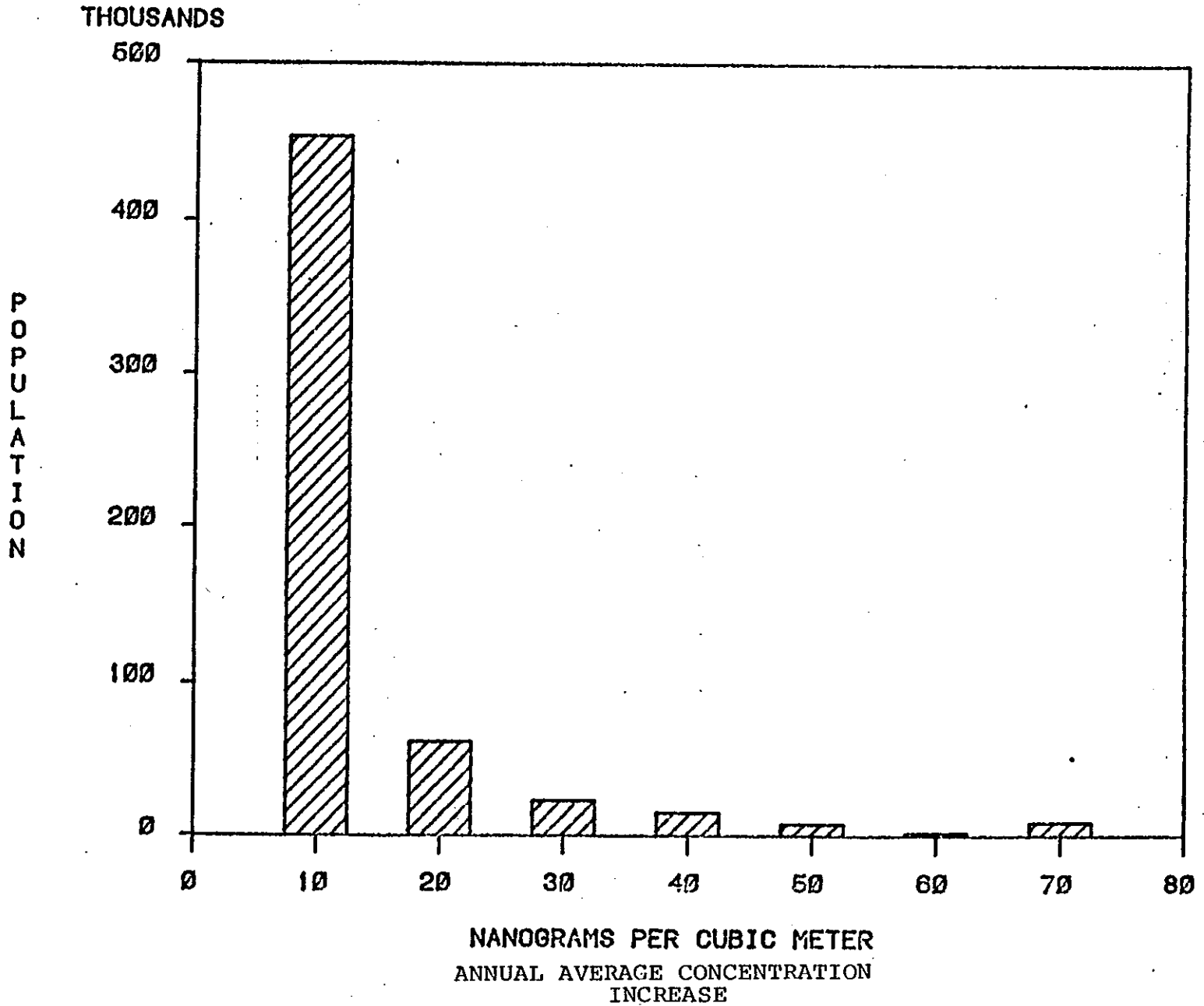
Table III-12

Increase in Population Exposure to Chromium
from a Plating Facility

<u>Annual Average Increase in Chromium Concentration, ng/m3</u>	<u>Population Exposed</u>	<u>Cumulative Population</u>
550	1,960	1,960
450	-0-	1,960
350	-0-	1,960
250	1,925	3,885
150	5,825	9,737
100	-0-	9,737
90	-0-	9,737
80	-0-	9,737
70	8,803	18,540
60	1,945	20,485
50	7,742	28,227
40	14,870	43,097
30	22,982	66,079
20	61,829	127,908
10	452,709	508,617
0.5 to 5.0	2,400,000	2,993,262

FIGURE III-11

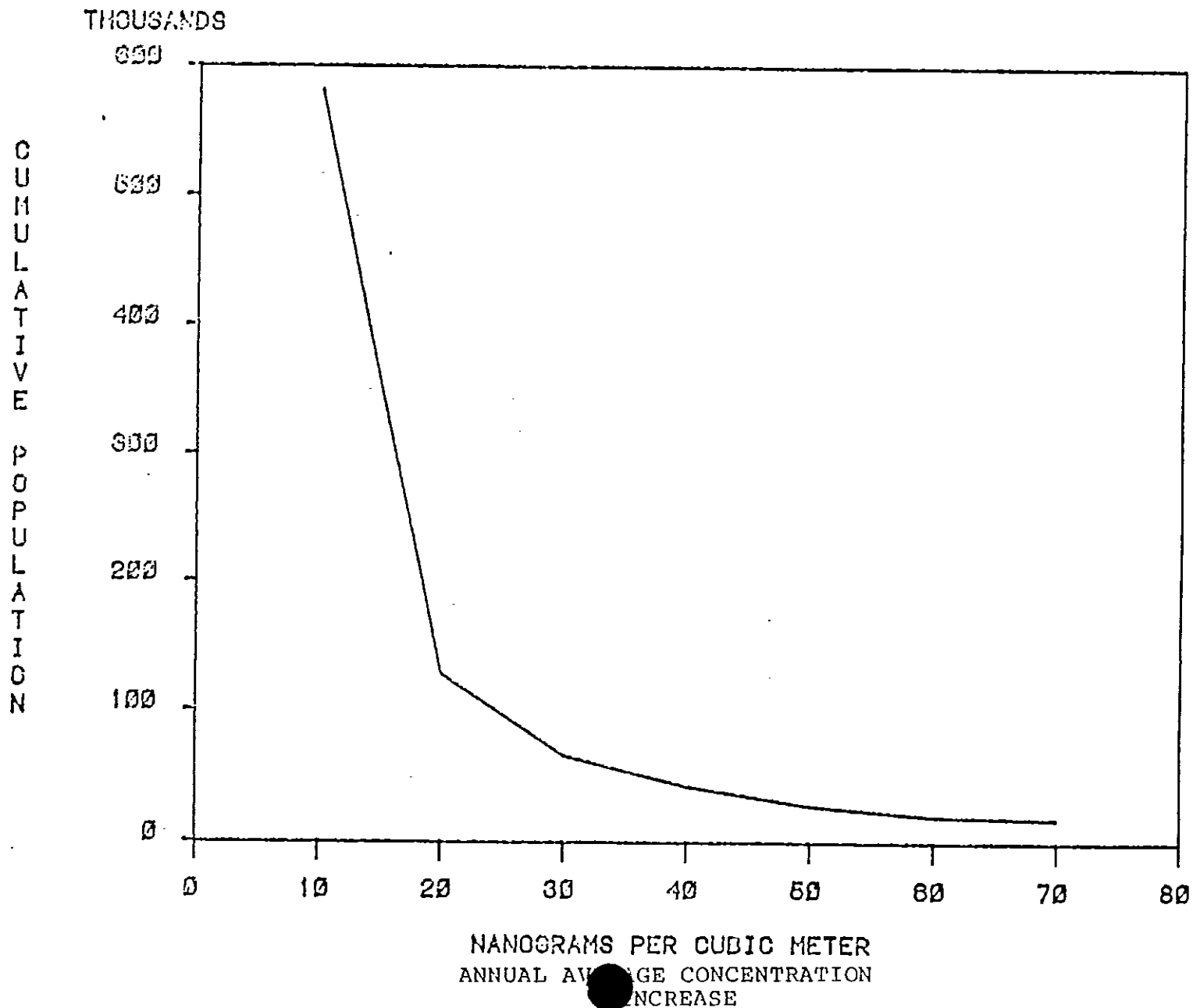
INCREASE IN
POPULATION EXPOSURE TO CHROMIUM FROM A PLATING FACILITY



III-35

FIGURE III-12

INCREASE IN
CUMULATIVE POPULATION EXPOSURE TO CHROMIUM FROM
A PLATING FACILITY



III-36

Relatively short distances are observed between the source and exposed population involved in this analysis; for instance, an elementary school is located within one kilometer of the source. Annual average concentrations of chromium at the school are estimated to fall between 100 and 500 ng/m³.

Emissions from a bank of industrial cooling towers were estimated based on recirculating water rate, average chromate treatment concentration in industrial towers, and information on the typical fraction of tower water emitted as drift. The annual emissions of chromium from these towers were estimated to be about 800 pounds. Results of modeling and exposure assessment are summarized in Table III-13 and shown in Figures III-13 and III-14. Values are reported as chromium because insufficient information exists to quantify the extent of reaction of emitted chromium(VI) occurring between the source and receptors.

TABLE III-13

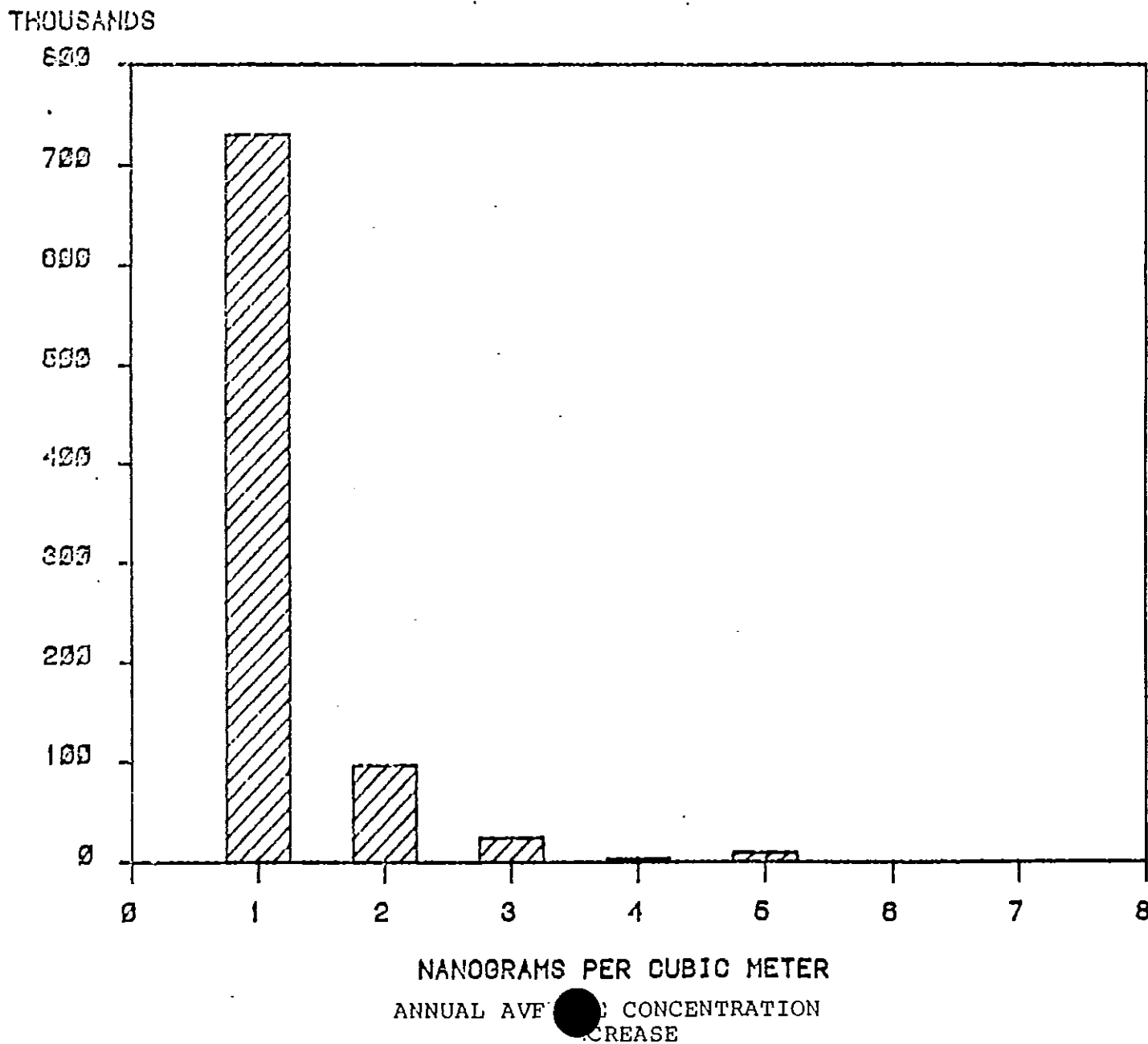
Increase in Population Exposure to Chromium from a Bank of Industrial Cooling Towers

Annual Average Increase in Chromium Concentration, ng/m ³	Population Exposed	Cumulative Population
5.0	8,886	8,886
4.0	2,993	11,879
3.0	23,942	35,821
2.0	96,565	132,386
1.0	730,336	862,722

In summary, estimates of concentrations of chromium close to sources of chromium(VI), and resulting population exposures have been made for two typical sources of chromium(VI) emissions. These health conservative estimates indicate that significant increases in population exposure to chromium may occur close to large sources.

FIGURE III-13

INCREASE IN
POPULATION EXPOSURE TO CHROMIUM FROM A BANK OF
INDUSTRIAL COOLING TOWERS

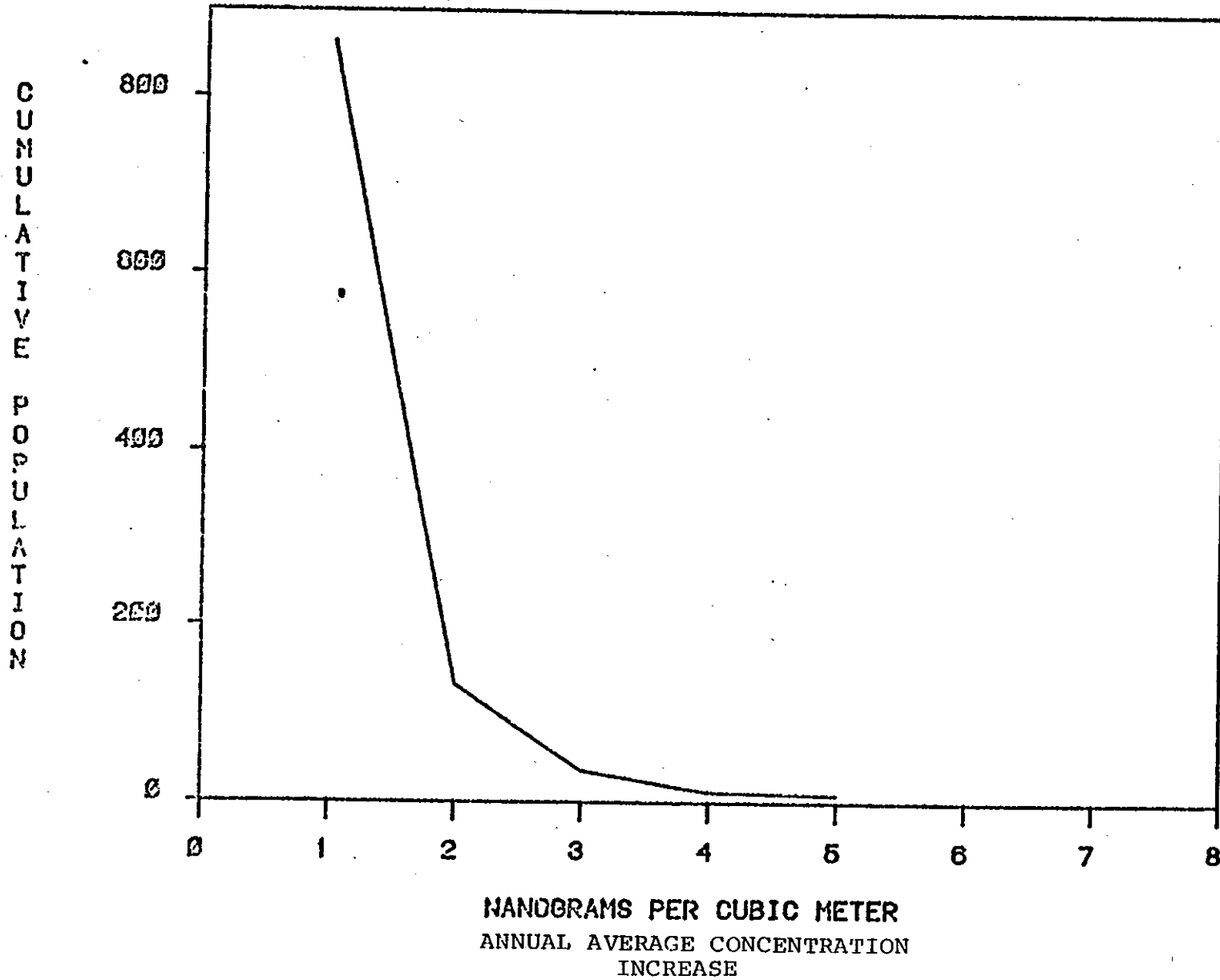


III-38

FIGURE III-14

INCREASE IN
CUMULATIVE POPULATION EXPOSURE TO CHROMIUM FROM A BANK
OF INDUSTRIAL COOLING TOWERS

THOUSANDS



III-39

D. EXPOSURE BY ROUTES OTHER THAN AMBIENT AIR

Human intake of chromium(III) occurs through consumption of chromium-containing foods. Chromium is found as a trace element in various foods. Data on the oxidation state of chromium in food are unavailable; only chromium or total chromium concentrations have been reported. Because chromium(VI) is a strong oxidizing agent, it is reasonable to expect that in the presence of bulk organic matter and water in food, chromium(VI) would be reduced to chromium(III). The chromium concentration in different types of foods has been measured at between 0.02 ug/g and 0.51 ug/g (Thomas, 1974). Chromium intake from a typical American diet of 43 percent fat was determined to be 62 ± 28 ug/day; from a typical American diet of 25 percent fat, intake of chromium was determined to be 89 ± 56 ug/day (EPA, 1984a). The DHS has found that trivalent chromium is an essential nutrient and is necessary for maintenance of normal glucose metabolism. Also, it is known that chromium(III) compounds are poorly absorbed from the gastrointestinal tract of animals, and that they are practically non-toxic when administered orally.

There is some evidence that human exposure to chromium may occur from drinking water. Chromium has been measured at low concentrations in some surface and groundwaters in California. Concentrations of up to 21 ppb were found in four of 72 spring water and three of 63 well water samples taken in the state (Silvey, 1967). In other California studies, no chromium was detected in 65 stream and 24 seawater samples (Soukup, 1972). The average chromium concentration in United States water supplies was determined to be 2.3 ppb (Schroder, 1962). A national mean daily intake of 17 ug/day of chromium in drinking water has been reported, with a range of 1 to 224 ug/day based on 2 l/d drinking water consumption (NAS, 1980). Chromium in water is

virtually all in the chromium (III) state, although chromium (VI) has been known to exist in natural waters with extremely low organic content. The extent to which anthropogenic sources are responsible for the presence of chromium detected in the hydrosphere is not known.

The extent of exposure to airborne chromium in the indoor environment, other than in the workplace, is not known. There are no direct consumer uses of chromium which could lead to emission of chromium compounds. Although cigarettes are known to contain chromium, the intake of chromium from smoking is not known.

The intake of chromium via these routes is summarized in Table III-14.

TABLE III-14
Intake of Chromium by Exposure Routes
Other Than Ambient Air

<u>Exposure Route</u>	<u>Chromium Oxidation State</u>	<u>Mean Daily Intake, ug (range, ug)</u>
Ingesting of Food	+3	62 (37-130)
Ingestion of drinking water	+3	17 (1-122)

Because chromium intake from food and water is in the trivalent state, chromium (as chromium (VI)) from ambient air represents the exposure route having the most significant public health effect.

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APPENDIX A

INFORMATION REQUEST LETTER WITH
ATTACHMENTS AND RESPONSES

AIR RESOURCES BOARD

1300 O STREET
BOX 2815
SACRAMENTO, CA 95812



July 31, 1984

Dear Sir or Madam:

Subject: Request for Information Regarding Chromium

I am writing to request information on the health effects of chromium as part of our toxic air contaminant program. This program is based on Health and Safety Code Sections 39650, et seq. which require the ARB to identify compounds as toxic air contaminants and once identified to develop and adopt control measures for such compounds. After consultation with the staff of the Department of Health Services (DHS), we have selected chromium as a candidate toxic air contaminant to be evaluated in accordance with the provisions of Health and Safety Code Sections 39650, et seq. During our evaluation of chromium, we will consider available health information on all forms and compounds of chromium. Additionally, we are soliciting information regarding environmental and biological transformations of chromium and its compounds.

Before the ARB can formally identify a compound as a toxic air contaminant, several steps must be taken. First, the ARB must request the Department of Health Services to evaluate the health effects of candidate compounds. Second, the ARB staff must prepare a report which includes the health effects evaluation and then submit the report to a Scientific Review Panel for its review. The report submitted to the Panel will be made available to the public. Information submitted in response to this request will be considered in the ARB report to the Panel. Although any person may also submit information directly to the Panel for its consideration, I urge you to submit all information at this time for our consideration in the development of the report for the Panel. The Panel reviews the sufficiency of the information, methods, and data used by the DHS in its evaluation. Lastly, after review by the Scientific Review Panel, the report with the written findings of the Panel will be considered by the Air Resources Board and will be the basis for any regulatory action by the Board to officially identify a compound as a toxic air contaminant.

Prior to formally requesting the DHS to prepare a health effects evaluation of chromium, we are providing, pursuant to the provisions of Section 39660(e) of the Health and Safety Code, an opportunity to interested parties to submit information on the health effects of chromium which he or she believes would be important in DHS's evaluation of chromium as a candidate toxic air contaminant.

July 31, 1984

In July 1984, ARS staff received a reference search on chromium health effects using the MEDLARS II and DIALOG Information Services. These information services include material available to the public on or before December 1983. The attached bibliography lists the references from this information search. We are requesting pertinent information on chromium health effects, including any material that may not be available to the public, that is not included in the attached bibliography.

Pursuant to the provisions of the Public Records Act (Government Code Sections 6280 et seq.), the information you provide will be a public record and subject to public disclosure, except for trade secrets which are not emission data or other information which is exempt from disclosure or the disclosure of which is prohibited by law. The information may also be released to the Environmental Protection Agency, which protects trade secrets and confidential information in accordance with federal law, and to other public agencies, which are also required to protect such information.

To expedite the review process, we ask that any information which you believe should be regarded as "trade secret" be clearly marked and separated from other information. You may identify portions of the information you submit as "trade secret" in accordance with Health and Safety Code Section 39660(e). The claim of trade secrecy must be supported upon the request of the Air Resources Board. Other information claimed to be trade secret and information otherwise claimed to be exempt from disclosure may be identified as confidential in accordance with Section 91011, Title 17, California Administrative Code. Section 91011 requires that the claim of confidentiality be accompanied by specified supporting information.

I would appreciate receiving any relevant information you wish to submit by August 31, 1984. Your help in expediting our review will be greatly appreciated. Please send the information to the attention of:

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

If you have any further questions regarding health effects information, please contact Mr. John Batchelder at (916) 323-1505. For any other questions, please contact Mr. Robert Barham at (916) 322-7072.

If you are not the person to whom this request should be addressed, please forward it to the appropriate person in your organization. Also, please let us know whether you would like to continue to receive information inquiries

July 31, 1984

for other candidate compounds, and if not, if there is anyone in your organization to whom such requests should be sent.

Sincerely,



Peter D. Venturini, Chief
Stationary Source Division

cc: Alex Kelter, DHS
Lori Johnston, DFA
Wayne Morgan, President, CAPCOA
Jan Bush, Executive Secretary, CAPCOA
David Howekamp, EPA Region IX
Assemblywoman Sally Tanner
APCOs

Attachment

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DOUGLAS AIRCRAFT COMPANY

3855 Lakewood Boulevard Long Beach, California 90846
TWX: 9103416342
Telex: 674357

August 13, 1984
C1-711-WB-84-177

William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Subject: Request for Information Regarding Chromium

Dear Mr. Loscutoff:

Douglas Aircraft Company, a division of the McDonnell Douglas Corporation, acknowledges receipt of the subject request.

Concerning information on the health effects of chromium as a candidate toxic air contaminant, Douglas Aircraft Company can be of no help.

Although Douglas Aircraft uses chromic acid in anodizing operations, the only physical fallout that Douglas experiences is the discharge of gaseous components expressed as hydrocarbons, particulate matter, sulfur dioxide and nitrogen dioxide. The discharge of these compounds arise from the painting, degreasing, abrasive blasting, oven use, and other manufacturing operations in which the Douglas Aircraft Company is involved.

Very truly yours,

W. Barnack, Jr.

W. Barnack, Jr.
Environmental Control Engineer
Plant Engineering

CONCURRENCE:

G. M. French

G. M. French
Manager - Plant Engineering
Design & Facilities Acquisition

WB/scc



IT CORPORATION

August 14, 1984

Mr. William V. Loscutt, Chief
Toxic Pollutants Branch
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Dear Bill:

CHROMIUM

A quick review of your bibliography on chromium indicates a couple of things:

a. The data bases you are searching may not include books and monographs. Two examples are:

Paul B. Hammond and Robert P. Bellies "Metals" - Chapter 17 In "Casarett and Doull's Toxicology: The Science of Poisons" 2nd Edition. MacMillan Publishing Co. (New York) 1980. Pages 409-467.

Marshall Sittig "Toxic Metals" Chapter on Chromium, pages 97-131. Noyes Data Corporation (Park Ridge, N.J.) 1976.

b. The data bases and/or search strategy are not picking up papers that discuss substances such as Cr in connection with another, perhaps broader topic. As you know, these are people who assert that a threshold for carcinogenesis must exist for metals, particularly trace metals that are found in all humans in measureable concentrations. Without prejudging that issue, it seems important that your bibliography at least include such papers from the literature. Two important examples that deal with Cr are:

William V. Loscutoff
August 14, 1984
Page 2

IT CORPORATION

George Claus and Karen Bolander "Environmental Carcinogenesis: The Threshold Principle: A Law of Nature", in "Pollution and Water Resources" (G. J. Halaj-Kun, Editor) Pergamon Press (New York) 1982. Pages 153-182.

Thomas H. Jukes "Chasing a Receding Zero: Impact of the Zero Threshold Concept on Actions of Regulatory Officials". J. Amer. Coll. Toxicol. 2 (3): 147-160, (1983).

Another paper on this subject, although not explicitly discussing Cr, is:

R. Koch "A Threshold Concept of Environmental Pollutants" Chemosphere. 12(1): 17-21 (1983).

I hope these references are helpful. Please continue to send me your data requests and exposure and health effects reports.

Very truly yours,

Nick

R. N. Hazelwood, Ph.D.
Project Manager
Environmental Affairs

RNH/sp

This could be very useful for calculating actual doses at the tracheal level as f (concentration) in air glass

Chromate Inhibition of Metabolism by Rat Tracheal Explants II. *In Vivo* Exposures

UNIVERSITY OF CALIFORNIA

Last

CPRC

DAVIS, CALIFORNIA 95616

#8704

RECEIVED
AUG 20 1984
Stationary Source
Division
Air Resources Board

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

4515
xplan

animals.

In an earlier study (Last *et al.*, 1977), we demonstrated that the secretion of mucus glycoproteins by tracheal slices incubated for 24 hr in tissue culture is inhibited by inclusion of Na_2CrO_4 in the culture medium. The extent of such inhibition was dependent upon the concentration of chromate in the medium; a biphasic dose-response curve was observed. In the second phase, at higher concentrations of chromate (above 0.27 mM), we also observed inhibition of precursor [^3H]glucosamine uptake and gross cytotoxicity. In the present study, analogous studies have been performed with tracheal

explants from rats exposed to Na_2CrO_4 *in vivo*, administered as an aerosol. We find that for equivalent concentrations of Na_2CrO_4 administered *in vivo* and *in vitro* (calculated as described below), there is equivalent inhibition of glycoprotein secretion rate in the tracheal explant assay (Last *et al.*, 1977). In addition, we have extended the previous findings of chromate-induced cytotoxicity by histochemical staining techniques.

Such a quantitative comparison of pollutant effects *in vivo* and *in vitro* is, to the best of our knowledge, a completely novel approach with no published precedents.

August 16, 1984

William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Reference: Chromium

Regarding July 31, 1984 ARB request for information on the health effects of Chromium. We have no data to submit at this time.

We would like to continue to receive information inquiries, etc. for other potential toxic air contaminants.

Sincerely,

Dale B. Hanson
Dale B. Hanson
Director, Engineering

DBH/dpc

cc: P. Charley
G. Sweeney

adcoat, inc.

172 East La Jolla Road, Placentia, California 92670 — (714) 630-7311

August 17, 1984

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P.O. Box 2815
Sacramento
CA. 95812

Dear Mr. Loscutoff:

Adcoat, Inc. does not, at this time, use any chromium or chromium compounds in its products.

We have, from time to time, considered the use of chromium containing pigments, so we would like to remain on your mailing list for information on chromium.

Very truly yours,
ADCOAT, INC.



HUGH H. MULLER
PRESIDENT

HHM/mw

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF BIOPHYSICS
AND MEDICAL PHYSICS
BERKELEY, CA 94720

UNIVERSITY OF CALIFORNIA, BERKELEY
6701 SAN PABLO AVENUE
OAKLAND, CA 94608
TELEPHONE (415) 642-7160

17 August 1984

Mr. Peter D. Venturini
Stationary Source Division
Air Resources Division
1102 Q Street
PO Box 2815
Sacramento, CA 95812

Dear Mr. Venturini:

Thank you for your letter of July 31 regarding chromium.

Any discussion or regulation concerning chromium should include consideration of the fact that, in small amounts, it is a nutritionally essential element. The recommended dietary allowance is 0.05 to 0.20 milligrams per day (National Academy of Sciences). See Recommended Dietary Allowances, 9th ed., 1980, National Research Council, Washington, D.C.

Chromium deficiency in human beings causes disturbances of carbohydrate metabolism, and marginal deficiency states may exist in the USA.

Kindly refrain from throwing the baby out with the bathwater. Thank you.

Enclosed is a publication by me.

Sincerely yours,

A handwritten signature in cursive script that reads "Thomas H. Jukes".

THOMAS H. JUKES

cc: William V. Loscutoff
R.N. Hazelwood
Assemblywoman Sally Tanner

Oil, Chemical and Atomic Workers
International Union

J. E. (JACK) FOLEY
DIRECTOR, DISTRICT NO. 1



304 FREEWAY CENTER BUILDING
3605 LONG BEACH BOULEVARD
LONG BEACH, CALIFORNIA 90807
PHONE: (213) 426-6961

August 10, 1984

State of California
Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Attention: Peter D. Venturini, Chief
Stationary Source Division

Dear Mr. Venturini:

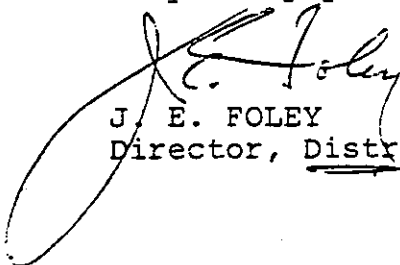
In response to your communication of July 31, 1984,
please continue to send this, and like correspondence to this
office and I would appreciate your forwarding the same
material to:

Mr. Dan Edwards, Director
Health and Safety Dept.
Oil, Chemical & Atomic Workers
International Union
P. O. Box 2812
Denver, CO 80201

I have taken the liberty of forwarding a copy of your
July 31st letter to him at our Denver office.

May I take this opportunity to thank you in advance for
your cooperation on the above request.

Very truly yours,


J. E. FOLEY
Director, District 1

JEF:ajs
cc: Dan Edwards
File

RECEIVED
AUG 14 1984
Stationary Source
Division
Air Resources Board

August 24, 1984

Mr. William V. Loscutoff
Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P. O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

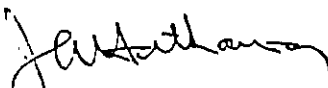
Re: Request for Information Regarding Chromium

We are enclosing copies of comments provided last year to the EPA's Science Advisory Board during their deliberations on the EPA's Health Assessment Document for Chromium. A number of the specific references mentioned in our comments were not listed in your bibliography and should be reviewed. The concerns we expressed to the EPA should also apply to both your review and that of the Department of Health Services.

Also enclosed is a copy of a lifetime intratracheal injection study in rats. A manuscript for publication related to this study is currently in preparation and will be forwarded when available. Additional studies on detoxification mechanisms for chromates have also been completed and manuscripts are in preparation. These studies provide substantial additional support for a threshold phenomenon for chromate carcinogenesis and will also be forwarded when available.

Please be sure we are included in future mailings related to chromium.

Sincerely,



J. A. Hathaway, M. D.
Director - Medical Services
Chemical Sector

JAH/hmw
Enclosures



Chevron Environmental Health Center, Inc.

A Chevron Research Company Subsidiary
15299 San Pablo Avenue, Richmond, California
Mail Address P.O. Box 4054, Richmond, CA 94804

R. D. Cavalli
Manager
Product Evaluation

August 22, 1984

William V. Loscutoff
Chief, Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

This letter is in response to your request for information on the health effects and environmental fate of chromium and its compounds. Upon review of our files we did not identify any in-house toxicology or environmental fate data on these materials. Several published reports were identified, however, which we believe will significantly contribute to the information already collected by the Air Resources Board. These references are listed below:

Ecological Analysts, Inc. (November 1981). The Sources, Chemistry, Fate and Effects of Chromium in Aquatic Environments. Available from API Publications, order No. 847-89600.

Environmental Protection Agency (July 1983). Health Assessment Document for Chromium, EPA 600/8-83-014A.

National Institute for Occupational Safety and Health (1975), Criteria for a Recommended Standard. Occupational Exposure to Chromium VI, HEW Publication No. 76-129.

National Institute for Occupational Safety and Health (1973), Criteria for a Recommended Standard. Occupational Exposure to Chromic Acid, HEW Publication No. 73-11021.

Please contact R. M. Wilkenfeld of my staff at (415) 231-5018 should you have questions concerning the information we are submitting.

Sincerely,

RDCAVALLI
JWE

**KAISER ALUMINUM
& CHEMICAL CORPORATION**

August 24, 1984

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Subject: CHROMIUM

Dear Mr. Loscutoff:

Kaiser Aluminum & Chemical Corporation thanks you for the opportunity to respond to your request for information regarding chromium. We are interested in chromium compounds because some are the basis for the manufacture of heat and chemical resistant materials known as refractories, which is the business of our Refractories Division.

Our concern centers exclusively around trivalent chromium present in the ore of chromium. We call this ore "chromite." Chromite is among the materials most resistant to chemical change. It is insoluble in water and in all common bases and acids including aqua regia. It is also relatively insoluble in most of the aggressive leaching substances designed to categorize hazardous wastes. Examples of such leaching substances include citric and acetic acids.

Many of the references cited in the attachment to the "Request for Information Regarding Chromium" attest to the absence of exposed worker health effect from chromite.

Battelle Memorial Institute, Columbus, Ohio, published a study in February 1983 regarding their investigations to determine the extent of health hazard from trivalent chromium compounds used in the refractories industry. We suggest you refer to a copy of that study (Exhibit A, attached) and add their bibliography to the chromium references provided with the State's request for information on chromium.


Exhibit B, attached, is a report by Joseph J. Durek, Ph.D., which was part of a submission to the Department of Health Services in the latter part of 1983. Dr. Durek's report indicates the permanence of chromite, since the mineral is found unaltered in the environment.

The third attachment, Exhibit C, by Dr. Harry Mikami, an acknowledged expert on chromite, is further substantiation for the permanence of chromite in the environment. Dr. Mikami's paper and the references he cites should be part of the references used in rule making.

Because of potential concern about trivalent chromium in solution (water) we hired a Bay Area engineering company to perform preliminary toxicity tests on rainbow trout using 750 grams of chromite per liter of water. Rainbow trout are exceedingly sensitive to toxic substances and are a good choice for delicate testing. There were no fatalities in the 96 hours of exposure.

Kaiser Aluminum & Chemical Corporation believes that any regulation on chromium compounds emitted to the atmosphere should recognize the distinct difference in health effects between trivalent and hexavalent compounds.

Sincerely,



Rod E. Ewart, CIH
Industrial Hygiene Manager

Attachments: Exhibit A, "Report on Evaluation of the Potential Health Effects of Trivalent Chromium Compounds in the Refractories Industry," by Joiner, Rench, Zanetos, and Brauning, Battelle Columbus Laboratories, Columbus, OH, February 18, 1983

Exhibit B, "Chromite Distribution in California," by J. J. Durek, Kaiser Aluminum & Chemical Corporation, Oakland, CA, August 24, 1984.

Exhibit C, "Chromite," by H. M. Mikami, from Industrial Minerals and Rocks, 4th Ed., A.I.M.E., 1975



Diamond Shamrock
Chemicals Company

Technical Center

August 23, 1984

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

In response to Mr. Peter Venturini's solicitation for information on the toxicity of chromium, I have included several pieces of information to aid in your review. These include:

1. "Chromates Symposium 80"
2. U.S. EPA list of references taken from a 7/83 draft of their health assessment document on chromium.
3. "Testing Sodium Dichromate and Soluble Calcium Chromate for Carcinogenicity in Rats" - final draft.

Another study, sponsored by the American Wood-Preservers' Institute, titled "Effects of Chemical Preservatives on the Health of Wood Treating Workers in Hawaii, 1981 - Clinical and Chemical Profiles and Historical Prospective Study - July, 1983" was not included but contains findings related to worker exposure to chromium containing wood preservatives. A copy of this study can be obtained by contacting:

J. E. Wilkinson
Reichold Chemicals, Inc.
2340 Taylor Way
Tacoma, Washington 98401

The proceedings from the Industrial Health Foundation's "Chromates Symposium 80" is an excellent collection of pertinent information describing the acute & chronic toxic effects that have been attributed to exposure to chromium containing compounds.

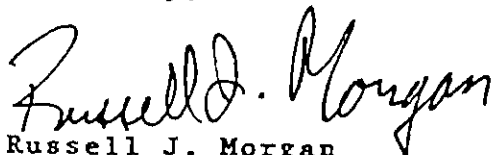
Mr. William V. Loscutoff, Chief
California Air Resources Board
August 23, 1984
Page 2

The list of references is from an external draft of the Office of Health and Environmental Assessment's (OHEA) "Health Assessment Document for Chromium" which was released for review and comment in July, 1983. The document itself was returned to EPA for further revision and is expected to be released shortly. This health assessment document was developed for use by the Office of Air Quality Planning and Standards to support decision-making regarding possible regulation of chromium as a hazardous air pollutant. If you contact Dr. Si Duk Lee of OHEA of the U.S. EPA, I'm sure he'd be happy to provide you with a copy of the revised document when it is available.

The study "Testing Sodium Dichromate and Calcium Chromate for Carcinogenicity in Rats" conducted by Bayer AG, Institute of Toxicology is a final draft and should be regarded as confidential until its publication in the journal, Cancer. I have included it because the findings are significant and the study itself is one of the best done on this subject to date. This work was planned, designed and sponsored within the framework of the Industrial Health Foundation by a number of the world's chromium chemicals producers.

In closing, we here at Diamond Shamrock appreciate the opportunity to participate and contribute toward your evaluation of air borne chromium. Please don't hesitate to contact me if we can be of any further help.

Sincerely,



Russell J. Morgan
Chromium Chemicals Group
Research & Development

kjv

PACIFIC GAS AND ELECTRIC COMPANY

PG&E + 77 BEALE STREET • SAN FRANCISCO, CALIFORNIA 94106 • (415) 781-4211 • TWX 910-372-6587

H. M. HOWE
CHIEF SITING ENGINEER

August 29, 1984

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Information Inquiries Mailing List
Requests for Public Health Information

Pacific Gas and Electric Company received your July 31, 1984 request for additional public health information regarding chromium. We reviewed the bibliography and concluded that we are unaware of any additional public health effects information which would be of use to you.

It is generally recognized that hexavalent chromium is far more potent than trivalent chromium. In fact, your bibliography includes references addressing such differences. However, by requesting information on "chromium" you appear to be overlooking such differences.

As a matter of general principle, PG&E thinks that any risk assessment document forwarded to the Science Review Panel for their review should include separate risk assessments for each compound or valence state of concern -- particularly when the available data suggest that such differences may be significant.

Please continue to send future information inquiries to me at the above address.

Thank you.

Sincerely,

*B. B. Woobleski for /
J. F. McKenzie*

J. F. MCKENZIE
Supervising Civil Engineer



3801 West Temple Avenue
Pomona, California 91768
Telephone (714) 598-4592

August 29, 1984

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Pursuant to your request for information regarding chromium health effects, I have determined that the University does not have any information which I believe would be important in the Department of Health Services' evaluation of chromium as a candidate toxic air contaminant.

Sincerely,

Michael R. Ceser
Environmental Health & Safety Officer

MRC:cb

cc: President La Bounty
Dorothy Roberts

Agriculture
Arts
Business Administration
Engineering
Environmental Design
Science
Teacher Preparation

301 Pigeon Point Road
New Castle, Delaware 19720
(302) 652-3301
Telex 905033
Answerback: AMMIN NCST
Cable AMINPAR Newcastle, DE

American Minerals

September 4, 1984

Mr. William Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
Box 2815
Sacramento, Ca. 95812

Dear Mr. Loscutoff:

This is in reply to your request for information concerning the toxicity of Iron Chromite. We have just received a copy of the letter from Mr. Venturini and, therefore, were not able to respond by the indicated deadline. It is hoped that you will consider our evidence in spite of it being late.

American Minerals is a supplier of Iron Chromite to the glass industry in California, so these hearings are very important to us. Iron Chromite is really a natural ore of Chromium which we import from South Africa and grind in our plants in El Paso, Tx. and Wilmington, Del. Although we have been involved with Iron Chromite for more than 25 years, we have never noted an unusual incidence of cancer in any of our plants.

Iron Chromite has the essential formula of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ which means that the Chromium is in the trivalent state. We should like to submit in evidence, pages 18 to 29 of a report by Battelle Institute entitled, "Evaluation of the Potential Health Effects of Trivalent Chromium Compounds in the Refractories Industry".

The pages enclosed contain a good summary of the experimental work that has been carried out in this field. Please note on page 27, "The information available on human exposure to chromium compounds suggests that exposure to the trivalent chromium

Received
SEP 07 1984
A.W.

American Minerals

301 Pigeon Point Road
New Castle, Delaware 19720
(302) 652-3301
Telex 905033
Answerback: AMMIN NCST
Cable AMINPAR Newcastle, DE

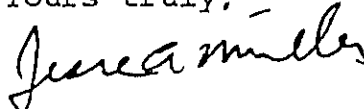
compounds does not produce a significant increase in cancer incidence."

We can send you a copy of the entire report if this would be of interest to you, but we did not want to burden your files.

We are also enclosing a copy of a letter from Dr. L.E. Thompson who serves as a consultant for us. His opinion is that "The probability of hexavalent chromium being produced in any substantial quantity in the reactions assumed in the fusing of glass, is relatively small."

Please place my name on your mailing list to receive notifications of hearings concerning Chromium. If we can supply you with any further information, please write or call us.

Yours truly,



Jesse A. Miller
Vice President

15
OCAW

Oil, Chemical & Atomic Workers
International Union, AFL-CIO



Joseph Misbrenner, President
Michael Ricigliano, Secretary-Treasurer
L. Calvin Moore, Vice President
Robert E. Wages, Vice President

International Offices:
255 Union Blvd., Lakewood, CO 80228
303/987-2229

Mail: P.O. Box 2812, Denver, CO 80201

→ Bill
Adjunct
Mechanist
[Signature]

August 27, 1984

RECEIVED

SEP 4 1984

Stationary Source
Division
Air Resources Board

Peter D. Venturini, Chief
Stationary Source Division
State of California,
Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Re: Request for Information
Regarding Chromium

Dear Mr. Venturini:

Reference is made to your letter of July 31, 1984, regarding the above, addressed to Director Foley, and Director Foley's August 10, 1984, response to you (copy attached).

First, I concur with Director Foley's request to direct future requests of this nature directly to this office, while continuing to direct a copy of such requests to his office.

Regarding Chromium, this office has no unpublished or other information other than that contained in the standard reference literature, which I'm sure you already have. We also have no information regarding environmental and/or biological transformations of chromium and its compounds.

Thank you for the opportunity to provide information.

Yours truly,

[Signature: Dan C. Edwards]

Dan C. Edwards, Director
Health and Safety Department

c-R. E. Wages, Vice President
J. E. Foley, Director



CALIFORNIA CAST METALS ASSOCIATION

1722 J Street • Suite 14 • Sacramento, CA 95814 • (916) 442-6233

Frederick J. Simonelli
Executive Director

William P. Conway, Jr.
Administrative Director

Hazel Kagan
Legislative Analyst

September 5, 1984

Mr. Peter D. Venturini
Stationary Source Division
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Venturini:

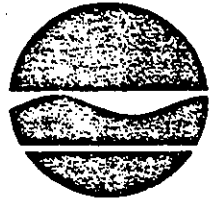
I have no information regarding the toxicity of chromium, but wish to continue to receive inquiries for other candidate compounds.

Sincerely,

Jay Dyer, Jr.
Administrative Assistant

JD:em

New York State Department of Environmental Conservation
50 Wolf Road, Albany, New York 12233-0001



Henry G. Williams
Commissioner

September 6, 1984

Mr. William V. Loscutoff, Chief
Toxics Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

At your request for information regarding Chromium as a toxic air contaminant (TAC), we are enclosing copies of "New York State Air Guide-1 - Guidelines for the Control of Hazardous Ambient Air Contaminants" and "Part 212 - Processes and Exhaust and/or Ventilation Systems" for environmental ratings in the State of New York.

After extensive research done by New York State Department of Environmental Conservation and the Department of Health, hexavalent chromium and derivatives have been classified as high toxicity air contaminants. After reviewing your enclosed references, I do not think that we could add any more useful information at the present time. We are enclosing the above documents that our Regional Air Pollution Control Engineers (RAPCEs) use as a reference guide in trying to minimize the hazards of toxic contaminants in our environment.

We would be very interested in receiving a copy of your report on Chromium when available.

Sincerely,

Carlos L. Montes
Asst. Research Scientist
Bureau of Air Toxics
Division of Air

Enc.

SEP 15 1984

7/15/84



DEPARTMENT OF THE ARMY
U. S. ARMY ENVIRONMENTAL HYGIENE AGENCY
ABERDEEN PROVING GROUND, MARYLAND 21010-5422

REPLY TO
ATTENTION OF

05 SEP 1984

Occupational and Environmental
Medicine Division

Mr. William V. Loscutoff
Chief, Toxic Pollutants Branch
California Air Resources Board
P. O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

This Agency has no information which would be pertinent to your evaluation of the health effects of chromium. However, we are aware of a recent EPA draft document which you may want to review if you have not already done so. The draft document, Health Assessment Document for Chromium, SRC TR-84-628, May 7, 1984, and any public comments thereto should provide important information on the current assessment of chromium's health effects. This document was published by the U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina 27711. Project coordinator is Si Duk Lee, Ph.D.

Questions or comments to this Agency should be addressed to Major Robert W. Petzold, M.D., M.P.H., telephone (301) 671-2464.

Sincerely,

Joel C. Gaydos
Joel C. Gaydos, M.D.
Colonel, Medical Corps
Director, Occupational and
Environmental Health

SEP 11 1984

19/8

Memorandum

To : William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Date : September 6, 1984

Place : Sacramento

From : Department of Food and Agriculture

Subject: Response to Request for Information Relevant to DOHS Evaluation of Chromium as a Candidate Toxic Air Contaminant

In response to your request, I am enclosing a copy of the print-out of references in the Department of Food and Agriculture's Registration Library. Please be advised that some of these references may be confidential access and as such may fall under the Department's policy on such matters.

Lori Johnston, Assistant Director
Pest Management, Environmental
Protection and Worker Safety
(916) 322-6315

Attachment



HEUBACH INC.
256 VANDERPOOL STREET
NEWARK, NEW JERSEY 07114
201-242-1800

Stett

September 24, 1984

Air Resources Board
1102 Q Street
P.O. Box 2815
Sacramento, CA 95812
ATTN: Mr. Peter Venturini

Dear Mr. Venturini:

We received through our California sales office a request for information on Chromium. I suggest that this request be directed to the Dry Color Manufacturers' Association who should be in a position to provide you with comprehensive information on health effects of chromium based pigments. You may wish to address this request to:

Dry Color Manufacturers' Association
P.O. Box 931
Alexandria, VA 22313
ATTN: Mr. J. Lawrence Robinson
Executive Vice President

I am sure this will enable you to get pertinent information for your study.

Sincerely,

P. A. Wriede

P. A. Wriede
Vice President, R&D

PAW:mr

cc: J. L. Robinson - DCMA

RECEIVED
OCT 1 1984
Stationary Source
Division
Air Resources Board

Representing the Color Pigments Industry

SUITE 202, 206 NORTH WASHINGTON STREET
ALEXANDRIA, VA 22314 (703) 684-4044

Mailing Address:
P.O. BOX 931, ALEXANDRIA, VA. 22313

December 20, 1984

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P.O. Box 2815
Sacramento, California 95182

Dear Mr. Loscutoff:

The Dry Color Manufacturers' Association is pleased to provide you with additional references as a result of your request of October 4 concerning information regarding chromium.

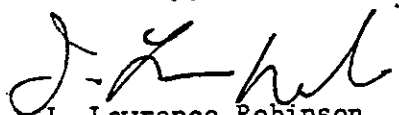
The Dry Color Manufacturers' Association is an industry trade association representing small, medium and large pigment color manufacturers throughout the United States and Canada, accounting for approximately 95% of the production of color pigments in this country. Foreign pigment manufacturers with sales in the United States and Canada and suppliers of intermediates to the pigments industry are also members of the Association. The Lead Chromate Committee of the DCMA represents manufacturers of lead chromate pigments and the enclosed comments are prepared by that committee.

You will find enclosed a copy of a report entitled, "The Effect of a Range of Chromium-Containing Materials on Rat Lung", a study conducted by the University of Aston in Birmingham, England, sponsored by the DCMA and others. You will note that this study indicates significant differences in different chromium compounds. In particular, the solubility of chromium pigments is much lower than other chromium compounds, and their impact on the environment is significantly less.

Also enclosed is a paper entitled, "Mutagenicity of Chromium Compounds" by F. L. Petrilli and S. De Flora which appeared in the Proceedings of the Chromate Symposium 1980. In that paper you will note the importance that the authors place on threshold levels.

We trust that this information is of assistance to you. Should you have any questions concerning lead chromate pigments, please feel free to call upon us.

Sincerely,


J. Lawrence Robinson
Executive Vice President

Enclosures

DEC 27 1984

APPENDIX B


HEALTH EFFECTS REQUEST TO
THE DHS AND LETTER OF RESPONSE

Memorandum

Peter Rank, Director
Department of Health Services
714 P Street
Sacramento, CA 95814

Date : October 3, 1984

Subject: Evaluation of
Chromium


James D. Boyce
Executive Officer
From : Air Resources Board

I am writing to formally request that the Department evaluate the health effects of chromium as a candidate toxic air contaminant in accordance with Assembly Bill 1807 (Tanner). According to Health and Safety Code Sections 39660-62, your Department has ninety days to submit a written evaluation and recommendations on the health effects of chromium to the Air Resources Board and may request a thirty day extension.

Attached for your staff's consideration in evaluating chromium are: Attachment I - a suggested list of topics that we believe should be included in your chromium evaluation and recommendations; Attachment II - a list of references on chromium health effects which were identified in an ARB letter of public inquiry; Attachment III - additional references received from the public in response to the inquiry letter; Attachment IV - comments provided by Allied Chemical to EPA's Science Advisory Board during SAB's deliberations on EPA's Health Assessment Document for Chromium; and Attachment V - ambient chromium concentration data and emission trends which should be used to estimate the range of risk to California residents as required in Health and Safety Code Section 39660(c).

My staff is available for consultation in conducting this health effects evaluation. We look forward to continuing to work closely with you and your staff in carrying out this legislative mandate. If you have any further questions regarding this matter, please contact me at 445-4383 or have your staff contact Peter D. Venturini, Chief of the Stationary Source Division, at 445-0650.

Attachments

cc: Gordon Duffy
Alex Kelter w/attachments
Raymond Neutra w/attachments
Peter D. Venturini
Assemblywoman Sally Tanner
Claire Berryhill
Emil Mrak, Chairman and Members
of the Scientific Review Panel

CHROMIUM: TOPICS TO BE INCLUDED IN FINAL STAFF REPORT ON CHROMIUM

I. CHEMICAL AND PHYSICAL PROPERTIES

- A. Valence States
- B. Chromium Containing Compounds
- C. Environmental Transport
- D. Industrial Uses

II. INHALATION TOXICOLOGY OF CHROMIUM

- A. Occurrence of Chromium in Particulate Matter
- B. Deposition in the Lung
- C. Defense Responses of the Lung
- D. Inhibition of Normal Pulmonary Functions
- E. Fibrogenic Potential of Chromium

III. CARCINOGENICITY (REVIEW ARTICLES: U.S. EPA, DRAFT DOCUMENT, 1983; IARC, 1980)

- A. Human Evidence (Hayes, 1982; Norseth, 1981; Langard, 1983; and Leonard and Lauwerys, 1980)
 - 1. Epidemiologic studies of workers in the production of chromium compounds
 - a. Strong association between industrial exposure and respiratory cancer
 - b. Undefined exposure levels
 - c. Exposure may include chromite ore, Cr(III) and Cr(VI) compounds with various solubilities.
 - 2. Epidemiologic studies of workers in the production and use of chromium pigments
 - a. Some indication that workers in chromium pigment production had increased respiratory cancer.
 - b. The risk associated with the use of such pigments and products containing such pigments is less certain.
 - c. Major exposure is to Cr(VI) in compounds such as lead and zinc chromates.
 - 3. Epidemiologic studies of workers in chrome plating industry
 - a. Data are inconclusive to determine the risk of respiratory cancer
 - b. Chromium oxides are the major exposure
 - 4. Epidemiologic studies of workers in ferro-chromium industry
 - a. Some indication of increased lung cancers
 - b. Exposure to Cr(III), Cr(VI) compounds and possibly other carcinogens such as asbestos and benzo(a)pyrene

- B. Animal Evidence (Hayes, 1982; Norseth, 1981; Langard, 1983; and Leonard and Lauwerys, 1980)
 1. The carcinogenicity of different compounds containing chromium has been studied in laboratory animal species through various routes of exposure.
 2. Sufficient evidence exists for Cr(VI) compounds in causing cancer in animals--e.g., calcium chromate, strontium chromate and zinc chromate.
 3. Chromium (VI) compounds have been shown to be carcinogenic by different routes of exposure--e.g., intrabronchial, intrapleural, intramuscular implantation and subcutaneous injection.
 4. Both Cr(III) and Cr(VI) compounds have been ineffective in producing lung tumors in animals.
 5. Cr(III) compounds have not been shown to be carcinogenic in animals by oral administration.

IV. SHORT-TERM TESTS FOR GENOTOXICITY

IARC (1982) considered the evidence for the genotoxic activity of hexavalent chromium to be sufficient and the evidence for trivalent chromium to be inadequate.

The most recent review articles on the genotoxicity of chromium compounds include those by: Levis and Bianchi (1982); Sirover (1981); Hatherill (1981); and EPA (1983). The following outline on the genotoxicity of chromium compounds emphasizes articles published subsequent to the IARC monograph review (1980) and complements the above-listed reviews. The outline is not meant to be comprehensive. Representative articles in each category are listed.

- A. Gene Mutation or DNA Damage in Bacteria or Fungi
 1. Gene Mutations - Hexavalent Chromium (Cr VI) was mutagenic in several Salmonella strains. Trivalent chromium (CrIII) was negative. (Bennicelli, et al., 1983; Petriilli and DeFlora, 1981.)
 2. DNA Damage - Cr(VI) induced DNA damage as determined by B. Subtilis rec repair assay. (Kada, et al., 1980.)
- B. Gene Mutation or DNA Damage in Mammalian Cells (excluding human cells)
 1. Gene Mutation - Cr(VI) was mutagenic in V79 Chinese hamster cells in culture (Paschin, et al., 1983; Newbold, et al., 1979). Cr(III) was inactive in V79 cells (Newbold, et al., 1979).
 2. DNA Damage - Cr(VI) induced DNA cross-links, strand breaks, and DNA-protein cross links in chick embryo hepatocytes (Tsapakos, et al., 1983). Rainaldi, et al. (1982) reported that Cr(VI) induced sister chromatid exchanges in V79 cells in vitro in a dose-dependent manner.
- C. DNA Damage in Human Cells
 1. In vitro - Stella, et al. (1982) reported that Cr(VI) induced sister chromatid exchanges (SCE) in human lymphocytes in culture in a dose-dependent manner. Cr(III) was inactive.

2. In vivo - Workers exposed to chromic acid (Cr[VI]) had increased SCE's compared to unexposed controls (Sarto, et al., 1982).

D. Chromosomal Effects

1. Stella, et al. (1982) reported significant increase in chromatid-type aberrations (gaps and breaks) in human lymphocytes in vitro at Cr(VI) concentrations above $2.5 \times 10^{-7}M$. One hundred times more Cr(III) was required compared to Cr(VI) to increase the frequency of chromosomal aberrations.
2. Sarto, et al. (1982) reported increased chromosomal aberrations in workers exposed to chromic acid (Cr[VI]).

E. Other Short-Term Tests for Genetoxicity

1. Dominant lethal assay - Cr(VI) was positive in mice. There was a dose-dependent relationship (Knudsen, 1980).
2. Mouse spot test - Welding fumes and Cr(VI) were positive (Knudsen, 1980).

V. REPRODUCTIVE EFFECTS

A. Animal Studies

1. Teratogenesis:

<u>Species</u>	<u>Method of Administration</u>	<u>Oxidation State</u>	<u>Author(s)</u>	<u>Effects</u>
a. Mice	I.P. Injection	Cr(III)	(Matsumoto, <u>et al.</u> 1976)	Fetal deaths exencephaly, open eyelids, cleft palate, skeletal malformations
b. Hamsters	I.V. Injection	Cr(VI)	Gale, 1978)	Fetal deaths, cleft palate, skeletal defects
c. Hamsters (pregnant)	I.V. Injection days 7,8,9	Cr(VI)	Gale and Bunch, 1979)	Fetal deaths, cleft palate
d. Mice/Blastocysts & egg cylinders	In Vitro	Cr(VI)	Ijima, <u>et al.</u> 1983)	Degeneration of Inner Cell Mass, ↑ in No. of S.C.E.'s, ↓ in development and crownrump length
e. Mice (pregnant)	I.P. Injection day 8	^{51}Cr (III)	(Ijima, <u>et al.</u> 1983)	Neural tube defects

1. Teratogenesis (continued):

<u>Species</u>	<u>Method of Administration</u>	<u>Oxidation State</u>	<u>Author(s)</u>	<u>Effects</u>
f. Chicken Eggs	Air Sac Injection	Cr(VI)	(Gilano & Marano, 1979)	Skeletal Malformations, exencephaly, microphthalmia, evisceration/ decreased body size
g. Chick Fibroblast	In Vitro	Cr(III), Cr(VI)	(Denker, et al., 1983)	Inhibition of cartilage formation (skeletal defects)

2. Impaired Fertility

<u>Species</u>	<u>Method of Administration</u>	<u>Oxidation State</u>	<u>Author(s)</u>	<u>Effects</u>
a. Sea Urchin	Pre-treatment of sperm Gametes	Cr(VI) Cr(III)	Pagano, et al. 1983)	↓ Fertilization No Malformation
b. Marine Polychaete	2-Generation Toxicity Test	Cr(VI) Cr(III)	Oshida & Word, 1982	↓ # of Offspring Change in Spawning Time No Change
c. Rabbit	IP, 2 mg/kg	Cr(III), or Cr(VI)	Behari, 1978 (From Lee, 1983)	↓ Testicular Succinic dehydrogenase ↓ ATP-Ase Multi-nucleated Germ Cells Degeneration of Spermatocytes

- B. Human Effects
1. Chromium levels in placentas and in maternal and fetal blood in 25 maternal-fetal sets from each of eight geographic areas in the United States. Stable maternal-fetal chromium ratio demonstrated in spite of geographic variation. (Creason, et al. 1976)
 2. Lack of relationship between levels of chromium in drinking water in 48 local areas in South Wales and increased CNS malformation rates. (Elwood, et al. 1974)

- C. Discussion of Animal Data
1. Mechanism of Action - Maternal Toxicity
 2. Effects on Fertility

D. Human Data (insufficient)

VI. ACUTE TOXICITY (REVIEW ARTICLE: IARC, 23 (1980))

- A. Cr(VI)
1. Fatal ingestion (1.5 - 6 g) causes hemorrhage in various organs, shock and death
 2. Toxic to renal tubules and liver
 3. Corrosive to nasal septum
 4. Contact sensitivity in the skin
 5. Bronchial asthma and pulmonary edema
 6. Irritation of mucus membranes (including conjunctivitis and corneal injury and respiratory irritation)
- B. Cr
1. Chromium metal is relatively nontoxic
- C. Cr(III), Cr(II)
1. Inhalation of insoluble chromite dust produces pneumoconiotic changes consisting of thickening of interstitial tissue, fibrosis and hyalinization of the lungs.
 2. Inhalation of soluble chromic and chromous salts have produced no established acute toxicity with the exception of dermatitis.

VII. PHARMACOKINETICS

A. Absorption, Distribution and Excretion

Chromium is absorbed from the gastro-intestinal tract and the airways of the lungs. Following inhalation exposure, it may deposit in the pulmonary tissues. Chromium is excreted in the urine and also from the GI tract where biliary excretion plays an important role (Langard, 1982).

B. Metabolism

Chromate, Cr(VI), is reduced in the cells of the body to produce Cr(III). Molecules containing sulfhydryl groups easily reduce chromate. Several proteins contain chromate-reductase activity. This activity is found in the microsomes and mitochondria. (Connett and Wetterhahn, 1983.)

VIII. RISK ASSESSMENT (REVIEW ARTICLES: U.S. EPA, DRAFT [1983]; IARC, VOL. 23 [1980]; AND SUPPLEMENT [1982])

- A. Threshold Determination
 - 1. Solubility of Compounds
 - 2. Valence States
 - 3. Route of Administration
- B. Dose-response Assessment Based on:
 - 1. Available Animal Data
 - 2. Human Epidemiology and Monitoring
 - 3. Workplace Evidence
- C. Range of Potential Risks
 - 1. Study of Manușco (1975) - See EPA Draft
 - 2. CAG Estimate
 - 3. Population at Risk

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Additional references submitted by the public at large:
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Submitted by J. A. Hathaway, M.D. Director - Medical Services Chemical
Sector Allied Chemical

Streinhoff, D., Gad, Sn.C., Hatfield, G.N., and Mohr, V. (Sept. 1983). Testing sodium dichromate and soluble calcium chromate for carcinogenicity in rats. Bayer AG. Institute of Toxicology. (submitted for publication)

Submitted by Thomas H. Jukes, Ph.D., Dept of Biophysics and
Medical Physics and the Dept. of Nutritional Sciences, U.C. Berkeley:

Jukes, T.H. (1983). Chasing a receding zero: Impact on the zero threshold concept on Actions of Regulatory officials. J. Amer. Coll. Toxicol. 2(3):147-160.

Submitted by R.D. Cavalli Manager Product Evaluation Chevron
Environmental Health Center, Inc.

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Submitted by Rod E. Ewart, CIH Industrial Hygiene Manager
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Submitted by Russell J. Morgan Chromium Chemicals Group Research
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Chromates Symposium 81. see original bibliography

EPA Health Effects References. See original bibliography.

Testing Sodium Dichromate and soluble Calcium Chromate for carcinogenicity in rats.
See reference submitted by J.A. Hathaway.

August 24, 1984

Mr. William V. Loscutoff
Chief
Toxic Pollutants Branch
Re: Chromium
California Air Resources Board
P. O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

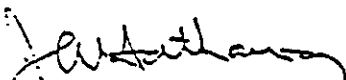
Re: Request for Information Regarding Chromium

We are enclosing copies of comments provided last year to the EPA's Science Advisory Board during their deliberations on the EPA's Health Assessment Document for Chromium. A number of the specific references mentioned in our comments were not listed in your bibliography and should be reviewed. The concerns we expressed to the EPA should also apply to both your review and that of the Department of Health Services.

Also enclosed is a copy of a lifetime intratracheal injection study in rats. A manuscript for publication related to this study is currently in preparation and will be forwarded when available. Additional studies on detoxification mechanisms for chromates have also been completed and manuscripts are in preparation. These studies provide substantial additional support for a threshold phenomenon for chromate carcinogenesis and will also be forwarded when available.

Please be sure we are included in future mailings related to chromium.

Sincerely,



J. A. Hathaway, M. D.
Director - Medical Services
Chemical Sector

JAH/nmw
Enclosures



Allied Corporation
Corporate Health,
Safety and Environmental Sciences
P.O. Box 2332R
Morristown, New Jersey 07960

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Reference: Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

Allied Corporation is a major United States producer of basic chromium chemicals. In the very limited time available to us, we have tried to review the above referenced document. We have identified numerous areas where we disagree with the interpretations, methods of analysis, and/or conclusions expressed. In a few instances we have noted errors in the factual information presented in the document, or omissions of recent pertinent scientific papers related to chromium compounds. We would like to stress that our review is limited in scope due to the short time-frame allowed by the Environmental Protection Agency. We were unable to review most of the references in their original form and suspect that had more time been available, additional errors in fact or interpretation would have been discovered.

In addition to our specific concerns noted below we would make the general observation that the document has internal inconsistencies related to interpretation of scientific data. While we can appreciate the difficulty of preparing a cohesive document of this size when numerous authors are drafting different sections, we believe that it was premature of the Environmental Protection Agency to present the document to the Science Advisory Board in its present condition. It would have seemed advisable for the Agency to reexamine the document for editorial consistency as well as consider the comments of external reviewers before submitting it to the Scientific Advisory Board. The summary, which can be expected to be relied upon by the public and regulatory agencies to a large degree, is particularly troublesome inasmuch as the conclusions expressed therein are usually incomplete or unrepresentative of important scientific studies and interpretations discussed in the body of the report.

We do agree with one of the major conclusions of the report that there is sufficient evidence for the carcinogenicity of calcium chromate, strontium chromate and zinc chromate from animal studies and for similar moderately insoluble chromates from epidemiology studies. But we disagree with many other interpretations and conclusions. Of particular concern is that both the qualitative and quantitative risk assessments for all chromium compounds are unsupported by the available scientific data and clearly exaggerate the risk to human populations exposed to low doses. We also believe that the scientific data supports the conclusions that chromates do not pose a human teratogenic risk and that trivalent chromium compounds are not mutagenic or carcinogenic in

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

man. In contrast the document, particularly the summary, implies that the evidence is inconclusive on these issues. Our specific comments will address these concerns as well as other issues in more detail.

1. Epidemiology Studies of Chromate Production Workers

Sixteen epidemiology studies of chromate manufacturing plants are reviewed in the document (pages 7-36 to 7-55). While the studies clearly demonstrate an increased risk of lung cancer associated with work in these plants, the qualitative risks as discussed in the summary on pages 7-64 and 7-65 implies a far greater risk than actually exists for current workers. Relative risks quoted in the summary are 29, 32, 23, and 38. These relative risks are from studies with small sample sizes, inappropriate controls and/or reflect studies performed in the 1940's or 1950's which included workers whose exposures were primarily in the 1910-1930 time frame. Unfortunately no mention is made in the summary of the three studies of more contemporary cohorts. The three more current studies discussed in the body of the EPA document demonstrate much lower risks for workers initially hired from the 1940's to about 1960. For workers hired since 1960 two of the three studies show no excess risk of lung cancer. All three studies compared cohorts initially exposed during different time periods corresponding to improvements in industrial hygiene or modification of processes. The cohorts correspond to the following time frames:

	<u>I</u>	<u>II</u>	<u>III</u>
Leverkusen	approx. '40-'48	'48-'57	'57-'79
Uerdingen	approx. '40-'48	'48-'63	'63-'79
Eaglescliff	* '49-'60 (only)	+ '49-'60 (or later)	'61-'77
Baltimore	'45-'49	'50-'59	'60-'74

* 1949-1960 cohort includes workers hired after 1949 with no exposure after 1960. + 1949-1960 includes workers hired during this period but who also worked after 1961. All other cohorts in this Table include workers hired exclusively during the indicated time periods.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

The results of the studies are summarized below:

<u>Author</u>	<u>Country</u>	<u>Location</u>	<u>S M R</u>		
			<u>Time Frame</u>		
			<u>I</u>	<u>II</u>	<u>III</u>
Korallus, et al.	W. Germany				
		Leverkusen	2.76	2.60	0.96
		Uerdingen	2.85	1.97	0.54
Alderson, et al.	Great Britain				
		Eaglescliff	3.03	2.03	1.87
Hayes, et al	United States				
		Baltimore			
		Short-term	1.8	1.8	No Cases
		Long-term	3.0	3.4	No Cases

When the three studies are considered together there is a clear trend showing a decreasing risk for more recently hired cohorts. The rates even for workers initially hired in the 1940's and 1950's are much improved over those quoted in older studies whether one looks at the relative risks of 20-30 or the SMR of 8.5 observed by Taylor (page 7-44) using more modern epidemiology methods. Rates for workers hired since about 1960 are even more favorable and excess risks may have been eliminated in the German and United States plants studied.

The authors of the document noted that the favorable trends within each study are not statistically significant but the identical trend in all three studies should be considered strongly suggestive of a substantial decrease if not elimination of excess lung cancer risk in these plants. Another argument raised by the authors is that the amount of time that has passed since 1960 may be an insufficient latent period for lung cancer in chromate production workers. We concur that this is a possibility; however, in

October 28, 1983.

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

reviewing several older epidemiology studies the authors noted a higher relative risk for lung cancer in workers less than 45 years of age compared to older workers. This situation clearly does not exist in the cohorts first hired since 1960 since many of these individuals would now be approaching age 45 even if hired at age 20. It is our opinion that even though the risk of lung cancer has not been proven to have been eliminated in these workers, it is certainly markedly reduced from early time periods. This conclusion should be adequately addressed in both the body of the document and its summary.

2. Quantitative Risk Assessment

Allied Corporation strongly disagrees with both the methodology used in making the quantitative risk assessment as well as the final result. Based on animal studies and mutagenicity tests we believe the lifetime estimate₃ of cancer of 1.2×10^{-2} for continuous exposure to 1 ug/m³ of chromium is overestimated by several orders of magnitude or even more probably that there is no risk whatsoever at that level of exposure. Our opinion is based on the following points, several of which we understand will be discussed in even more detail by the Industrial Health Foundation's Chromium Chemicals Environmental Health and Safety Committee.

- The one-hit model used by the EPA to estimate risk is inappropriate.
- Any of the commonly discussed mathematical models, including the one-hit model, used to estimate low dose exposures to carcinogens are designed for systemic acting carcinogens. Since carcinogenic effects for chromates are a local phenomenon, none of these models are appropriate for quantitative risk assessment.
- The EPA did not seriously consider the substantial amount of pharmacokinetic information on chromates that support the concept of a threshold for carcinogenesis.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

- All chromium compounds, regardless of valence or solubility, were inappropriately considered of equivalent toxicity in calculating the quantitative risk assessment.
- The exposure levels used from the Mancuso epidemiology study to develop risk estimates were too low.
- Comparisons to real-life exposures to chromium compounds demonstrate that the quantitative risk estimate does not reflect reality.

(a) One-Hit Model

The use of this model appears to follow outmoded policy and outdated methodology rather than current scientific judgment. One would have expected a more balanced presentation on this issue in pages 7-66 and 7-67. There is insufficient discussion of arguments against the one-hit model. Further discussion on the substantial controversies that exist in selection of mathematical models to predict low exposure cancer risks, should be made in the document.

In fact, there are numerous articles that make significant points against the blind political use of the one-hit model in scientific risk assessment. A few of these include:

- (1) Final Report of the Scientific Committee of the Food Safety Council, June 1980, Food Safety Council, 1725 K Street, N.W., Washington, DC 20000.
- (2) Ryzin, J.V., Quantitative Risk Assessment, Journal of Occupational Medicine, 22:321-326, 1980.

October 28, 1983

Members, Science Advisory Board.
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

- (3) Park, C.N. and R.D. Snee, Quantitative Risk Assessment: State-Of-The-Art for Carcinogenesis. Fundamental and Applied Toxicology, 3:310-333, 1983.

In addition, there are several articles in the January-February 1981 issue of Fundamental and Applied Toxicology that discuss the ED₀₁ study performed at the National Center for Toxicology Research which was referenced on page 7-67 in support of using a one-hit model. These articles clearly point out the inappropriateness of the one-hit model as it relates to exposure to 2-acetylaminofluorene and bladder cancer. When time to tumor considerations are applied the one-hit model is also not supported by the data on liver cancer, contrary to the claim made in the EPA's draft document.

(b) Inappropriateness of Mathematical Models in Predicting Low Dose Risks from Chromate Exposures

Chromates have been shown in animal or epidemiology studies to only produce tumors at the site of initial contact; that is, at implant sites or respiratory tract surfaces. Despite numerous animal experiments, no tumors have been seen at distant sites. Mathematical models implicitly assume random and even distribution of dose to the animal or man. This is simply not the case with chromates. The animal chromate inhalation versus implant studies reinforce this point when lung cancer is manifested in the latter and not the former. Any risk assessment that works with average exposures or time-weighted average exposures based on samples with extreme variations in time and space, cannot be expected to give reliable risk extrapolation estimates. This point will become clearer when the exposures in the Mancuso study and similar industrial hygiene experience at Allied's Baltimore Plant is discussed later.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

(c) Pharmacokinetic Data on Chromates

Contrary to the statement on page 5-22, there is a substantial amount of information on the pharmacokinetics of chromate metabolism. In addition to the numerous studies referenced in the document, the following should be added:

Petrilli, F. L. and S. DeFlora,
Interpretations on Chromium Mutagenicity and
Carcinogenicity in Mutagens In Our
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Inc., 150 Fifth Ave., New York, NY 10011,
1982.

This information, along with the results of a recently completed life-time intratracheal injection study (to be provided with the submission from the Industrial Health Foundation's Chromium Chemicals Environmental Health and Safety Committee), provide substantial evidence for a threshold for mutagenic and carcinogenic responses to chromate exposure.

Hexavalent chromates can be effectively reduced to the much less toxic and nonmutagenic (in vivo and using whole cells in vitro) trivalent chromium. This reduction takes place rapidly in the skin, saliva, gastric juice, red blood cells, and liver. Chromate can also be reduced by compounds normally present in cytoplasm such as ascorbic acid and reduced glutathione. Lung cells can also reduce chromates to a small degree and with repeat exposures this reduction is enhanced in a manner suggestive of enzyme induction.

The knowledge of these pharmacokinetic mechanisms provides understanding to the observations that chromates do not produce cancers at distant sites and do not enter fetal tissues from reasonable routes of maternal exposure. This knowledge and the further observation that it is difficult to produce tumors in the respiratory tracts of animals unless material is held directly in contact with tissue (intratracheal implantation) or by large dose bolus

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

administration (Industrial Health Foundation Study) provides good evidence of a threshold effect for chromate carcinogenesis.

(d) Solubility and Valence State

The EPA document does not differentiate between different forms of chromium compounds in its quantitative risk assessment. This is acknowledged to be inappropriate but is justified by lack of separate exposure information on hexavalent chromates. It is our opinion that this justification is unsupportable scientifically. If there is insufficient information to make a quantitative risk assessment because of lack of exposure information, this fact should have simply been acknowledged and no attempt at risk assessment should have been made. In fact, as previously discussed, there are ample additional reasons for not performing the risk assessment using mathematical models and certainly for not using the one-hit model.

The numerous references on trivalent chromium throughout the document provide sufficient information to conclude that trivalent chromium is not a carcinogen or mutagen. This is in contrast to the statement in the document that the data on these effects relative to trivalent chromium are inconclusive. In fact, studies on trivalent chromium have consistently shown a lack of carcinogenic activity and lack of mutagenic activity. While some interaction of trivalent chromium with DNA has been demonstrated, these have been in artificial cell extracts. Whenever whole organism including yeast and bacteria have been used the results have been negative. The inability of trivalent chromium to penetrate cell membranes has been clearly established by the studies cited in the draft document. This fact, coupled with the lack of mutagenic activity in vitro and the negative results in carcinogenicity studies, should logically lead to the conclusion that trivalent chromium compounds do not pose a carcinogenic or mutagenic risk to humans.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

Solubility considerations are discussed in the document, it is even stated that the authors believe some chromates do pose greater carcinogenic risk than others. In general they express agreement that intermediately soluble compounds such as calcium, strontium, and zinc chromates pose a greater carcinogenic risk than aqueously soluble materials. It seems totally inappropriate to us to then lump all chromium compounds, regardless of solubility or valence statement, into one category for risk assessment. Any result of such an assessment can only yield scientifically invalid results. We are not persuaded by the authors' arguments attempting to justify their approach (see pages 7-69 and 7-70). We see no reason to perform a risk assessment at all if one knows the results will be invalid.

(e) Exposure Levels used in Quantitative Risk Assessment

The exposure levels used in the draft document are based on those presented in Mancuso's 1975 paper, which are in turn based on levels reported by Bourne and Yee in their 1950 paper. Although it is difficult to be absolutely certain, a careful review of Mancuso's reported exposure levels strongly suggests they were based on Figures 1-4 from the Bourne and Yee study. The exposure levels reported in these figures represent time-weighted average exposures for nine different departments under "normal operating conditions." It appears that no consideration was given to reported exposures under maintenance and repair conditions even though such work occurred very frequently. Thirty percent of the workforce was reported as maintenance workers and their time-weighted average maximum exposures as reported in Table 5 varied from 0.13 to 5.67 mg/m³ with most over 1.0 mg/m³. The minimum exposures also listed in this table are related to "normal operating conditions" and are similar to Figures 1-4. Bourne and Yee state that "it was observed huge volumes of dust were generated during the repair and cleaning of dust collectors, [and] process equipment or building structure [was] overlaid with an accumulation of dust." Any risk assessment that does not consider these frequent excursions of much higher exposures will grossly exaggerate the estimated risk from chromate exposure.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

Experience at Allied's Baltimore Plant in 1947, when over 2,500 industrial hygiene samples were taken, also supports our belief that exposures were much higher than estimated by Mancuso. The plant he studied in 1949 was similar in operation to ours and we believe exposures were similar. We suspect that even the "normal operating levels" reported by Bourne and Yee represent ideal conditions at the plant during visits by inspectors from the State of Ohio Health Department.

If the data collected in the first half of 1949 and reported by Bourne and Yee and Mancuso were similar in nature to that collected by Allied in 1947, no reasonably representative low dose risk estimates can be derived using simple models derived for average exposure. Based on samples taken at the Allied plant over a 12 month period in 1947, monthly average samples from 39 areas ranged from 0.01 to 50.0 mg/m³ hexavalent chromium expressed as CrO₃. The yearly average of all locations was 0.9 mg/m³. Individual samples show an even greater spread. Also, yearly area averages ranged from 0.03 to 6.8 mg/m³ hexavalent chrome as CrO₃, revealing large location differences of a factor of more than 200 fold. Representative exposures are difficult, if not impossible, to derive from such data because of the order of magnitude differences in average levels. We believe similar variations occurred at the plant studied by Mancuso and that the real exposures also varied in a similar manner. The extremely high levels of variation in workplace chromium levels and the enormously high exposure (often over 10.0 mg/m³) that existed at many plant locations in the late 1940's dramatize the serious problems in developing meaningful low dose risk extrapolations from average chromium levels that do not realistically represent actual exposures.

Besides the problem of extreme variation, there is a problem of data representativeness over time. The data that was collected in the first half of 1949 by Bourne and Yee and that has subsequently been used in the EPA's chromium risk assessment estimates, cannot be considered

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

representative of exposures for employees followed between 1931 and 1974 in the Mancuso study. Bourne and Yee point out such deficiencies and limitations of the data in paragraphs 4 and 5 of their paper. Any risk assessment model developed from such data is ignoring the fact that the data represents only a half year in a forty-three year follow-up period (1931-1974) and hence assumes conditions were "static". The static assumption is also presumed when using these types of models since there is a long lag time between dose (chromium exposure) and response (respiratory cancer). If the dose is not constant throughout the period then a lag relationship needs to be considered. Otherwise a biased or distorted relationship between dose and response can result. In the case of chromium exposures in the workplace, the assumption of constancy of dosage is probably the least supportable assumption that can be made.

(f) Comparison of Predicted Risks to Real-Life Situations

While the authors of the draft document caution on page 7-70 that the quantitative risk assessment should be only used for certain chromium compounds, the fact that it is derived without regard to solubility or valence considerations will undoubtedly leave others to apply it to all forms of chromium. The inappropriateness of the predicted risk of 1.2×10^{-2} at continuous exposure to 1 ug/m^3 for developing cancer can be illustrated by the following two examples.

The first example is normal ingestion of chromium in the diet which is estimated by the National Academy of Sciences (NAS, 1980) to be 62 ug/day in food and 17 ug/day in drinking water for a total of 79 ug/day. This compares to an intake of about 20 ug/day at 1.0 ug/m^3 if one assumes the chromium is 100 percent respirable and totally retained and that air exchange equals $20 \text{ m}^3/\text{day}$. From this normal dietary intake about five percent of the population ought to develop lung cancer as a result of this exposure according to the quantitative risk assessment. If this were valid, most of the lung cancer in the United States could be attributed to chromium ingestion. Obviously, this is not the case as numerous

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

epidemiology studies linking cigarette smoking and lung cancer have clearly demonstrated. The only conclusion one can reach is that the estimated risk predicted by the EPA model does not represent reality and should, therefore, be disregarded.

The second example involves a study in a Swedish County with two communities heavily polluted with chromium compounds from ferro-alloy industries. (Before discussing the article in detail, we would like to comment that it seems incredible that the EPA authors would omit such an epidemiology study from its consideration, particularly in a document developed for use by the Office of Air Quality Planning and Standards). The citation for this study is:

Axelsson, G. and R. Rylander,
Environmental Chromium Dust and Lung
Cancer Mortality, Environmental
Research, 23:469-476, 1980.

Two ferro-alloy industries are situated in the County studied. Chromium air levels are reported as 0.1 to 0.4 $\mu\text{g}/\text{m}^3$, which is 50-100 times higher than most other rural areas in Sweden. The plants started operations in 1912 and 1913. The quoted exposures refer to 1976-1979, and one could speculate that past exposures were likely to have been even higher since air pollution control has received considerable recent attention in Sweden.

If one assumes that the average exposure was 0.25 $\mu\text{g}/\text{m}^3$ for the communities studied then about 0.3% of the population would be expected to suffer lung cancer as a result of the air pollution using the results of the EPA risk assessment estimate. While this amount of lung cancer risk in males may not be enough to be statistically discernible, it should have caused at least a 50% increase over control groups for females. Such an increase was not seen, casting serious doubt on the credibility of the risk estimate. The study concluded that there was no excess risk of lung cancer in the two communities with higher levels of airborne pollution from chromium compounds.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

It is our opinion that risk estimates which do not conform to reality should be disregarded. Such is the case with the risk estimated for chromium in the draft document.

3. Errors in Airborne Chromium Levels Reported for Baltimore

The airborne chromium levels reported for Baltimore in the summary on page 2-2 and on pages 3-21 to 3-23 are in error. Copies of the 1977 and 1979 Maryland State Yearly Air Quality Data Reports, prepared by the State Department of Health and Mental Hygiene, are attached so that the actual levels can be verified.

In fact, the maximum observed value is not 2.48 ug/m^3 , as reported in the draft document for 1977, but is rather 0.247 ug/m^3 . The arithmetic average is actually 0.036 ug/m^3 not 0.1568 ug/m^3 , as reported in the draft document. For 1979 the data are also incorrect with a maximum value of 0.31 ug/m^3 (one value of 0.690 ug/m^3 was disregarded according to procedures specified by the Maryland Health Department when there was only one sample in a quarterly reporting period) and an arithmetic average of 0.0468 ug/m^3 . These levels are more in line with reports from other communities; however, in view of the errors noted for Baltimore, the EPA authors should review the reported results for all locations to verify their accuracy.

4. Allied's Epidemiology Experience

This discussion supplements comments made previously in paragraphs #1. and #2.e concerning results of epidemiology studies and exposure measurements at Allied's Baltimore facility. Allied's epidemiology experience since a major process change in 1961 (a new chromic acid plant) shows no significant excess of respiratory cancer among production workers who were first hired after this date. One case of respiratory cancer has been reported in this cohort and 1 to 2 cases would have been expected based on Baltimore City cancer incidence rates. Although five to ten more years of follow-up are desired to improve the power of the statistical test, there is no evidence of excess risk in the Allied production workers whose initial employment at the chromium facility occurred in the past 21-3/4 years based upon the Hayes et al. study on these workers through mid-1977 and our review of Company records on active employees and retirees through September 1983.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

Major process changes in 1951 (a new bichromate plant) and in 1961 (a new continuous chromic acid plant) have led to significant reductions in the average and peak chromium exposures at the Allied plant. These reductions correlate with no apparent respiratory cancer excess risk in production workers hired after 1961.

From samples collected in 1961 and 1962, the plant average level was estimated to be .07 mg CrO₃/M³ or a factor of at least 10 below the levels in 1947. The area averages ranged from .01 to .5 mg CrO₃/M³. These were followed by further reductions to an average of .02 mg CrO₃/M³ as evidenced in 1968 and also in the period 1976-1978. Area average readings typically ranged from nondetectable to .14 mg CrO₃/M³ in the years 1976-1978. During this period, the value of .1 mg CrO₃/M³ was only exceeded on the average in 4 of the 154 sampling areas (3%) where the worker density per workday was approximately 1 person for the four areas combined or .3% of the workforce. This contrasts with 30 of 39 sampling areas (77%) exceeding .1 mg CrO₃/M³ during 1947.

As seen above, over the past three and one half decades major changes have occurred in the average chromium exposure levels as well as in the size and number of extreme exposures.

In addition to the changes in dust levels of chromates, we believe the changes in the Chromic Acid Plant in 1961 may have had a major effect on the excess risk of lung cancer that previously was associated with work in that area. Both internal Company observations as well as the Hayes study identified the End Products area as having the highest lung cancer risk. Chromic acid is manufactured in this area and is sometimes referred to in our comments as the Chromic Acid Plant.

Prior to 1961, chromic acid was produced in batches. This method of production was accompanied by the production and evolution of large but unquantified levels of chromyl chloride in the workplace. Contamination of Soda Ash by salt used in the roasting of chromite ore resulted in chloride contamination of product streams. The chromate streams with the greatest contamination of chloride were directed to the Chromic Acid Plant where the chloride was removed essentially by boiling it off as chromyl chloride.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

We speculate that chromyl chloride may have been the major factor for the observed greater risk of lung cancer among workers in the old (pre-1961) Chromic Acid Plant. Since chromyl chloride was present as a vapor it might well be able to more easily penetrate the non-dividing layer of epithelial cells lining the lower respiratory tract than other chromates and once in contact with dividing cells exert a carcinogenic action. Another possibility is that chromyl chloride might have a carcinogenic action independent of the fact that it is a hexavalent chromium compound. In the attached article on the Chemistry of Chromyl Compounds by W. H. Hartford and M. Davrin, reaction of chromyl chloride with organic compounds resulting in chlorinated adducts is described. If such reactions occurred within DNA molecules a carcinogenic mechanism different from that of other chromates is possible.

Changes in the chromic acid manufacturing plant in 1961 eliminated chromyl chloride exposures. As previously discussed in paragraph #1 and earlier in this paragraph, no excess lung cancer has been observed at our Baltimore Plant since this time.

5. Systemic Toxicity of Chromates

Discussion of this subject on pages 7-1 and 7-140 to 7-143 do not cover the known acute toxicity of chromates very well. Acute renal failure is the predominant finding following either accidental ingestion or cutaneous exposure to chromates (typically in conjunction with a thermal or acid burn). A few recent literature citations are provided so the authors of the document may improve this section.

- (a) Schiff, H., P. Weidmann, M. Weiss, and S. G. Massry, Dialysis Treatment of Acute Chromium Intoxication and Comparative Efficacy of Peritoneal versus Hemodialysis in Chromium Removal, Mineral Electrolyte Metabolism, 7: 28-35, 1982.

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

- (b) Ellis, E.N., B. H. Brouhard, R. E. Lynch, E. B. Dawson, R. Tisdell, M. M. Nichols, F. Ramirez, Effects of Hemodialysis and Dimercaprol in Acute Dichromate Poisoning. J. Toxicol: Clin Toxicol 19: 249-258, 1982.
- (c) Leonard, L.G., J. J. Scheulen, A.M. Munster, Chemical Burns: Effects of Prompt First Aid. The Journal of Trauma, 22: 420-423, 1982.
- (d) Korallus, U. C., Harzdorf, and J. Lewalter, The Experimental Bases for Ascorbic Acid Therapy of Poisoning by Hexavalent Chromium Compounds. International Archives of Occupational and Environmental Health (in press) - prepublication copy attached.

In addition to the above references, Allied's Department of Toxicology has recently completed an animal study demonstrating the efficacy of ascorbic acid in the treatment of acute dichromate exposures.

Acute accidental exposures to chromates can produce serious and sometimes fatal kidney failure. Conversely there does not appear to be a similar chronic effect. Mortality studies have not identified chronic renal disease, nor has renal damage been seen in lifetime carcinogenesis animal bioassays. Clinical testing of employee groups has also not demonstrated chronic renal problems. This has been Allied's experience in its medical examinations and is the result reported in the paper by Satoh et al.

6. Epidemiology Study of Ferrochromium Industry

The remarks on page 7-64 of the document referring to a study of ferrochromium industry employees in Sweden by Axelsson et al (1980) are an incorrect interpretation of the data reviewed on page 7-63. Although the negative results of this study are correctly reported by the EPA authors, their comment that "because of the confounding due to smoking and exposure to asbestos, no definite conclusions can be drawn from this study." is incorrect. In fact, any confounding from these two variables was in the direction of an increased risk of lung cancer among exposed workers. This type of

October 28, 1983

Members, Science Advisory Board
Environmental Health Committee
U. S. Environmental Protection Agency

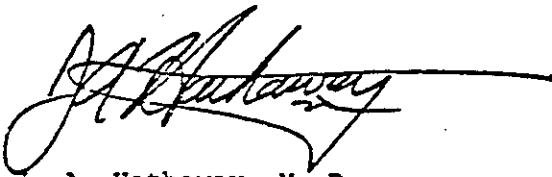
Health Assessment Document for Chromium,
Review Draft, EPA-600/8-83-014A

confounding in a negative study only strengthens the conclusion that there was no association between work in the Swedish ferrochromium industry and lung cancer.

The subsequent comment in the summary on pages 7-64 and 7-65, that two studies of the ferrochromium industry reported an increased risk of lung cancer mortality is obviously inaccurate.

7. Summary

Allied Corporation would hope that this document would receive extensive and careful revision before approval by the EPA's Scientific Advisory Board. Errors in fact, and editorial inconsistencies need to be corrected. The review of the literature needs to be expanded in many areas -- a number of citations are provided in our comments to assist with this effort. The views expressed by Allied as well as those of the Industrial Health Foundation's Chromium Chemicals Environmental Health and Safety Committee need to be seriously addressed, particularly as they relate to interpretation of epidemiology studies and the inappropriateness of mathematical models to assess low exposure cancer risks. Finally, the results of the Industrial Health Foundation's lifetime intratracheal study needs to be considered along with more recent mutagenicity studies that provide substantial evidence for a threshold of chromate carcinogenicity.



J. A. Hathaway, M. D.
Director-Medical Services
Chemical Sector
Allied Corporation

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Diamond Shamrock

T. R. Evans Research Center

October 5, 1983

Project Officer for Chromium
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

Dear Sir:

The Chromium Chemicals Environmental Health and Safety Committee of International Health Foundation appreciates the opportunity to comment on the draft Health Assessment Document for Chromium (EPA 600/ 8-83-014A July 1983). The time period allowed for review of the document has limited our initial comments to the Summary and Conclusions Section, and the Cancer Assessment Group estimated lifetime cancer risk. We feel the Summary and Conclusions Section will be widely read and will be the basis for decisions made concerning possible chrome regulations at the Federal and local levels. The estimated lifetime cancer risk will also be an important factor in possible regulatory action; therefore these sections have been the major focal point of our present review. Although a line-by-line critique was not possible at this time, the committee will submit further comments and additional information in the future. We have requested an extension of the comment period so as to permit input from studies just completed and to allow time for comments from European members of the committee.

Our conclusion is that studies of the chrome industry and recent animal studies show that exposure to high levels of chromium are of concern to human health, but ambient levels of chromium do not pose a concern for human health or the environment. Further, the data does not support the theory of linear extrapolation from high to low levels of exposure, thus the assessment of carcinogenic risk is inappropriate as applied to chrome.

2. Summary and Conclusions

General: The Summary and Conclusions section ineffectively summarizes the main text of the document and the section does not present any conclusions. The organization of the total document is poor in that certain sections and even subsections of the main body contain summaries and conclusions, the contents of which are not represented in this overall Summary and Conclusions section. The organization of the headings in this section does not follow the main document and makes little sense.

For example: 2.3 Biological Significance and Adverse
Health Effects of Chromium
2.5 Human Health Risk Assessment of Chromium

It would seem that the risk assessment should be a sub-part of the biological significance.

References to material discussed are given in some paragraphs and not in others.

2.1 Background Information

The text should indicate that Cr (0) as well as Cr (III) and Cr (VI) states are the most stable. The word anthropogenic is good and correctly used in the document but it would be clearer to refer to man made sources.

2.2 Analysis of Chromium

X-ray fluorescence is only able to analyze large amounts of chrome in compounds and would not be useful for environmental analysis.

The section should include the colormetric method using diphenylcarbazide. This method is widely used by industry. The method is accurate and precise at levels of 10 ppb and greater.

2.3 Biological Significance and Adverse Health Effects of Chromium

2.3.1 Chromium Pharmacokinetics: This subsection offers little in understanding chrome absorption, metabolism and excretion. The discussion does not even indicate, as does the main body of the report, that inhalation is an important route of exposure to chromium compounds. The background information on particulate inhalation is inappropriate for a summary section. Speculation should not be included in a summary section such as:

"Reduction of Cr (VI) to CR (III) appears to occur rapidly in biological systems, while the mechanism and kinetics are not completely understood."

2.3.2 Subcellular and Cellular Aspects of Chromium Toxicity: The document should avoid the use of jargon, such as "critical levels" without an explanation. The paragraph on mutagenicity neither summarizes the studies completed nor offers any understanding of valence state or solubility as factors in the conduct and interpretation of the results. It is doubtful that one looking for a summary of mutagenicity or genotoxicity would find the material under this organization.

2.3.3 Systemic Toxicity of Chromium: Adds nothing to the understanding of this topic.

2.3.3.1 Animal Data: To use the words ingestion/orally and soluble CR (VI) solutions/chromium salts in one sentence does not aid the reader, even a technically astute one, to gain an understanding of what the document is trying to say.

"Ingestion of soluble Cr (VI) solutions can cause local irritation but, generally chromium salts are relatively non-toxic when administered orally."

The main body of the document (7-2) states:

"Kidney effects are the primary result of acute exposure to chromium by various routes."

The summary section states:

"Acute exposure (intraperitoneal) result in kidney failure, liver, heart and brain micro pathology."

It would appear that the understanding of the experiments in demonstrating the kidney as a target organ for acute chrome toxicity was lost on the individuals summarizing the document.

2.3.4 Chromium Carcinogenesis: This section can be easily summarized by stating as in the second sentence:

"Animal studies have provided sufficient evidence for the carcinogenicity of the following Cr (VI) compounds calcium chromate, strontium chromate and zinc chromate."

Speculation about other forms of Cr (VI) and unfounded statements on solubility modification of carcinogenicity does not have a place in a summary.

Many statements in this section could be omitted, but one sentence in particular should be deleted.

"Cr (VI) is mutagenic in multiple tests while the data for Cr (III) is inconclusive."

To attempt to bring a one sentence discussion of chromium mutagenicity into the section on carcinogenicity shows a naive understanding of proposed genotoxic mechanisms as they may apply to metals.

It is interesting to note the many references to IARC criteria (3 times in this section). If EPA is accepting this criteria for evaluation of a chemicals carcinogenicity, then I think it should be stated and applied to all chemicals.

2.3.5 Dermatological Aspects of Chromium: The section should point out that adherence to personal hygiene practices have been shown to reduce the industrial incidences of ulceration and have in general eliminated chrome dermatitis.

2.4 Human Biological Monitoring: The section should clearly differentiate environmental measurements from those taken in industrial settings.

2.4.1 Chromium in Blood: Reintroduces points included in the pharmacokinetics section but in a much more positive manner.

Section 2.3.1 "Chromium may be absorbed via the skin, lungs or gastrointestinal tract."

Section 2.4.1 "Chromium is absorbed through both the respiratory tract and gastrointestinal tract."

2.4.2 Chromium in Urine; 2.4.3 Chromium in Human Hair: These sections present data but do not summarize or offer a conclusion. The presentation of values without any discussion or indication of meaning is not placing the information in perspective.

2.5 Human Health Risk Assessment of Chromium

2.5.1 Health Effects Summary: If the CAG estimated lifetime cancer risk is to be included in this document the uncertainties, as discussed in the main body 7-77 and 7-82, must be included in the summary section.

2.5.2 Populations at Risk: This section offers nothing to be included in a Summary Section.

The Summary and Conclusions section is a very important part of the Health Assessment Document. The section must represent the main body of the document and the conclusions must be well founded in the data and must be clearly stated. The present section does not represent the main body of the report (for example no mention of teratology or other reproductive effects), fails to include conclusions and should be redone.

RISK ASSESSMENT

The Industrial Health Foundation's Chromium Chemicals Committee has sponsored the conduct of an extensive program of toxicology studies on chromates during the past five years, including studies to develop therapies and first aid treatment for the nephrotoxicity of accidental poisonings and studies to characterize the acute toxicity, mutagenicity, and carcinogenicity of chromium compounds. These last two sets of studies have, of course, direct bearing on the question of a risk assessment for chromium.

The entire issue of a risk assessment for chromium as presented in the Health Assessment Document is one which requires extensive review and revision. The model used for the risk assessment and the data to which this model was applied are open to numerous questions. The agency document itself, on pages 7-44 and 7-44a, states that both the data and conclusions of Mancuso (the basis for the risk estimate which is presented) are of limited value, particularly in that the exposures are not well characterized. New information now available from the IHF studies may provide a better data base on which to base a risk assessment.

The final report and a manuscript for publication on the carcinogenicity study are in the final stages of review. These describe the results of a carcinogenesis bioassay of sodium bichromate and calcium chromate, administered intratracheally in solution form. Benzopyrene and dimethylcarbamoyl chloride were included as positive controls. Intratracheal administration provided direct exposure to the lungs. Separate groups of rats were dosed with calcium chromate or sodium dichromate at lifetime total dose levels approximating one half the present TLV, three and fourteen times the present TLV. To test the effect of concentration, each total dose was administered to one group of animals either once per week or as a divided dose to a different group of animals five times per week. The method of administration, in a single bolus, resulted in peak concentrations delivered to the target tissue approximately 10^3 times what would be expected from continuous exposure by inhalation. Even at the highest tolerated doses, the frequency of tumor formation was low compared to the positive controls; no tumors were observed within the first 27 months of chrome administration; there was excellent survival, and none of the tumors, which were small, caused the death of the test animals.

Significant tumor incidences were observed only in the lungs of the highest dosage once-per-week groups and in the positive controls, there being no lung tumors in negative control animals. The same amount administered five days per week did not produce any tumors. Hence, at the maximum tolerated dose (1.25 mg/kg administered once per week), tumorigenic effect is related to peak concentration of repeated doses rather than the total administered dose.

This study strongly supports the conclusion that there is a no-effect level for chromate carcinogenesis, based on multiple physiological and biochemical defense mechanisms. It also helps explain the progress which

has been made over the past 35 years within the chromate-producing industry in control of lung cancer by advanced engineering and process improvements, and the lack of credible evidence of abnormal lung cancer risk in consuming industries other than pigment manufacture.

Mutagenicity testing (Ames Test) has indicated that Cr (VI) compounds had a similar mutagenic potency. Cr (VI) elicited both frameshift errors and basepairs substitutions in *S. typhimurium*. Cr (III) compounds were negative in Ames Tests. Cr (VI) mutagenicity was decreased by S9 fractions from various tissues through NADPH - requiring pathways reducing Cr (VI) to Cr (III). The findings may contribute to interpret carcinogenicity data; for example, reduction of Cr (VI) to Cr (III) by gastric juice is consistent with the lack of carcinogenicity following ingestion of chromates (Cr VI). Also the reversal of Cr (VI) mutagenicity by erythrocyte lysates is consistent with Cr (VI) detoxification in the blood and supports the finding of tumors only at implant sites. Since Cr (III) is trapped by cytoplasmic ligands, this may also indicate an intracellular detoxication mechanism; that is, a barrier affecting the ability of Cr (VI) to enter the nucleus and then to interact with DNA (probably as Cr III).

In view of this information, the following points about the risk assessment presented in the agency's document need to be addressed.

- 1) Chromium is an essential dietary component for man, with an estimated adequate and safe intake (EASI) and recommended daily allowance (RDA) of 200 micrograms per day. The level of intake for which the agency is here proposing a risk of 1.2×10^{-2} of cancer is only 10% of this EASI/RDA.
- 2) The linear extrapolation model utilized, and in fact, any pure linear model is inappropriate. The model is not one of the agency's "standard" models and even though used by the agency for arsenic, it is not a generally accepted total body burden model.
- 3) Further the model used projects a risk based on total chromium exposure, not on exposure to hexavalent chromium. Hexavalent chromium is now generally accepted to be the source of concern. The extensive mutagenicity data base developed under the sponsorship of the IHF also supports the view that it is hexavalent chromium, at high local concentrations, which must be viewed with concern.
- 4) The original data base the agency's estimates are based on is not accurate. The base does not differentiate in exposures between the different valence states of chromium, just as importantly, it does not in any manner account or allow for the episodic high exposures of workers to chromium which did occur in the older plants. The resulting predicted risk of 1.2×10^{-2} incidences of cancer per $\mu\text{g}/\text{m}^3$ of total chromium is contrary to observed lung cancer incidence levels.

- 5) One microgram of chromium per cubic meter of air equals 20 ug/day in the average man, or a total of approximately 300 ug per year and about 36.5 mg over the course of fifty years. In a seventy kilogram "standard" man this amounts to 0.521 mg/kg. The high dose in the final intratracheal study was equivalent to 541.7 mg/kg over the course of the study, or 10^3 times greater total exposure. Fifty years at the EASI is equivalent to 52.14 mg/kg, or 10^2 times greater exposure. The observed results from either of these situations, occurring as doses distributed over the course of a life time, do not correspond at all to what the model purposed in this document would predict.
- 6) Using the background levels of chromium in urban areas presented in the document, one would expect matching variations in the lung cancer rates. The variation in mean chromium levels (page 3-4) are 30 fold, yet no corresponding variations in lung cancer incidence has been reported.
- 7) Based on total body burdens of chromium and using the IHF rat carcinogenicity study, one would expect a cancer rate in the high dose, once a week exposure group (the worst case from the intratracheal study) some 10-20 times higher than was found. In addition, one would expect significantly greater tumor incidence levels in all of the groups in the study. Every group would have been expected to show a significant incidence of tumors.

In summary, based on the IHF rat study data, and other recent epidemiology data (Franchini, et al, Scand J Work Environ Health 9 (1983) 247-252) a linear model is inappropriate. However, using the EPA linear model with the IHF rat data (1x per week) an upper bound risk of approximately 6.75×10^{-5} was calculated. An appropriate model should not however be based on total chromium but rather on hexavalent chromium.

Members of the Chromium Chemicals Environmental Health and Safety Committee would like to expand on the points of concern with the HAD as indicated in this letter and further would like to share the data of the several studies recently completed. Copies of completed reports will be submitted to the project officer by the end of 1983. The Committee would be prepared to present and discuss the results of these reports and other new data with appropriate agency people as soon as a meeting can be arranged.

Sincerely,

David M. Serrone, Ph.D.
dlg

David M. Serrone, Ph.D.
for the Chromium Chemicals
Environmental Health and
Safety Committee

DMS/dlg/9.13

ATTACHMENT V

Ambient Chromium Concentrations and Emission Trends

Data from the U.S. EPA's National Aerometric Data Bank show mean concentrations of total chromium between 0 (below detectable limit) and 29.9 ng/m³, with 68 percent (59 of 87) of the means falling above 4 ng/m³. This data represents total particulate chromium 50 um and smaller collected from ambient air at sites throughout California from 1965 to 1983.

Data on total chromium in particulate matter 10 um and smaller, collected at ten sites throughout the state by the ARB in 1983 and 1984, show mean concentrations of chromium from 1.6 to 14.9 ng/m³. At most (7 of 8) of the urban sites, mean chromium concentrations fell between 3.0 and 4.2- ng/m³.

The contribution of the various uses of chromium compounds in California to the presence of chromium in the ambient air is currently being investigated by ARB staff. Chromium compounds are used in chrome plating, refractory brick production, glass manufacture, wood preservatives, paint pigments, and cooling towers as anticorrosion agents. Other potential sources of chromium in air are emissions from fuel combustion, sewage sludge incineration, refractory brick wear from the glass, cement and secondary steel production furnaces, and entrainment of chromite-bearing soil.

National consumption of chromium has decreased steadily due to continued weak demand for steel and reduced need for refractory materials. Whether this trend is reflected in California is uncertain; primary steel production facilities do not exist in this state.

Memorandum

To : James D. Boyd
Executive Office
Air Resources Board
1102 Q Street
B-4

Date : FEB 25 1985

Subject: Health Effects
Chromium (CR)

3/12/85 J. Leung

From : Office of the Director
714 P Street, Room 1253
B-1248

Attached is the document prepared in response to your memo requesting the assistance of the Department of Health Services in evaluating the health effects of chromium (CR).

Stanley Cubanski
Stanley Cubanski
Director

Attachment

cc: C. Berryhill
G. Duffy
Assemblywoman Tanner
P. Venturini

Memorandum

To : William V. Loscutoff, Chief
Toxics Pollutants Branch
Air Resources Board
1102 Q Street
B-4

Date : September 18, 1985

Subject: Chromium Health
Evaluation Document

From : Public Health
8/1253 5-2927

Attached please find the revised chromium health evaluation document to be sent to the Science Review Panel.

Maridee Gregory
Maridee Gregory, M.D.
Acting Deputy Director

Attachment

SEP 19 1985

APPENDIX C
DISCUSSION OF EMISSION ESTIMATES

1. Chrome Plating Emissions

A. Emission Factors

Emission factors were derived based on data presented in the Naval Shipyard Study,^{1/} from information provided by industry representatives, and using certain assumptions.

Emission factors were calculated as follows:

$$\text{Emfac} = E_i / S_i \quad (1)$$

Where:

Emfac = Emission factor, lb/hr. ft.²

E_i = Emission rate of the i th tank, lb/hr.

S_i = Surface area of the i th tank, ft.²

Emission rate of the i th tank is calculated according to equation 2 below:

$$E_i = E_T * \left(S_i / \sum_{i=1}^n (S_i f_i) \right) * f_i \quad (2)$$

Where:

E_T = Total emission rate for each test, lb/hr.

f_i = Fractional current density applied in the i th tank, unitless (for hard chrome, $f_i = 1.0$, for decorative, $f_i = 0.4$).

For uncontrolled emission factors, emission rates, E_i 's were calculated from the emission rates at the inlet of the scrubber.. The emission rates at the outlet of the scrubber were used to calculate the controlled emission factors.

The emission rates and resulting emission factors are shown in the table below:

Test-Run	Emission Rate, E_T (lb./hr) ¹		Emission Factors (lb/hr.ft ²)			
	Inlet	Outlet	Decorative		Hard	
			Uncontrolled	Controlled	Uncontrolled	Controlled
4-1	0.0674	0.00316	2.05×10^{-4}	9.60×10^{-6}	5.12×10^{-4}	2.40×10^{-5}
4-2	0.0338	0.00534	1.03×10^{-4}	1.62×10^{-5}	2.56×10^{-4}	4.05×10^{-5}
4-3	0.171	0.00215	5.20×10^{-4}	6.53×10^{-6}	1.30×10^{-3}	1.64×10^{-5}
4-4	0.0639	0.00592	1.94×10^{-4}	1.80×10^{-5}	4.85×10^{-4}	4.50×10^{-5}
Ave.	0.0840	0.00414	2.56×10^{-4}	1.26×10^{-5}	6.37×10^{-4}	3.15×10^{-5}
sd	0.0599	0.00178	1.82×10^{-4}	5.41×10^{-6}	4.54×10^{-4}	1.35×10^{-5}

B. Estimates of Emissions

An average size chromic acid tank used in chrome plating has been estimated by an industry association representative to be about 1,000 gallons with the dimensions of 12 feet long, 4 feet wide and 3 feet deep.^{2/} The number of these tanks used by each company is estimated to range from at least one, to four. The Long Beach Naval Shipyard has four chrome plating tanks and was assumed to have the most number of chromic acid tanks per plater. For calculation purposes, it was assumed that the platers used an average of 1.5 tanks for chrome plating.

Using the estimated number of chrome platers (400 platers) in California and an industry association estimate^{3/} that three-fourths of chromium used for plating is used for for hard chrome, and one-fourth for decorative chrome, the surface area, S's are calculated as follows:

$$\text{Average surface area per plater} = 1.5 \text{ tanks } (12' \times 4') = 72 \text{ ft}^2$$

Hard chrome:

$$S_{\text{Hard}} = (400 \text{ platers})(3/4)(72 \text{ ft}^2/\text{plater}) = 21,600 \text{ ft}^2$$

Decorative chrome:

$$S_{\text{Decorative}} = (400 \text{ platers})(1/4)(72 \text{ ft}^2/\text{plater}) = 7,200 \text{ ft}^2$$

Emissions were calculated assuming that on the average chrome plating is done 8 hours per day, 250 days per year. Emissions from chrome platers are tabulated below:

	Hexavalent Chromium Emissions (tons/year)	
	Controlled	Uncontrolled
Hard Chrome	0.68	13.8
Decorative Chrome	0.09	1.8
Total	0.77	15.6

NOTE: The controlled emissions were calculated based on an average scrubber efficiency of 92 percent as reported in the Naval Shipyard Study^{1/} The figures presented here for controlled emissions represent estimates based on technically achievable control efficiencies, and not on control efficiencies observed in the industry. On the average, we would expect lower than 92 percent control efficiency for typical wet scrubbers.

2. Cooling Towers Emissions

Chromium emissions from cooling towers were estimated using two sources of information. Method 1 is based on a survey conducted by SAI^{5/} on emissions from cooling towers in California. Method 2 is based on information from a Radian report^{4/} on the national population exposure to ambient chromium emissions. Both methods divide cooling towers into two groups, industrial and those associated with electrical power plants (utilities). This division is maintained in the following summary of methods used to calculate chromium emissions.

Where upper and lower estimates are given, the lower estimate was determined by using the lowest reported values for each parameter in an equation and the highest reported value was used for the upper estimate.

Method 1:

Based on an SAI report^{5/}, equation (1) was used to estimate chromium emission from cooling towers. The fraction of cooling towers using chromates, the concentration of chromium in the cooling tower water and the circulating water flow rate were determine from a survey of utilities and industry.

$$\text{Cr. Ems} = C_f * F * Q * D_f * C_{Cr} \quad (3)$$

Where:

Cr. Ems = tons per year

C_f = units conversion factor (0.563 ton/min/year. M^3)

F = fraction of cooling towers using chromates

Q = Circulating water flowrate in cubic meters per minute

D_f = Fraction of circulating water lost to the atmopshere (drift fraction)

C_{Cr} = Weight fraction of chromium in circulating water in parts per million

To calculate the conversion factor, it was assumed that cooling towers operated 24 hours per day, 355 days per year. Ten days were allowed for maintenance or holiday stoppage. The drift losses, D_f , reported ranged from 10^{-5} to 10^{-4} gallons lost per gallon of circulating water. The concentration of chromium in the circulating water varied from 15.5 ppm to 16.1 ppm by weight. The fraction of all cooling towers, F, reported to be using chromates was 0.191. Using the above values, equation (1) can be simplified to yield the following equations for lower and upper estimates:

$$\text{Lower estimate} \quad \text{Cr. Ems} = 1.67 \times 10^{-5} Q_l \quad (4)$$

$$\text{Upper estimate} \quad \text{Cr. Ems} = 1.73 \times 10^{-4} Q_u \quad (5)$$

The average circulating water flow rate was different for industrial and utilities cooling towers and was determined separately as follows:

a) Utility Cooling Towers

The total circulating water flow rate was estimated to be 7,670 M³/minute for cooling towers associated with electrical power plants in California.^{5/} This does not include the Geysers, Magnolia, Olive or the Grayson plants (chromium emissions of these plants are negligible as calculated by Rogozen). Using equations (2) and (3), the contribution of chromium emissions from utility cooling towers is estimated to range from 0.12 ton to 1.3 tons per year.

b) Industrial Cooling Towers

SAI estimated that there are between 874 and 1,887 cooling towers in use in California. Of this total, it was reported that 392 towers had a total circulation rate of 2,960 M³/min or an average circulation rate of 7.55 M³/min tower.^{5/} Using the average circulation rate and the estimates for the number of towers in California, upper and lower estimates for the total amount of water circulating in towers, Q, can be calculated.

Lower estimate $Q_l = 7.55 \text{ M}^3/\text{min tower} (874 \text{ tower}) = 6600 \text{ M}^3/\text{min}$

Upper Estimate $Q_u = 7.55 \text{ M}^3/\text{min tower} (1,887 \text{ tower}) = 14250 \text{ M}^3/\text{min}$

Substituting the appropriate values into equations (2) and (3) gives a range of estimates emissions from 0.11 ton to 2.5 tons per year of chromium for industrial cooling towers. Adding the upper and lower estimates for both utilities and industrial towers gives the following estimate for the total emission rate:

	<u>Lower Estimate</u>	<u>Upper Estimate</u>	<u>Average</u>
Utilities	0.12	1.3	0.7
Industrial	<u>0.11</u>	<u>2.5</u>	<u>1.3</u>
Total Chromium Emissions (tons/year)	0.23	3.8	2.0

Method 2:

This method uses estimates from a Radian report^{4/} on chromium emissions from cooling towers and some values from the SAI report. Equation (6) was used to calculate chromium emissions.

$$\text{Cr Ems} = C_2 * F * D_w * C_{Cr} \quad (6)$$

Where:

C_2 = Units concersion factor (4.2×10^{-9} ton/gallon)

F = The fraction of cooling towers using chromates

D_w = The amount of water lost to drift

C_{Cr} = The concentration by weight of chromium in the circulating water

Because the Radian report estimated emissions nationwide, equation (6) was changed to include a correction factor for the number of towers in California compared to the nation. It was assumed the fraction of towers in California was the same as the fraction of the population in California. Thus, equation (5) was used for the California estimates.

$$\text{Cr. Ems} = C_2 * F * F_p * D_w * C_{Cr} \quad (7)$$

Where:

F_p = The fraction of the population in California

The fraction of the population in California is approximately 0.10. The fraction of cooling towers using chromate, F, was taken from Method 1. Because the chromium concentration, C_{Cr} , used in the Radian report was not specific to the measured concentration in California cooling towers, an average of chromium concentration of 15.8 ppm from method 1 was used in the method 2 equation. The water lost to drift nationwide in 1983 was estimated to be 1.436×10^9 gallons per year for industry and 2.656×10^9 gallons per year for utilities. Using the above values in equation (7) gives:

Industry estimate:

$$\begin{aligned} \text{Cr. Ems} &= (4.2 \times 10^{-9} \text{ ton/gal})(0.10)(0.191)(1.436 \times 10^9 \text{ gal/yr}) \\ &\quad (15.8 \text{ ppm}) \\ &= 1.8 \text{ tons/year} \end{aligned}$$

Utilities estimate:

$$\begin{aligned} \text{Cr. Ems} &= (4.2 \times 10^{-9} \text{ ton/gal})(0.10)(0.191)(2.65 \times 10^9 \text{ gal/yr}) \\ &\quad (15.8 \text{ ppm}) \\ &= 3.4 \text{ tons/year} \end{aligned}$$

The Radian report^{4/} also included a second estimate for the water lost from utility cooling towers. This second method estimates the drift based on the amount of water needed for cooling per kilo-watt-hour of power produced. The estimate for D_w from this approach is 5.83×10^9 gallons per year nationwide.

Using equation 5 the estimates for utility emissions is

$$\begin{aligned} (\text{Cr. Ems}) &= (4.2 \times 10^{-9} \text{ ton/gal})(0.10)(0.191)(5.83 \times 10^9 \text{ gal/yr}) \\ &\quad (15.8 \text{ ppm}) \\ &= 7.4 \text{ tons/year} \end{aligned}$$

Using the two estimates for utility emissions, an upper and lower estimate can be determined.

	<u>Lower Estimate</u>	<u>Upper Estimate</u>	<u>Average</u>
Utilities	1.8	1.8	1.8
Industrial	<u>3.4</u>	<u>7.4</u>	<u>5.4</u>
Hexavalent Chromium Emissions (tons/year)	5.2	9.2	7.2

Because there was no reason to select either method 1 or 2 as the "best" estimate, results from both methods were used for the report.

The estimate for the average chromium emissions from cooling towers was the average of the methods 1 and 2 estimate or $(2.0 + 7.2)/2 = 4.6$ tons/year. The possible upper and lower estimates were taken to be the highest and the lowest estimate determined by either method or 0.23 tons per year from method one and 9.2 tons per year from method two.

3. Waste Incineration Emissions

Chromium emission factors are usually presented as a weight percent of the particulate matter (PM) emissions. The chromium content of PM is highly dependent on the amount of chromium in the waste being burned. Unfortunately, the chromium content of waste is usually not known and an average emission factor has to be applied to the PM emissions.

A review of six reports indicates that the percent chromium in PM emissions can range from 0.017 percent to 0.13 percent with an average for refuse and/or sludge incinerators of 0.058 percent.^{6,7,8,9,11/} The total PM emissions from refuse/sludge incineration in 1981 was estimated to be 126.2 tons.^{10/}

Using the above numbers, the estimates for chromium emissions are:

Lower estimate Cr. Ems = $\frac{(0.017)(126.2 \text{ tons})}{100} = 0.021 \text{ tons/year}$

Upper estimate Cr. Ems = $\frac{(0.13)(126.2 \text{ tons})}{100} = 0.16 \text{ tons/year}$

Average Cr. Ems = $\frac{(0.058)(126.2 \text{ tons})}{100} = 0.074 \text{ tons/year}$

4. Residual Oil Combustion:

In 1981, 85.5 million barrels of residual oil were burned within California which resulted in an estimate of 18,300 tons of particulate matter (PM) being released to the atmosphere. Of this oil use, the electric utility industry consumed for 45.0 million barrels and released 9,000 tons of PM emissions.^{12/}

In 1983, electric utilities in California consumed 10.4 million barrels of residual oil^{13/} which are estimated to emit 2,080 tons of PM.

All other sections, except electric utilities, are estimated to consume 38.8 million barrels of residual oil and emit 8,730 tons of PM^{14/}; the total California consumption of residual oil and its PM emissions in 1983 would be 49.2 million barrels (10.4 MMbbl + 38.8 MMbbl) and 10,800 tons (8,730 tons + 2,080 tons) of PM emissions, respectively.

Chromium emissions based on residual oil combustion are estimates as follow:

$$\text{Cr Ems} = (8.47 \times 10^6 \text{ tons/yr})(1.2 \times 10^{-3} \text{ lb.Cr/ton oil})^{15/}$$
$$(\text{ton}/2,000 \text{ lb}) = 5.1 \text{ tons}$$

In another method, chromium emissions are calculated as a fraction of PM emissions. The emission factor was calculated based on tests using #6 fuel oil. The calculation is presented below:

$$\begin{aligned} \text{Cr Ems} &= (10,800 \text{ tons PM/yr})(1.85 \times 10^{-3} \text{ ton Cr/ton PM}) \frac{15}{100} \\ &= 20 \text{ tons} \end{aligned}$$

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APPENDIX D

ARB ANALYTICAL METHODS FOR SAMPLING AND ANALYSIS
OF ATMOSPHERIC TOTAL CHROMIUM AND
ATMOSPHERIC HEXAVALENT CHROMIUM

AIR RESOURCES BOARD
PROCEDURE FOR THE SAMPLING AND ANALYSIS
OF
ATMOSPHERIC TOTAL CHROMIUM, LEAD, MANGANESE AND NICKEL
METHOD 105

Haagen-Smit Laboratory Division
State of California
Air Resources Board
9528 Telstar Avenue
El Monte, CA 91731

Procedure for the Sampling and Analysis
of
Atmospheric Total Chromium, Lead, Manganese and Nickel
Method 105

1. Introduction

- 1.1 This procedure describes a method of sampling and analyzing atmospheric concentrations of total chromium (Cr), lead (Pb), manganese (Mn) and nickel (Ni).
- 1.2 Normal concentrations of total chromium usually are about 0.007 $\mu\text{g}/\text{M}^3$; lead usually is about 0.2 $\mu\text{g}/\text{M}^3$; manganese is about 0.01 $\mu\text{g}/\text{M}^3$ and nickel is about 0.005 $\mu\text{g}/\text{M}^3$.
- 1.3 With a sample volume of 24 cubic meters, the lower detectable limit for Cr, Mn, and Ni is 0.002 $\mu\text{g}/\text{M}^3$, while the lower detectable limit for Pb is 0.005 $\mu\text{g}/\text{M}^3$.

2. Method

- 2.1 A low-volume sampler is used to collect ambient suspended particulates containing total chromium, lead, manganese and nickel in air parcels.
- 2.2 A measured volume of air passes through a Teflon filter where particulates are collected.
- 2.3 The procedure and apparatus for low-volume sampling is described in Appendix C, "Procedure for Lo-Volume Sampling."
- 2.4 The Teflon filter is removed from the sampler and returned to the laboratory for elemental measurement by X-ray fluorescence (XRF) analysis:
 - 2.4.1 The sample is irradiated with X-rays, which knock out inner-shell electrons.
 - 2.4.2 When the inner-shell vacancies are filled by valence electrons, the excess energy may be released in the form of (fluorescent) X-rays whose energies are characteristic of the atom from which they originate.
 - 2.4.3 Both the number and characteristic atomic energies of the fluorescent X-rays are measured by a solid-state detector.
 - 2.4.4 The XRF simultaneously measures concentrations of most elements, including Cr, Pb, Mn, and Ni, at the nanogram to microgram level.

3. Apparatus

- 3.1 The XRF analyzer consists of the following:
 - 3.1.1 A sample holder which contains an X-ray tube, detector, preamplifier and liquid nitrogen trap.
 - 3.1.2 Amplifier
 - 3.1.3 Multichannel analyzer
 - 3.1.4 Buffer unit
 - 3.1.5 Calculator with printer
 - 3.1.6 The buffer unit and calculator can be replaced by a computer.
 - 3.1.7 A separate unit houses the X-ray tube power supply and control.
- 3.2 Figure 3.2 is a block diagram of the instrumentation employed. The detector is solid-state, lithium-drifted silicon. Its resolution is about 150 electron volt (eV) full width half maximum (FWHM) at an X-ray energy of 2.3 KeV; its resolution decreases with increasing X-ray energy. The multichannel analyzer sorts the pulses from the amplifier into channels according to the energy of the pulse, which is proportional to the energy of its parent X-ray. It may be used to process the spectrum in a number of ways. The buffer stores pulses from the analyzer and feeds them into the calculator at an acceptable rate. The calculator is programmable; its program subtracts the background of the raw spectrum, removes contributions from secondary X-rays, calculates net atmospheric concentrations and sends them to the printer.

4. Procedure

- 4.1 The sample is placed in the X-ray sample holder where a molybdenum X-ray tube irradiates the sample.
- 4.2 The resulting fluorescent X-rays are detected and converted into electrical pulses, amplified, and sent into a multi-channel analyzer.
- 4.3 After a scan is completed, the pulses are converted into elemental concentrations of Cr, Pb, Mn, and Ni and the results are typed out automatically on the printer.

5. Calculations

- 5.1 Elemental concentrations are obtained assuming a proportionality between net counts and concentration; the proportionality constant is obtained from calibration standards, stored in cassette tapes and entered into the Tektronix 31 calculator.
- 5.2 The standards are thin films obtained from Umatter Company or dried solutions on filters obtained from Columbia Scientific Industries.

5.3 Fluorescent count rates from these standards are proportional to elemental concentrations of Cr, Pb, Mn and Ni expressed in micrograms per cm².

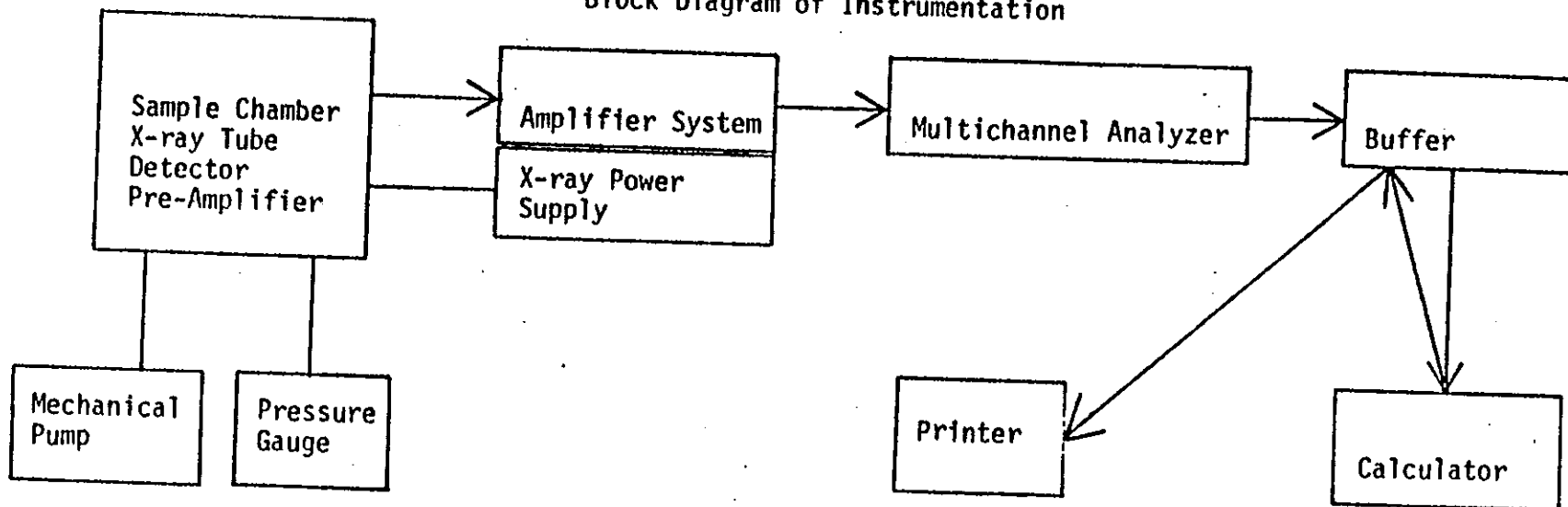
6. Critiques and Comments

6.1 Molybdenum L X-rays were chosen to maximize count rates from elements which fluoresced in the region between 5 and 12 KeV, particularly manganese and lead. The molybdenum L X-rays near the sulfur K region were absorbed using two thicknesses of Whatman 41 filter paper.

6.2 X-ray fluorescence analysis is a rapid, non-destructive analytical method.

Figure 3.2

Block Diagram of Instrumentation



DRAFT

D R A F T

ADDLOG6

METHOD FOR THE SPECIATION AND ANALYSIS OF
HEXAVALENT CHROMIUM AT AMBIENT ATMOSPHERIC LEVELS1. SCOPE

This document describes the determination of chromium +6 in aqueous media after sampling ambient air. The method has been tailored to concentrations which would be expected in ambient air. Although the procedure described is known to complex other metal ions, the procedure has not been validated for any metal species other than hexavalent chromium.

2. SUMMARY OF METHOD

If sampling is performed by aqueous impinger, the water may be treated directly. If sampling by low volume filter, the filter is added to 100 ml of water and the complexation procedure carried out in the presence of the filter.

The aqueous solution is buffered to pH 7 and an aqueous solution of APDC added. After mixing, the solution is filtered through a disposable cartridge containing C₁₈-bonded silica gel. The complex is absorbed onto the gel. The water, remaining ions, and uncomplexed APDC are passed through into a filtering flask and discarded. The absorbed Cr+6-complex is desorbed with acetone, the acetone evaporated, and the resultant residue diluted to 1.0 ml with 10% nitric acid in water.

This solution is then analyzed by flameless atomic absorption spectrophotometry (FAAS) for chromium.

3. LIMITATIONS AND INTERFERENCES

- 3.1 The concentration ranges expected for Cr+6 in ambient air (1-5 ng/m³) require that extreme care must be taken to insure that glassware and reagents do not contribute to the measured levels. Blanks must be analyzed with every batch of samples.
- 3.2 Trivalent chromium at levels ten times the Cr+6 concentration does not interfere in the method. Iron (Fe+3) does not interfere, except that excess ferric ion will compete with Cr+6 for available complexing agent. This effect has been minimized by performing the complexation step at pH 7. The other metals known to form APDC complexes at pH 7 (copper and cobalt) do not occur at sufficiently high levels to deplete the complexing agent.
- 3.3 Matrix effects have been reduced or eliminated by the extraction of the complex into an organic solvent and matching the final aqueous diluent to the 10% nitric acid solution used for diluting standards.

4. APPARATUS

- 4.1 Varian Model 375 Atomic Absorption Spectrophotometer equipped with a CRA-90 flameless accessory and strip chart recorder.

- 4.2 Vacuum filtering apparatus equipped with Sep-Pak C₁₈ cartridge adaptor and teflon tubing.
- 4.3 micro-Snyder concentrator, 5 ml capacity.
- 4.4 Sep-Pak cartridge: Waters Assoc. #51910. Prepare cartridge for use by first filtering 5 ml of methanol through it, then washing with 10 ml distilled water.

5. REAGENTS

- 5.1 Nitric acid, Ultrex grade.
- 5.2 Stock standard, 250 mg/l: Dissolve 141.4 mg K₂Cr₂O₇ in 10% nitric acid solution and dilute to 200 ml in a volumetric flask. 1 ml = 0.25 mg Cr+6.
- 5.3 Intermediate standard, 0.5 mg/l: Dilute 100 ul of the stock standard in 50 ml of 10% nitric acid in a volumetric flask. 1 ml = 0.5 ug Cr+6.
- 5.4 Working standard: Dilute 2.0, 4.0, 8.0, 12.0 ml in 100 ml of 10% nitric acid. These correspond to 10 ng/ml, 20 ng/ml, 40 ng/ml, and 60 ng/ml Cr+6. Prepare working standards daily.
- 5.5 Buffer, pH 7: 0.05 M KH₂PO₄/NaOH buffer, Fisher Scientific.

5.6 APDC solution: Dissolve 3 gms ammonium pyrrolidine dithiocarbamate in 100 ml distilled water. Filter the solution through a glass fiber to remove the insoluble sediment. The resultant solution will be a clear yellow. Filter entire 100 ml through a prepared Sep-Pak C₁₈ cartridge. The resultant solution will be colorless.

6. INSTRUMENT CALIBRATION

- 6.1 Prepare instrument for the flameless analysis of chromium. Insure that the carbon tube is properly aligned.
- 6.2 Inject 10 ul of 10% nitric acid solution. Start CRA-90 heating cycle. Auto zero the data system using this value. The absorbance value should be no more than 0.005.
- 6.3 Inject 10 ul of 60 ng/ml standard. After the analysis, calibrate the data system to 60 ng/ml. Repeat Step 6.2 to insure that the system reads 0.0.
- 6.4 Inject 10 ul of 60 ng/ml standard twice more. Recalibrate if values differ from 60 ng/ml by more than +15%.
- 6.5 Inject 10 ul of 40 ng/ml, 20 ng/ml, and 10 ng/ml standards in triplicate. Determine the least squares fit of the resultant data; the analysis must result in a slope of $1.00 \pm 15\%$. This calibration procedure must be performed weekly.

6.6 The blank and 60 ng/ml standard must be analyzed at least every ten samples.

7. SAMPLE ANALYSIS

- 7.1 If the sample has been taken using a 37 mm glass fiber or teflon filter, place the filter in a 125 ml glass stoppered flask, add 100 ml deionized water, 2 ml of pH 7 buffer, and 1 ml of APDC solution. Place on horizontal shaker for 30 minutes.
- 7.2 If sample has been collected in a liquid impinger, add 2 ml/100 ml solution pH 7 buffer; mix well, and then add 1 ml/100 ml solution APDC solution. Mix well.
- 7.3 Aspirate aqueous solution through a prepared Sep-Pak C₁₈ cartridge.
- 7.4 Using a 10 ml syringe, desorb the trapped Cr+6-APDC complex with 5 ml acetone directly into a micro-Snyder concentrator.
- 7.5 Using a hot water bath (more than 80°C), concentrate the acetone solution to dryness. Note: There will be a small liquid residual, mostly residual water. As much acetone must be removed as possible, since it causes problems during the analysis step.
- 7.6 While hot, add 0.1 ml concentrated Ultrex nitric acid (2 drops); let cool.

- 7.7 Add deionized water to the micro-Snyder receiver and quantitatively transfer the solution to a 1.0 ml volumetric flask. Dilute to 1.0 ml.
- 7.8 Inject 10 ul of the concentrate in triplicate for analysis using the calibrated FAAS system.
- 7.9 Record the analysis results on the strip chart trace with identifying laboratory identification number and dilutions, if any. Record results and calculations in the AAS laboratory workbook. Record the calculated concentration in nanograms/m³ on the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium +6, ng/m}^3 = \frac{\text{Concentration Found, ng/ml}}{\text{Volume Sampled, m}^3} \times \text{Dilution Factor}$$

8. METHOD VALIDATION

- 8.1 The calibration curve from 10 ng/ml to 60 ng/ml was constructed. The results of this procedure are shown in Table I.
- 8.2 Deionized water was spiked with 20 ng, 40 ng, and 50 ng Cr+6. The analysis was performed using this method with the following results:

Spike, ng	Recovered*, ng	% Recovery*	RSD, %*
20	14	70	17
40	37	92	6.5
50	48	96	11

* Results of three spike sample analyses.

8.3 Field spike studies have not yet been performed, results to be submitted at a later date..

TABLE I
Chromium +6 by Flameless Atomic Absorption
Results of Standard Analysis

Concentration (ng/ml)	Average Recovery, ng/ml	RSD**, %
10	8.9	25
20	24.4	6.6
40	39.0	3.2
60 (calibration)	60	7.2

** Relative Standard Deviation, $n = 4$

Correlation Coefficient: 0.994

Slope: 0.978

Intercept: 1.2 ng/ml

LOD: $(i + 3\sigma) = 2.1 \text{ ng/ml}$ (0.21 ng/m^3 , 10 m^3 sample, but may be higher due to sample media contamination).