Chromium Speciation: Key to Reliable Control of Chromium Toxicity to Aquatic Life

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Abstract

Chromium exists in aquatic systems in two principle oxidation states, Cr(III) and Cr(VI). Cr(VI) is highly toxic to aquatic life, where in some waters it is toxic to zooplankton at less than 0.5 μg/L. Cr(III) has a low toxicity to aquatic life. Current regulatory approaches allow Cr(III) to be discharged to ephemeral streams with limited dilution at 50 μg/L, i.e. the drinking water MCL. Cr(VI), however, is regulated in discharges to 10 μg/L, i.e. the US EPA National Toxics Rule ambient water quality criterion. There are a variety of chemical and photochemical processes that occur in ambient waters that control the speciation of chromium and, therefore, its toxicity.

Current regulatory approaches are not protective of aquatic life from Cr(VI) toxicity. Current regulation of

Cr discharges to the environment ignores aquatic chemistry of Cr where Cr(III) converts to Cr(VI) in sufficient amounts to be toxic to aquatic life. There is need to regulate Cr based on a risk assessment approach that incorporates mid-1990 aquatic chemistry and aquatic toxicology information. The key to technically valid regulation is the development of a comprehensive, reliable receiving water monitoring program that determines whether aquatic life toxicity is present in the receiving waters for Cr discharges above an ambient water concentration of 1 μg/L. If chronic toxicity is found to zooplankton used in the toxicity tests, then TIEs should be conducted to determine if the toxicity is due to Cr(VI).

Thermodynamic Equilibrium

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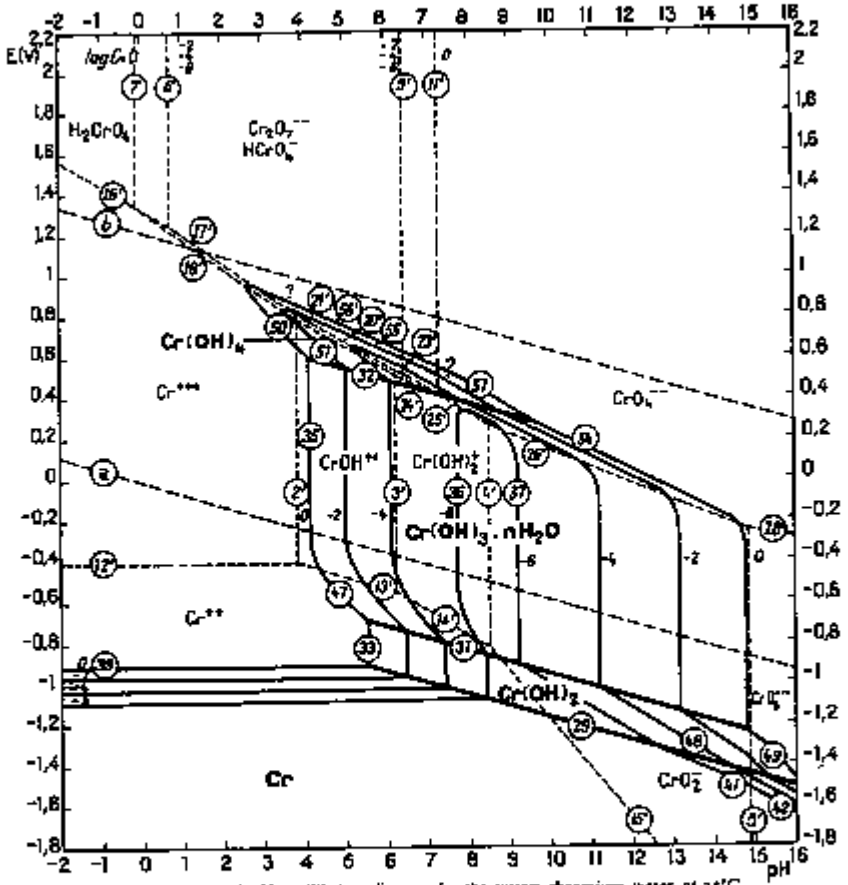


FIG. 4. Potential–pH equilibrium diagram for the system chromium–water, at 25°C.
In solutions containing chloride.
[Approximate representation made by considering $Cr(OH)_3 . nH_2O$.]

Pourbaix, M., "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, London (1966)

Pourbaix, M., "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, London (1966)

Aquatic Chemistry Issues

Poorly Understood

Cr(VI) Thermodynamically Stable Species in Oxygen Containing Surface Waters

Cr(III) Present Under Reducing - Anoxic (Oxygen Free) Conditions

Cr(VI) Highly Soluble - Limited Tendency for Sorption, Precipitation and Complexation

Cr(III) High Tendency for Sorption, Precipitation and Complexation with Organics

- Tends to Accumulate in Bedded Sediments Under Low Flow - Low Velocity Conditions
- Bedded Sediment Cr Subject to Scour During High Flows (Storm Conditions)

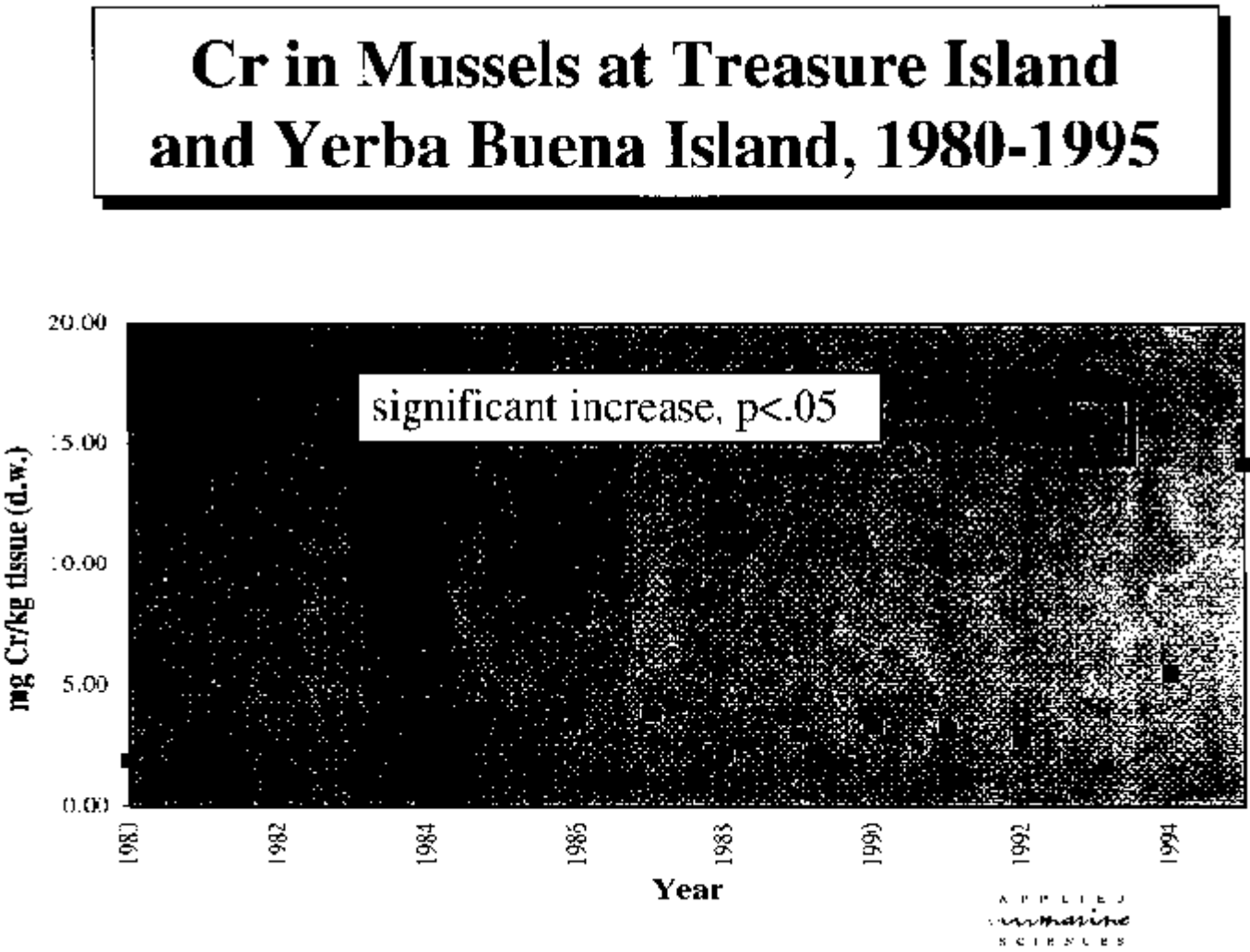
Cr(VI) Photochemistry - Reduction by Light Produced Free Radicals

- Is This a Significant Factor in Cr(VI) Concentrations in Ambient Waters?
- Magnitude of Photoreduction Site Specific
  - Water Quality Significance Unknown

Cr(III) Oxidized by Variety of Known and Unknown Substances

- MnO_2 Known "Catalyst" - Can Rapidly Oxidize Cr(III)
- Role of Cu as Catalyst - Free Radical Promoter Likely
- Significance of Aged vs. Freshly Precipitated MnO_2 Needs to Be Considered

Impact of Increased Stream Flow Scour of Sediments on Water Column Chromium



Mytilus edulis," In preparation (1997)

Chromium Oxidation State and Toxicity

US EPA Fresh Water Quality Criterion (μg/L)

Oxidation State	1 Hour Average	4 Day Average
Cr(III)	1,700	210 (100 mg/L $CaCO_3$)
Cr(VI)	15	10 (dissolved)

Not to Be Exceeded More than Once in Three Years

Cr(VI) Toxic to Zooplankton at 0.5 μg/L

US EPA Criterion For Cr(VI) Not Protective

Total Cr Drinking Water MCL = 50 μg/L

Environment Canada (1995):

"Based on reviews by the United States Environmental Protection Agency (U.S. EPA, 1985) and the Canadian Council of Resource and Environment Ministers (CCREM, 1987), Daphnia *spp. appear to be particularly sensitive to chromium. The average number of young produced per adult* Ceriodaphnia reticulata *was reduced by about 30% following 7 days of exposure to 0.5 μg/L of Cr(VI), while the decrease was 20% for* D. magna *exposed to 1.5 μg/L of Cr(VI) for 14 days (Elnabarawy* et al.*, 1986). Exposure of* D. magna *to 2.5 μg/L of Cr(VI) for 7 days caused a 28% reduction in juvenile survival and a 22% reduction in the number of young produced (Trabalka and Gehrs, 1977; U.S. EPA, 1985). Elnabarawy* et al. *(1986) reported a 20% death rate for adult* D. pulex *exposed to 1.5 μg/L of Cr(VI) for 14 days. The lowest reported median lethal concentration (LC_{50}) of Cr(III) for* Daphnia magna *was 6 μg/L (Janus and Krajnc, 1990.)"*

US EPA (1985):

"Six chronic values are available for five species of daphnids and they range from less than 2.5 to 40 μg/L (Table 2). The results of Trabalka and Gehrs (1977) support those of Mount (1982)."

Canadian Environmental Protection Act

Priority Substances List
Assessment Report

Chromium and its Compounds

Government of Canada / Gouvernement du Canada
Environment Canada / Environnement Canada
Health Canada / Santé Canada

Canada

CANADA'S GREEN PLAN

United States Environmental Protection Agency

Office of Water Regulations and Standards Criteria and Standards Division Washington, DC 20460

EPA 440/5-84-029 January 1985

EPA

Ambient Water Quality Criteria for

Chromium - 1984

Additional Information on Toxicity

Environment Canada, "Priority Substances List Assessment Report: Chromium and its Compounds," Canadian Environmental Protection Act, Quebec, Canada (1994)

US EPA, "Ambient Water Quality Criteria for Chromium - 1984," Office of Research and Development, Environmental Monitoring and Support

Laboratory, EPA 440/5-84-029, Cincinnati, OH, January (1985)

Environment Canada (1995)

Regulatory Approaches for "Controlling" Chromium Toxicity

Central Valley Regional Water Quality Control Board (CVRWQCB) 1996

Permitted Wastewater Discharge Containing Up to 50 μg/L Cr to Putah Creek

at Times Putah Creek, Is 100% Wastewater Effluent (Effluent Dominated)

Putah Creek Designated Beneficial Uses

Fish, Aquatic Life, Wildlife, Domestic Water Supply, Groundwater Recharge, Etc.

CVRWQCB Basin Plan Regulatory Requirements

"All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life. This objective applies regardless of whether the toxicity is caused by a single substance or the interactive effect of multiple substances. Compliance with this objective will be determined by analyses of indicator organisms, species diversity,

population density, growth anomalies, and biotoxicity tests of appropriate duration or other methods as specified by the Regional Water Board."

1995 CVRWQCB Allowed 16 μg/L Cr(VI) for 1 Hour Average

No Chronic Cr Criterion Required

1996 CVRWQCB Allowed 10 μg/L Cr(VI) as 4 Day Average

Under Pressure From Public Required Toxicity Testing of Effluent

Measure Cr Concentrations in Putah Creek at 100 ft. Downstream of Discharge

No Toxicity Measurements of Putah Creek Waters Required

Problems with Regulatory Approach

Regulatory Approach Will Not Likely Prevent Aquatic Life Toxicity Due to Cr(VI)

- Ignores Aquatic Chemistry of Cr
- Ignores Post 1984 Information on Toxicity of Cr(VI)
- Ignores Hydraulic Characteristics of Putah Creek

CVRWQCB Executive Officer Stated at Permitting Hearing, Considering These Issues Would Be "Precedent Setting"

Evaluate Toxicity of Wastewater Effluent and Receiving Water

Monitor Effluent and Receiving Waters at Monthly Interval for Two years Using US EPA Three Species Aquatic Life Short-Term Chronic Toxicity Tests

Use Chronic End Point

If After Two Years of Monthly Testing No Toxicity Found - May Reduce Toxicity Testing to Bi-monthly

If Toxicity Found - Increase Frequency of Toxicity Testing to Weekly, If Toxicity Found on Weekly Sampling - Increase Frequency to Daily Until Toxicity Is Eliminated for One Year, Then Decrease Frequency to Monthly for Two Years

If Toxicity Found - Conduct Toxicity Investigation Evaluation (TIE) To Determine Cause

If Cr(VI) Above 0.5 μg/L - Screen Toxic Waters for Cr(VI) Toxicity

How? - Need Specific TIE for Cr(VI)

Regulatory Approach Should Incorporate 1997 Level of Risk Assessment for Regulating Cr in Discharges to Surface Waters

- Aquatic Chemistry
- Aquatic Toxicology
- Water Impact Assessment
- Water Quality Monitoring

Key to Reliable Regulation is Integration of Aquatic Chemistry and Auatic Toxicology

Reliable Monitoring of Chromium Discharges for Environmental Impacts

Do Not Select Sampling Station at Fixed Distance, i.e. 50 ft. or 100 ft., 300 ft.

Examine Receiving Water Hydrologic and Hydraulic Characteristics

Determine Distance and Travel Time to Dilute Discharge Plus Receiving Water Background Total Cr< 1 μg/L

Under Low Flow, Mid-Range Discharge i.e. 0.5" Precipitation per Day, and High Flow Greater than 1.0" Precipitation per Day in Stream Watershed Select Position of

Sampling Stations to Achieve < 1 μg/L Total Cr

Monitoring of Chromium Impacts

Measure Flow, Specific Conductivity at 25 Degrees, Temperature, pH, Turbidity, Suspended Sediments, Total Cr and Cr(VI) with Detection Limits of 0.5 μg/L

Toxicity Tests Use US EPA Three Species Fish Larvae and *Ceriodaphnia*

If Toxicity Found That is Not Due to Cr(VI) Allow Increased Cr Discharge After One Year of Testing to Allow a Total Cr Concentration of 5 μg/L - If After One Year of Testing of Receiving Waters at Various Locations at 5 μg/L Total Cr, Allow Total Cr to Increase to 10 μg/L

Should Continue at Least Quarterly Total Cr and Cr(VI) Toxicity Testing

Sample During Rising Hydrograph - Scour in First Major Storm of Season to See if Suspension of Deposited Cr(III) Leads to Excessive Cr in Water Column

Examine Downstream Clams and Mussels for Excessive Bioaccumulation of Chromium in Tissue

Sample Before and After First Major Storm of Season

Managing Chromium Solid Wastes

California Department of Toxic Substance Control Proposes to Allow a Solid Waste Containing High Levels of Cr(III) to Be Classified as "Non-Hazardous"

Ignores Environmental Chemistry of Cr(III) Which Can Convert to Cr(VI) Which Has High Levels of Toxicity to Aquatic Life

Should Require that the Manager of Any Waste Containing Total Cr that Could Result in Cr in a Waterbody Above About 1 μg/L that Proposes to Manage the Waste in Such a Way as to Possibly Lead to Surface or Groundwater Pollution by Cr,

Determine on a Site Specific Basis Whether the Management Approach Leads to Cr(VI) in Surface Waters at Potentially Toxic Levels

A Comprehensive Monitoring Program Required for as Long as the Waste Is a Threat

Research Needs

Toxicity of Cr(VI) to *Ceriodaphnia* and Other Zooplankton and Other Aquatic Life

What Factors Influence Cr(VI) Toxicity to Zooplankton?

Needs Toxicity Investigation Evaluation (TIE) For Cr(VI)

U.S. Urban Area Street Stormwater Runoff Typically Contains Total and Soluble Cr Above 1 μg/L (Pitt and Field 1990)

Is The Form of Chromium Cr(VI)? If so, Is it Causing Aquatic Life Toxicity to Zooplankton in Receiving Waters for Urban Area Stormwater Runoff?

Supplemental Information

Lee, G.F., *"Petition to the State Water Resources Control Board to Review the Waste Discharge Requirements, Order 96-227, Issued by the Central Valley Regional Water Quality Control Board on August 9, 1996 to the University of California at Davis for the UCD Campus Landfill Ground Water Cleanup System,"* submitted to State of California Water Resources Control Board, Sacramento, CA, September (1996)

Lee, G.F., *"Technical Deficiencies in the CVRWQCB Order No. 96-227 Discharge of the UCD 'West' Landfill Leachate-Polluted Groundwaters to Putah Creek Presented to CVRWQCB September 20, 1996 Hearing,"* Report G. Fred Lee & Associates, El Macero, CA (1996)

Lee, G.F., *"Supplement/Addendum to Petition of Order No. 96-227 Issued by the Central Valley Regional Water Quality Control Board on August 9, 1996 to the University of California at Davis for the UCD Campus Landfill Ground Water Cleanup System To address the New Information Provided by The University of California at Davis and the CVRWQCB Staff at the CVRWQCB September 20, 1996 Hearing Devoted to Chromium Technical Issues,"* submitted to State of California Water Resources Control Board, Sacramento, CA, October (1996)

Conclusions

- Typically Regulatory Agencies Ignore Aquatic Chemistry, Readily Available Toxicology and Transport Information in Regulating Chromium Discharges to Surface Waters
- Cr(VI) Is Likely More Toxic Than Reflected by the US EPA 10 μg/l Water Quality Criterion - Toxicity Found at 0.5 μg/L for Zooplankton

- Conditions Exist in Aquatic Systems that Can Convert Cr(III) to Cr(VI) at Potentially Toxic Concentrations
- Concentrations of Total Cr Above About 0.5 μg/L Should Be Considered Threat to Aquatic Live that Requires Site Specific Investigations of Potential Toxicity
- Cr Discharges Above 1 μg/L at the Edge of a Mixing Zone for the Discharge Should Require Intensive Properly Developed and Implemented Effluent and Receiving Water Monitoring for Aquatic Toxicity - TIEs and Cr Species to Protect Aquatic Life from Potential Adverse Impacts of Cr

References as:"Lee, G.F. and Jones-Lee, A., 'Chromium Speciation: Key to Reliable Control of Chromium Toxicity to Aquatic Life,' Presented at American Chemical Society national meeting, San Francisco, CA April (1997)."

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