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Subject: Under-Regulation of Chromium
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J. Bruns et. al., previously I have brought to your attention my concerns about chromium VI being under-regulated by the US EPA chronic criterion of 10 ug/L. Attached is a recent report on this issue. This report is serving as a basis for a paper that I have been asked to prepare for the SETAC newsletter. If you have questions or comments on this report, please bring them to my attention. Fred

Under-Regulation of Chromium in Ambient Waters
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The typical water pollution control regulatory approach used for chromium (Cr) is to limit discharges of Cr VI from NPDES permitted sources so the ambient waters receiving the discharge do not have a total Cr VI concentration above the US EPA chronic water quality criterion/state standard of 10 µg/L. This value was established as part of the US EPA (1995) National Toxics Rule. It is generally assumed that meeting the US EPA (1987) water quality criterion/state standard for Cr VI will be protective of aquatic life in the receiving waters from Cr toxicity. The US EPA (1985) aquatic life water quality criterion for Cr III is 120 µg/L for water with a hardness of 50 mg/L $CaCO_3$. The US EPA drinking water MCL for Cr III of 50 µg/L in the ambient waters receiving the discharge will be protective of drinking water supplies and aquatic life from toxicity due to Cr III. It is generally assumed that meeting the drinking water MCL for Cr III in ambient waters should be protective of domestic water supplies and aquatic life toxicity. The above general assumptions are valid under conditions where the ambient waters contain low Cr VI and provide rapid dilution of the NPDES-permitted discharges of Cr. There are, however, conditions, associated with low flow receiving waters (effluent dominated systems) where the assumptions of meeting Cr VI aquatic life water quality criteria/standards and Cr III drinking water MCL will not be protective of zooplankton for Cr VI aquatic life toxicity. Many effluent-dominated systems are classified for full aquatic life beneficial uses and therefore have to meet the same water quality criteria/standards as those systems that have large amounts of dilution available to dissipate the potential toxic effects of Cr VI. There can also be conditions where Cr III has accumulated in sediments to a sufficient extent so that when the sediments are exposed to oxidizing conditions, there can be sufficient conversion of Cr III to Cr VI to lead to aquatic life toxicity.

Cr VI Toxicity

A review of the Cr VI aquatic life toxicity literature shows that there is substantial evidence that Cr VI is toxic to zooplankton (daphnia species) at concentrations of a factor of 10 or less than the US EPA water quality criterion of 10 µg/L. The US EPA 1987 "Gold Book" criterion support document (US EPA, 1985) presents information that Cr VI is toxic to daphnia at concentrations less then 2 µg/L. There was insufficient information to establish the toxicity level. Environment Canada (1995) presents a review of Cr toxicity and concludes Cr VI can be toxic to several forms of zooplankton at less than 0.5 µg/L. The US EPA (1996) updated water quality criterion presents information that shows that Cr VI is toxic to several zooplankton at about 1 µg/L. The US EPA, in establishing the water quality criterion development approach, as implemented today, does not protect all forms of aquatic life from adverse impacts associated with meeting the criterion value. In the case of Cr VI, there is substantial evidence in the literature that Cr VI is toxic to several common forms of zooplankton that are typically considered important species at concentrations of a factor of 10 or so less than the chronic criterion value. Therefore, the typical assumptions that meeting the ambient water quality chronic criterion for Cr VI of 10 µg/L will be protective of zooplankton and fish populations that depend on the zooplankton as food can be under- protective of aquatic life resources in a waterbody.

In August 1997 the US EPA Region 9 proposed the California Toxics Rule (CTR) (US EPA 1997) for establishing water quality criteria for toxic constituents that are to be used by California as the state's water quality standards (objectives). The criterion values proposed in the CTR are, in general, updated based on US EPA (1996) reviews from the US EPA (1987) "Gold Book" values. They are also updated from the US EPA (1995) National Toxics Rule implementation guidance. The US EPA (1997) promulgated a revised Cr VI chronic (four-day average) criterion of 11 µg/L. This represents an increase in the chronic criterion from the US EPA (1996) value of 10 µg/L to 11 µg/L. While based on the way the US EPA water quality criteria are developed they do not necessarily protect the most sensitive aquatic life, generally, when these criteria are implemented into state standards and NPDES wastewater discharge limits, it is assumed by the local regulatory agencies that meeting a criterion/objective value in ambient waters would be protective of common zooplankton such as daphnia species. However, a review of the literature on the toxicity of Cr VI to various daphnia species, including the documents cited by the US EPA in developing the 1987 as well as 1995 water quality Cr VI criterion values, that a number of investigators have found that Cr VI is toxic to several daphnia species at less than 1 µg/L. Therefore, meeting the US EPA Cr VI chronic criterion of 11 µg/L proposed for adoption in the State of California may not protect a number of important zooplankton from chronic toxicity. Since Cr VI does not enter into precipitation, complexation, sorption reactions that tend to detoxify many heavy metals, it may be concluded that Cr VI is being under-regulated with respect to protecting zooplankton as a source of food for larval fish and other aquatic life.

While the US EPA claims in its 1997 and 1995 documents that the 11 µg/L chronic criterion will be protective of fisheries resources, such claims ignore situations where ambient waters could contain sufficient Cr VI to be toxic to zooplankton at less than 0.5 µg/L which are important sources of larval fish food. Such toxicity could, therefore, be adverse to fish populations through impacting larval fish development.

Cr III to Cr VI Conversion

Schroeder and Lee (1975) were among the first to demonstrate that Cr III in ambient waters can slowly convert to Cr VI. Lee (1996a,b,c) has reviewed the literature on Cr III to Cr VI conversions where it is concluded that under oxic conditions, the thermodynamically stable species of Cr is Cr VI. Further, Cr III can be converted to Cr VI in oxygen-containing ambient waters, especially in the presence of a catalyst such as manganese. There are also a number of reactions that tend to convert Cr VI to Cr III in oxic conditions, including photoreduction. While generally, it can be concluded that in most situations, the rate of conversion of Cr III in an ambient water from a wastewater discharge to Cr VI is sufficiently slow so that the dilution of the discharge with low Cr ambient waters allows the Cr VI criterion/standard to be met in the receiving waters, there can be situations, associated with low flow, effluent-dominated conditions, where discharging Cr III at the drinking water MCL of 50 µg/L could result in the conversion of sufficient Cr III to Cr VI to be toxic to zooplankton. The issue is not that typically assumed of conversion of Cr III to Cr VI to exceed the ambient water chronic criterion of 10 µg/L, but one of conversion of Cr III to Cr VI where the concentrations of Cr VI would be toxic to zooplankton which could occur at less than 0.5 µg/L.

Inadequate Monitoring Programs

One of the major problems in regulating Cr wastewater discharges is that regulatory agencies allow dischargers and those conducting ambient water monitoring programs to use analytical methods that measure Cr with a detection limit of the ambient water chronic criterion of 10 µg/L. Obviously, under these conditions, it is not possible to detect Cr VI at potentially toxic levels for zooplankton. The analytical methods that are used Cr VI should have reliable detection limits of less than 0.5 µg/L in order to use the US EPA's chemically-based approach for regulating potentially toxic chemicals.

A more reliable, readily implementable approach for regulating Cr toxicity in ambient waters is the effects-based approach where ambient water toxicity to zooplankton, such as Ceriodaphnia dubia, is used to determine whether the ambient waters receiving a Cr III and/or Cr VI discharge are toxic to the zooplankter under the standard US EPA test conditions (Lewis et. al. 1994). If toxicity tests are conducted at appropriate locations to address the Cr III to Cr VI conversion in ambient waters considering the dilution available in the receiving waters for a Cr III-Cr VI discharge, then it would be possible to detect Cr VI toxicity problems arising either directly from the discharge alone or in combination with background Cr VI as well as those associated with Cr III to Cr VI conversions.

The required ambient water monitoring program is significantly different than those typically permitted by regulatory agencies which involve a limited number, usually one, downstream monitoring station 100 to 200 meters downstream of the discharge point. Such monitoring programs have limited reliability in detecting Cr III to Cr VI conversion which can be toxic to zooplankton in effluent-dominated systems.

With respect to using the US EPA's chemically-based water quality protection approach, it will be necessary that the analytical methods used for Cr VI have reliable detection limits of less than 0.5 µg/L. According to Standard Methods, APHA et. al (1995), there are several analytical procedures that can be used for measuring Cr VI at about 1 µg/L. These methods include ion chromatography which has reported to be able to determine Cr VI at a few tenths of a µg/L. The frequently used inductively coupled plasma (ICP) method typically does not have the sensitivity to measure chromium at levels that are potentially toxic to aquatic life. The ICP standard methods of 1995 list the estimated detection limit for Cr using ICP as 7µg/L. Therefore, ICP is not adequate for measuring Cr in many wastewaters and ambient waters.

Cr III Accumulation in Sediments

Another potential problem with allowing Cr III discharges to occur at concentrations up to 50 µg/L is that Cr III tends to accumulate in sediments through sorption and precipitation reactions on particulates. The sediment-accumulated Cr III represents a potential source of Cr that under certain oxic conditions can be converted to Cr VI and lead to aquatic life toxicity. Of particular concern is sediment scour during a period of time where the increased flows typically associated with sediment scour are not sufficient to dilute the Cr VI toxicity that would arise from the conversion of Cr III to Cr VI at concentrations of 0.5 µg/L. The resuspension of Cr III in sediments may also occur due to fish and other aquatic life activity in the waterbody. Carp and some other fish resuspend sediments through their foraging and reproductive activities. This type of situation could result in the presence of the suspension of Cr III into the watercolumn where it could be oxidized to Cr VI and represent toxicity to zooplankton.

Gunther et al. (1997) have shown that associated with sediment scour conditions following a long period of drought in the Sacramento - San Joaquin River system, there was a readily discernible accumulation of Cr in San Francisco Bay mussels associated with the elevated flows at the end of the drought. It appears that the Cr III that has been accumulating in the San Francisco Bay watershed sediments during the low flow conditions was scoured and transported into the Bay to a sufficient extent to raise the overall level of Cr in the Bay waters. This in turn resulted in biouptake of the Cr by mussels. The significance of the accumulated Cr in the mussels is unknown at this time. This is an area that needs consideration as part of permitting Cr III discharges that lead to sediment accumulation of Cr III in the receiving waters. While Cr III in aquatic sediments probably, based on what is known now, not significantly toxic to aquatic life, the possibility of the conversion of Cr III to Cr VI under conditions of sediment suspension, as well as the bioaccumulation of Cr, in aquatic life tissue are areas of concern.

Suggested Regulatory Approach

While the water pollution field has been aware that it is possible that the discharge of a form of a chemical constituent could through transformations lead to greater toxicity in the receiving waters, this type of condition is largely ignored in the permitting of wastewater discharges. Current permitting typically approaches the regulation of chemicals that can transform to different chemical forms as though the transformations do not occur in the ambient waters, i.e. are regulated based on the individual species in the discharge or the concentrations that are present in the mixing of the discharge with the ambient waters. The Cr III-Cr VI regulatory issues mandate that the aqueous environmental chemistry and toxicology of the discharge to ambient waters be reliably considered in issuing the discharge permit. Of particular importance is the requirement that a substantial monitoring program be incorporated into the permit for those discharges to effluent dominated systems where there is inadequate dilution of the receiving waters to keep the total Cr VI in the receiving waters below the toxic levels of about 0.5 µg/L. Under conditions where there is the potential for concentrations of Cr VI in receiving waters to be above 0.5 µg/L, the discharger should be required to conduct comprehensive toxicity testing of these waters using Ceriodaphnia and/or other Cr VI sensitive zooplankton to determine if toxicity is present in these waters due to Cr VI arising directly from the discharge and/or from conversion of Cr III to Cr VI in the ambient waters. Particular attention should be given in the monitoring program to low flow conditions where there is limited dilution as well as those associated with the rising hydrograph where there could be sediment scour of deposited Cr III. The monitoring program should not be a one-shot operation, but an on-going program in which there is a valid search made for water quality (aquatic life toxicity) problems associated with discharges of Cr to the watercourses.

Cr III is another Cr species that is currently being under-regulated with respect to its impacts on aquatic life. While the direct toxicity of Cr III to aquatic life is low compared to Cr VI, the fact that Cr VI is a thermodynamically stable species in oxygen-containing aquatic systems and that Cr III has been found by a number of investigators to convert to Cr VI, especially in the presence of manganese as a catalyst, raises significant questions about the approach that is frequently used by regulatory agencies of allowing Cr III to be discharged to surface waters so the concentration of Cr III in the receiving waters considering the wastewater discharge and upstream sources does not exceed the drinking water MCL of 50 µg/L. 50 µg/L of Cr III in a waterbody has a significant potential to convert to Cr VI to a sufficient extent to cause toxicity to zooplankton, i.e. about 0.5 µg/L. The regulation of Cr III discharges should incorporate the requirement of the discharger demonstrating on a site-specific basis that the Cr III discharge, coupled with any upstream sources of Cr will not result in aquatic life toxicity in the ambient waters. The regulatory approach should be based on actual toxicity measurements at appropriate locations "downstream" of the discharge.

Another area of potential concern about allowing large amounts of Cr to be discharged to the environment is the accumulation of Cr III through precipitation and sorption reactions. During periods of elevated flows or sediment scour the accumulated Cr III can be suspended in the watercolumn where there is the potential for oxidation of the Cr III to Cr VI at sufficient concentrations to be toxic to aquatic life. Therefore, it is necessary to consider the possibility of Cr III causing downstream toxicity under conditions of a rising hydrograph as well as through aquatic life activity in the waterbody under low flow conditions. Lee and Jones-Lee (1997) have reviewed the regulatory issues associated with Cr VI. Additional information on these issues is available in this review.

References

APHA et. al., "Standard Methods for the Examination of Water and Wastewaters," 19th edition, American Public Health Association, American Waterworks Association, Water Environment Federation, American Public Health Association, Washington D.C., (1995) Environment Canada, "Priority Substances List Assessment Report: Chromium and its Compounds," Canadian Environmental Protection Act, Quebec, Canada (1994)

Gunther, A.J., J.A. Davis, and M. Stephenson, "Evaluation of Long-Term Trends in Contamination in the San Francisco Estuary Using Transplanted Mussels, Mytilus edulis," (1997)

Lee, G.F., A. Jones-Lee, "Chromium Speciation: Key to Reliable Control of Chromium Toxicity to Aquatic Life," presented at American Chemical Society national meeting, Geochemistry Division poster session, San Francisco, CA, April (1997)

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)a

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)b

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)c

Lewis, P.A., D.M. Klemm, J.M. Lazorchak, T. Norberg-King, W.H. Peltier, and M.A. Heber. "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms." Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, Environmental Research Laboratory, Duluth, Minnesota, Region 4, Environmental Services Division, Athens, Georgia, Office of Water, Washington D.C., Environmental Monitoring Systems Laboratory, Cincinnati, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio (1994)

Schroeder, D.C. and Lee, G.F., "Potential Transformations of Chromium in Natural Waters," Water, Air, Soil Pollut. 4:355-365 (1975).

US EPA, "Quality Criteria for Water 1986," Office of Water Regulations and Standards, EPA 440/5-86-001, Washington D.C. (1987)

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)

US EPA, "Stay of Federal Water Quality Criteria for Metals; Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance-Revision of Metals Criteria; Final Rules," Federal Register, Vol. 60, No. 86, pp. 22228-22237, May 4 (1995).

US EPA, "1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water," Office of Water EPA-820-B-96-001, Washington D.C. (1996)

US EPA, "Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Proposed Rule," Federal Register 40 CFR Part 131, Part II, Tuesday, August 5 (1997)