

**CALFED Water Quality Technical Group Heavy Metals Control Strategy:
Heavy Metal-Caused Water Column Toxicity Control,
Sediment Toxicity Control Programs**

July 26, 1998
via email

Rick Woodard
Bruce Macler
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CALFED WQTG

Dear Rick, Bruce and Paul:

As part of the CALFED Water Quality Technical Group's (WQTG) efforts to develop strategies for the control of water quality problems within the Delta or that may impact Delta resources, I have provided detailed comments on significant technical problems with draft WQTG documents. Two of the areas of particular concern have been aquatic life toxicity caused by heavy metals in the Delta water column. The other has been the appropriate approach to define sediment quality problems within the Delta. Recently additional information has become available in both of these areas that should be considered in CALFED's formulation of a water quality management strategy for the Delta. These issues are discussed below.

Heavy Metals as a Cause of Water Column Aquatic Life Toxicity

Over the past couple of years that the CALFED Water Quality Technical Group has been active, I have repeatedly commented on the statements made in WQTG documents, including the draft EIR, that state that heavy metals are a major cause of water quality problems within the Delta. As I pointed out, based on discussions with Central Valley Regional Water Quality Control Board staff (Chris Foe and Val Connor), it appears that, except for mercury and possibly selenium, there are no identified heavy metal water column water quality problems within the Delta. I am contacting you on this matter at this time since recently I have been asked to review a draft staff report by the Cal EPA Central Valley Regional Water Quality Control Board entitled, "Metal Concentrations, Loads and Toxicity Assessment in the Sacramento/San Joaquin Delta Estuary: 1993-1995" dated June 1998. This report has been developed by Dr. Val Connor and Dr. Stephen Clark. The Executive Summary at the bottom of page xi states,

"Dissolved metal concentrations were compared to the USEPA National Ambient Water Quality Criteria and the USEPA Proposed California Toxics Rule Criteria to determine if water quality objectives were exceeded in samples collected from 15 stations during WY94 and WY95. In summary, water quality objectives to protect aquatic life were never exceeded for 549 individual metal analyses."

On page xii, second paragraph,

"Waters sampled from the Delta region were tested for toxicity during WY94 and WY95 using EPA Three Species Tests to determine if aquatic life was impacted. In brief, 34 and 58 toxic events were detected during WY94 and WY95, respectively. Metals were never implicated in TIE studies conducted on the toxic samples."

Based on these results and the characteristics of the Delta waters with respect to the detoxification capacity for heavy metals, it can be concluded that, based on current information, potentially toxic heavy metals, such as copper, zinc, cadmium, lead and possibly nickel are not likely causing significant water column water quality problems in the Delta. However, definitely mercury and likely selenium, are causing water quality problems in the Delta. CALFED should, therefore, place a low priority for funding on potentially toxic heavy metal water quality problems in the Delta. The CALFED resources available for addressing water quality problems in the Delta should be focused on other issues where there are indications that there may be water quality problems and there is a lack of data to define these problems.

It is important to note that no one can be absolutely certain that there are no water column heavy metal problems in the Delta. However, after reasonable study in which such problems have not been found, it is appropriate to give further work on such problems a low priority for current funding. Under these conditions I recommend that a small amount of funding be made available for ongoing searches for subtle water quality problems due to heavy metals in the Delta water column. The allocation of this funding should be based on an expert advisory panel's review of the issues.

An example of an area of potential heavy metal toxicity that needs attention is the Cr VI situation. In my previous recommendations to CALFED WQTG in developing a strategy for managing heavy metal toxicity, I indicated that Cr VI could be a cause of toxicity to zooplankton. I provided a preprint of a paper that is in press on this topic as attachment to my discussion of heavy metal toxicity management approaches. It is of interest to find that the CVRWQCB data for dissolved chromium in the Sacramento River Delta system between 1993-1996 shows that most of the values were above 0.5 µg/L. Since dissolved chromium in Sacramento River-type waters is likely Cr VI, and since Cr VI is toxic to several forms of zooplankton such as *Daphnia* and *Ceriodaphnia* at reported concentrations of 0.5 µg/L, it is possible that some of the *Ceriodaphnia* toxicity that has been reported for the Sacramento River that is now attributable to OP pesticides may be due to Cr VI. This does not mean that there is not an OP pesticide toxicity problem in the Sacramento River and the Delta. It is just that, based on the recently released data., part of the *Ceriodaphnia* toxicity may be due to Cr VI. This is an area that needs attention.

My previous comments on the approach for establishing a technically- valid, cost-effective heavy metal water quality management strategy are appended to these comments. The new information released by the Central Valley Regional Water Quality Control Board on heavy metal presence relative to water quality standards and toxicity strongly supports the approach that I advocated of first finding a real, significant water

quality problem in the Delta or its tributaries that is attributable to heavy metals and that significantly impacts the beneficial uses of the Delta. Where such problems are found, then develop an appropriate management strategy that reliably incorporates mid-1990-level science and engineering in managing the problem.

CALFED Sediment Quality Evaluation and Management Issues

In June 26, 1998 correspondence to Dr. Chris Foe (see attached), in connection with PWT review of Delta sediment quality issues, I discussed the importance of conducting comprehensive studies on Delta sediment toxicity issues. My correspondence on this matter was provided to you and is available from my web site. I am concerned about the statements being made that heavy metals in sediments entering the Delta were found to be causing toxicity. This work, however, is questionable, based on the procedures used. There is need to give a high priority to properly conducting sediment toxicity tests using a variety of sensitive species and appropriate reference sediment to determine first if the sediments of the Delta are toxic and, if so, through appropriately conducted TIEs, determine the cause of this toxicity.

Further, since sediment toxicity does not necessarily mean significantly impaired resource with respect to the beneficial uses of a waterbody, work should be initiated on determining the water quality significance to the public and the Delta ecosystem of any sediment toxicity. If sediment toxicity is found within the Delta and this toxicity is, through an expert panel in a full, public, interactive peer review process, judged to be significantly adverse to the beneficial uses of the Delta's resources, then work needs to be done to control the input of the constituents responsible for this toxicity. Based on having worked on issues of this type for many years, it will be highly unlikely that heavy metals transported into the Delta are a cause of significant sediment toxicity that impairs the beneficial uses of Delta waters.

In assessing the potential sources of any heavy metal or, for that matter, other constituent toxicity found in the Delta sediments, it is important not to follow the guidance provided by the State Water Board BPTCP staff of assuming that all heavy metals from all sources contribute toxic metals to sediments in direct proportion to the total concentration of the metals that are present in the sediments. This approach has been known to be technically invalid since the 1960s. It is mandatory if CALFED is to develop a technically valid sediment toxicity control program, that fate transport studies between potential sources of heavy metals and other constituents in the toxic sediments be properly conducted to determine if what is discharged at a particular location does, in fact, either remain or become toxic at a location of concern in the Delta.

Previously I have pointed out that the CALFED WQTG staff approach of using co-occurrence based sediment quality guidelines is technically invalid in determining whether heavy metals and/or other constituents in sediments are causing or could be responsible for causing aquatic life toxicity or other adverse impacts in Delta waters and associated sediments. It is important that the CALFED WQTG not assume that, since the State Water Board BPTCP staff's final Functional Equivalent Document, "Water Quality

Control Policy for Guidance on the Development of Regional Toxic Hot Spot Cleanup Plans" dated July 1998, which lists the so-called sediment quality guidelines, provides technical validity to the use of these guidelines in Delta sediment quality evaluation. The State Water Board BPTCP staff lists these so-called guideline values as "NOAA" values, even though they were informed that they are not NOAA values, but are Long and Morgan values (two NOAA staff members). NOAA has not adopted these values as sediment quality guideline values that are to be used by NOAA or others. The State Water Board BPTCP staff failed to point out that, as discussed in NOAA reports and in several citations of these reports, such as presented in our report, "'Co-Occurrence' in Sediment Quality Assessment,"(1996), and in our paper, "Evaluation of the Water Quality Significance of the Chemical Constituents in Aquatic Sediments: Coupling Sediment Quality Evaluation Results to Significant Water Quality Impacts," Proc. Water Environment Federation National Annual Conference, (1996), which review this topic, the reliability of the Long and Morgan values is less accurate for predicting aquatic life toxicity than flipping a coin. The State Board staff, in their comments on the reviewers' comments on the BPTCP Draft Policy, also fail to point out that the US EPA independently reviewed the reliability of the Long and Morgan values and came to the same conclusion.

Long and Morgan's co-occurrence-based values, such as those that have been proposed to be used in some CALFED WQTG documents as suggested sediment guideline values are less reliable than flipping a coin in predicting sediment toxicity and have no reliability in predicting sediment-based bioaccumulation. A recent detailed discussion of these issues is provided in my comments on the significant technical errors made by the BPTCP staff in developing its proposed Policy. These comments are available as "Comments on 'Draft Functional Equivalent Document Water Quality Control Policy for Guidance on the Development of Regional Toxic Hot Spot Cleanup Plans,'" dated May 11, 1998. Also, supplemental comments have been provided in "Additional Comments on Technical Validity Issues for State Board Staff's Proposed Incorporation of Chemical Information into the Sediment Quality Triad for Designating, Ranking and Toxic Hot Spot Cleanup Plan Development and Implementation," dated June 26, 1998. These comments are downloadable from my web site (<http://members.aol.com/gfredlee/gfl.htm>) in the Contaminated Sediment section or available from me upon request.

The unreliability of Long and Morgan or, for that matter, MacDonald values is readily understood when individuals with an elementary understanding of aquatic chemistry, aquatic toxicology and water quality examine how the Long and Morgan values were developed. These values are based on a co-occurrence approach in which some kinds of impacts, such as aquatic life toxicity or numbers and types of organisms present in a sediment are compared to the total concentrations of heavy metals and other constituents in sediments. By assembling a number of databases of this type, as both Long and Morgan and MacDonald have done, it is possible to develop a concentration of a constituent in sediments where, at least thus far, no one has reported an adverse impact of the sediments in association with the concentrations of various constituents found in the sediments.

The approach that was originally used by Long and Morgan and subsequently by MacDonald in developing the co-occurrence relationship was fundamentally flawed from several perspectives. First and foremost, they left out of the database what has been known for many years to be the primary cause of aquatic life toxicity in sediments - namely, low dissolved oxygen, ammonia, and hydrogen sulfide. One of the data sets that Long and Morgan used in establishing their original co-occurrence-based values was part of a 50,000 data point set that my graduate students and I developed in the 1970s as part of the Corps of Engineers Dredged Material Research Program where we analyzed sediments taken from about 100 locations throughout the US for their chemical characteristics and aquatic life toxicity. There is little doubt that the primary causes of toxicity which Long and Morgan and MacDonald associated with certain heavy metal and other constituent concentrations, are actually ammonia and hydrogen sulfide. The co-occurrence-based approach has no technical validity in that it does not reliably incorporate cause and effect between the Long and Morgan values and the observed biological impacts.

Second, it has been well established after many millions of dollars of research that there is no relationship between the total concentrations of constituents in sediments and their toxicity to aquatic life. This situation arises from the fact that chemical constituents in sediments, as in the water column, exist in a variety of chemical forms, only some of which are toxic/available. In most aquatic sediment systems, only a very small part of the total concentrations of heavy metals and other potentially toxic constituents are in toxic forms. Most are present in non-toxic forms as the result of detoxification reactions between the potentially toxic constituents in the sediments and the sediment matrix. There are a number of constituents in sediments which are primarily responsible for detoxification. For some of the organics, binding with total organic carbon results in a detoxified, unavailable form of a constituent. For many of the metals, it is the sulfide content of the sediment that is primarily responsible for detoxification. Other constituents which can detoxify include clays, hydrous oxides, carbonates, etc.

Since the amount of detoxifying materials present in sediments is independent of the amount of total heavy metals or other potentially toxic constituents present in sediments, there can obviously be no relationship between the total concentration of a constituent, such as a heavy metal in sediments and its toxicity. This makes Long and Morgan, MacDonald and all other co-occurrence-based values highly unreliable in predicting aquatic life toxicity and, more importantly, determining its cause.

There have been several examples of misuse of Long and Morgan or similar co-occurrence-based so-called sediment quality guidelines where the public has been trapped into spending millions of dollars remediating contaminated sediments where, because of the potential toxicity predicted by these values. However, extensive, appropriately conducted toxicity tests show that the constituents in the sediments are in non-toxic forms. These types of situations will become more frequent in the future with the State Water Resources Control Board adopting its staff's recommended BPTCP Policy where the policy includes guidance that requires an "association" between the concentrations of a constituent in sediments as a cause of toxicity. The "association" approach

recommended is not a credible chemically-based approach in which a proper cause-and-effect relationship needs to be established through TIEs. Instead, the State Water Board BPTCP staff have recommended that this association be based on Long and Morgan or MacDonald values. This could mean that the public could be trapped into spending billions of dollars in cleaning up contaminated sediments because of elevated concentrations of constituents in sediments which exceed a Long and Morgan value but which, through proper investigation, would be shown to be in non-toxic forms.

It is important, as discussed in previous correspondence, that the CALFED WQTG not become trapped into using the technically invalid approaches where co-occurrence-based sediment quality guidelines are used to establish "cause and effect" between sediment toxicity or sediments as a source of bioaccumulatable chemicals and the presence of elevated concentrations of constituents in sediments. Techniques are readily available to properly incorporate chemical information into the sediment quality triad where rather than using total concentrations of constituents, the toxic available forms of the constituents are investigated and used as a basis for determining potential cause and effect relationship between toxicity and/or bioaccumulation and the presence of constituents in sediments.

It is appropriate to explore why individuals, such as members of the State Water Board BPTCP staff, perpetuate an obviously technically invalid approach for incorporating chemical information into assessing the cause of aquatic life toxicity. Basically, the situation is one in which the staff and others who support the use of the co-occurrence-based approach try to oversimplify the complexity of the chemistry of constituents in sediments, as those constituents may impact the beneficial uses of water. However, those with an understanding of aquatic chemistry, i.e. the chemical reactions that occur in sediments and how chemical constituents impact toxicity, know/understand that the total concentration of constituent approach is obviously technically invalid and can readily result in the development of unreliable sediment remediation programs.

The State Water Board BPTCP staff, as part of establishing the BPTCP and the expenditures of several million dollars per year of fee-based BPTCP-supported research, ignored recommendations of those who understand aquatic chemistry and the importance of focusing on toxic, available forms as opposed to total concentrations in the BPTCP data collection, with the result that after spending over \$10 million in data collection in the BPTCP since 1989, the Program has a massive deficit of information on true aquatic chemistry issues which could serve as the foundation for properly associating chemical constituents in sediments and various sources of these constituents in assessing impacts of chemicals in sediments on the beneficial uses of a waterbody. To acknowledge this inadequate database that evolved out of the BPTCP data collection program, would mean that the State BPTCP staff would have to acknowledge that they incorrectly established and conducted the BPTCP data collection program. It would also mean that the Regional Boards cannot implement the State Water Board's proposed Policy for developing toxic hot spot cleanup plans because they cannot reliably, from the information available, determine the cause of sediment toxicity or altered organism assemblages. Rather than admitting the significant errors that were made in developing and implementing the

BPTCP program by the State Water Board staff, they are trying to convince others that co-occurrence-based values can be used reliably to associate the presence of a constituent in a sediment with some biological impact. This approach is obviously technically invalid and can be tremendously wasteful of public and private funds in implementing the State Water Board's aquatic sediment "superfund" program (Aquafund).

While the BPTCP is an important, needed program, its development and implementation has in several respects been significantly technically deficient. It is important to understand that not all of the BPTCP be considered deficient; there are a number of notable exceptions, such as the work that was done on water column toxicity by the Central Valley Regional Water Quality Control Board staff and the work in the San Francisco Bay region on excessive bioaccumulation of hazardous chemicals in San Francisco Bay fish, as well as some aspects of sediment toxicity issues, with particular emphasis on the reference sediment approach. The work that was done by the Central Valley Regional Water Quality Control Board staff on toxicity issues under BPTCP support is an example of the kind of work that should have been done throughout the BPTCP, where appropriately conducted TIEs were used to determine whether the toxicity found which was "associated" with elevated concentrations of heavy metals was, in fact, due to heavy metals. It is through the appropriately conducted TIEs that it was demonstrated that the toxicity found was not due to heavy metals, but in fact due to organophosphate pesticides or constituents other than heavy metals.

If there are questions about these comments and the appropriate approach to incorporate them in the CALFED WQTG water quality management strategies, please contact me.

G. Fred Lee

**Recommended Approach For Development of CALFED Funded
Remediation Program To Control Heavy Metal Water Quality Use
Impairments
Associated With Exceedance of Quality Standards**

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CALFED is developing remediation programs to control water quality use impairments within the Delta and its watershed. Some heavy metals are present in CALFED jurisdiction waters above water quality standards based on worse case US EPA water quality criteria. It is known however, that for many waters the exceedance of a US EPA water quality criteria tends to overestimate the actual use impairments that occur in the waterbody. This is due to the highly conservative nature of the way in which US EPA

criteria are developed and implemented into state standards and discharge permits. Rather than assuming that the exceedance of a US EPA water quality criterion for a heavy metal represents a real significant water quality use impairment which requires remediation to achieve the criterion value with no more than one exceedance of any magnitude every three years, the approach that CALFED should follow in developing a technically valid, cost-effective heavy metal control program for potentially toxic heavy metals that are found to cause exceedance of water quality standards is to:

1) Critically define where heavy metals are the cause of water quality problems/use impairments in the waterbody of concern. A use impairment should be defined as heavy metals causing toxicity to aquatic life that significantly adversely alters the numbers, types and/or characteristics of desirable forms of aquatic life. Do not assume that the exceedance of a water quality criterion/standard represents a real use impairment that requires control of heavy metal inputs to achieve water quality standards. Conduct the necessary studies to determine whether the exceedance of a water quality standard for a potentially toxic heavy metal results in heavy metal caused toxicity in the ambient waters of concern.

2) Evaluate the water quality significance of the use impairments to the waterbody's resources and CALFED's interests. The stakeholders/public should be involved in determining what constitutes a significant use impairment of the beneficial uses of the waterbody. Evaluate how the beneficial uses of the waterbody would be improved if the heavy metal caused use impairment were controlled.

3) For those situations where there is a clearly defined use impairment that affects the waterbody's beneficial uses, formulate a heavy metal control program that focuses on the specific sources of the heavy metals that are toxic to aquatic life. Do not assume that this is in any way related to the total concentrations of the heavy metals or even their dissolved forms. A combination of toxicity tests and appropriately conducted TIE's should be used in a forensic study framework to define the sources toxic, available heavy metals that need to be controlled.

4) In those situations where there is insufficient information to define where the heavy metals at a particular location are causing a real significant water quality use impairment, develop a credible investigative program to determine whether the suspected water quality use impairment is a real use impairment. The areas where this will likely be most important are the areas where there is an exceedance of a US EPA water quality criterion (state standard) for a heavy metal or group of heavy metals. While the exceedance of a US EPA water quality criterion tends to significantly overestimate the toxic available forms, there are situations such as for chromium 6 where the US EPA water quality criterion is not protective of all desirable forms of aquatic life such as zooplankton which can be key components of larval fish food. There may also be situations where combinations of heavy metals or heavy metals with other constituents leads to toxic conditions that would not be predicted based on exceedance of water quality standards. It is for these reasons that if the toxicity testing of a waterbody shows toxic conditions, then

TIE studies should be conducted to determine the cause of the toxicity and in particular whether a heavy metal(s) is responsible for this toxicity.

Since CALFED municipalities and many other dischargers do not have sufficient funds to control all exceedances of water quality standards within the waterbody's watershed, it is essential that the funds available be used to control real significant water quality use impairments within the waterbody of concern and the watershed that adversely impacts the beneficial uses of the waterbody.

If this program shows that the exceedance of a water quality standard for a heavy metal does not result in a significant beneficial use impairment, CALFED should work with the stakeholders, regulatory agencies and others in developing a more appropriate approach for regulating heavy metals in the waterbody of concern than exists today.

A key component of a remediation program based on this approach is the availability of funding to conduct an ongoing program designed to detect more subtle water quality impacts than those investigated in the initial use impairment evaluation. Further this program would provide funds to detect new water quality problems due to heavy metals through their expanded use or the introduction of significant amounts of toxic forms of heavy metals associated with new activities in the waterbody's watershed.

This is the technically valid, cost effective approach for developing a remediation program for potentially toxic heavy metals. While the focus of this discussion is heavy metals, this same approach applies to all constituents that are regulated by US EPA water quality criteria/state standards.

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 CaCO₃. 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 than 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 zooplankton 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.

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June 26, 1998

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Dear Chris:

Following up on the last PWT meeting where a preliminary draft proposal for work on Delta contaminated sediment issues was made available prior to the meeting, but not discussed at the meeting, I have reviewed that proposal and wish to provide the following comments. The issue of contaminated sediments and their impacts on water quality is an area that has been a focal point of my 30-year university graduate-level teaching and research career where I conducted over several million dollars in research specifically directed toward evaluating the significance of chemical constituents in aquatic sediments as they may impact the beneficial uses of the associated waters.

The proposal made available prior to the PWT meeting focuses on obtaining funding for several specific Delta sediment-related research projects. For example, the first proposed research area - source of sediment contamination is one that I would give a low priority to until it has been found that there are significant Delta and Upper San Francisco Bay water quality use impairments due to chemical constituents in sediments. At this time, there is such a poor understanding of water quality issues in the Delta, much less the role of contaminated sediments in impacting water quality that it is my recommendation that CALFED should initially fund an effort to define whether contaminated sediments within the Delta are likely having an adverse impact on the beneficial uses of the Delta and its resources. Where potential use impairments are found, the cause of the use impairments and their significance to the aquatic ecosystems/water quality should be determined.

For example, it should not be assumed, as is often done, that any aquatic life toxicity is significantly adverse to the fisheries and other aquatic life-related beneficial uses of aquatic systems. Those familiar with the characteristics of waterbody sediments know that high levels of aquatic life toxicity exist naturally in eutrophic lakes which are some of the most productive waterbodies in the world. Several years ago I published an invited paper, "Evaluation of the Water Quality Significance of the Chemical Constituents in Aquatic Sediments: Coupling Sediment Quality Evaluation Results to Significant Water Quality Impacts," at a Water Environment Federation conference where I discussed the

importance of natural toxicity in aquatic sediments as a cause of toxicity as well as gaining an understanding of what sediment toxicity means to the beneficial uses of a waterbody. This paper is available from our web site (<http://members.aol.com/gfredlee/gfl.htm>).

I agree that contaminants in sediments within the Delta could play an important role in impacting the beneficial uses of the Delta and its resources. However, at this time, there is such limited information on these issues that there is need to start from scratch with a highly directed program focusing on searching for potentially significant water quality use impairments caused by sediment-associated constituents.

My recommendations to CALFED would be to make sufficient funds available to appoint an expert panel who would develop guidance on the specific research effort that should be undertaken to begin to define the water quality significance of chemical constituents and pathogenic indicator organisms in Delta aquatic sediments. I would not include Suisun Bay as a high-priority area for initial attention, but instead would focus on the overall Delta system in order to define through appropriately conducted toxicity tests, where the sediments in the Delta are toxic to aquatic life. It is important that several individuals who have high degrees of expertise in sediment chemistry and toxicology be part of this panel. The failure to incorporate modern-day aquatic chemistry/toxicology into sediment quality evaluation has resulted in highly inappropriate approaches being used for incorporation of chemical information into regulatory programs for sediments, such as the BPTCP. The State Board staff, as part of the BPTCP, are using approaches based on total concentrations of chemical constituents that were known to be technically invalid in the 1960s for evaluating the significance of chemicals in sediments.

Where significant sediment toxicity is found to several types of sensitive organisms using appropriate reference sites, then studies need to be conducted to determine the cause of the toxicity. Under no circumstances should the approaches being advocated by the State Board staff and the BPTCP based on co-occurrence values of Long and Morgan be used to estimate cause and effect or even imply that there is any relationship between elevated concentrations of a chemical constituent in sediments and toxicity or other adverse impacts. The determination of the cause of toxicity must be based on properly conducted sediment TIEs.

In those areas where high levels of toxicity are found, an intensive benthic organism assemblage sampling program should be conducted to determine whether the toxicity is apparently influencing the numbers and types of aquatic organisms present in or associated with the sediments. Based on this information, again operating through the expert advisory panel, a specific assessment should be made of the potential water quality significance of the sediment-associated constituents and their impacts on the beneficial uses of the Delta and its aquatic resources. In those situations where it appears that one or more constituents present in sediments is having a potentially significant adverse impact on the beneficial uses of the Delta or significant part thereof, then studies should be conducted on the sources of the constituents responsible for the use impairments. Through appropriate transport fate forensic studies using sediment toxicity and sediment

TIEs, it would be possible to trace back to the principal sources the origin of the constituents that are causing the water quality problems in the Delta due to sediment accumulation.

These problem definition type studies of focusing on sediment aquatic life toxicity would likely lead to a variety of specific research projects somewhat along the line of those proposed in the PWT Delta sediment research write-up. However, these projects would be focused then on the most significant water quality problems that evolve from the problem definition studies. It is my recommendation that before any of the specific sediment quality studies are undertaken, however, it is necessary to determine whether there is a significant water quality problem associated with contaminants in the Delta sediments.

I separate the mercury bioaccumulation issues which is a sediment phenomenon from the sediment toxicity issues. I have previously provided detailed comments to you and others on the work that needs to be done to determine the role of mercury in Delta sediments as a source of excessive mercury bioaccumulation in edible fish. The first step that needs to be done in that program is determine what the current levels of excessive mercury are in edible fish within the Delta. If as suspected, excessive levels are found which represent a human health threat compared to US EPA Region IX guidance for one meal per week or even two to three meals per week, I recommend that benthic invertebrate sampling be done using the Slotten procedures to determine those areas of the sediments within the Delta where there are high rates of methylmercury formation. Next there is need to conduct the incubation studies I have described earlier of where high-flow Cache Creek mercury is added to the sediments and studies conducted under laboratory conditions to see if the addition of Cache Creek high-flow particulate mercury changes the rate of methylmercury production. Through studies of this type, it should be possible to gain considerable insight into the potential benefits of spending CALFED funds in controlling Cache Creek and Sacramento River mercury inputs to the Delta. It is important to note, however, that there may be such a mercury reservoir there now that the current additions are having little or no impact in maintaining any excessive bioaccumulation that occurs.

One of the issues that needs to be considered in providing guidance on future Delta sediment water quality-related work is the potential relationship between the proposed work discussed herein and that of the CALFED-sponsored work that is being conducted under the guidance of the California Resources Agency Delta Levee and Habitat Advisory Committee. The background to that Committee's activities arises from a long-standing problem that exists where those who wish to dredge and use dredged sediments in the Delta for levee enhancement and now shallow water habitat development find that the regulatory requirements implemented through the Central Valley Regional Water Quality Control Board for obtaining dredging permits are significant impediments to dredging and beneficial uses of dredged sediments within the Delta. This situation is being seen by CALFED as a potentially significant problem in development of the alternatives for improved conveyance of Sacramento River water to central and southern California, especially through in-Delta channel improvements. It is also a potentially

significant impediment to the development of shallow water habitat within the Delta since one of the primary sources of fill material is Delta channel sediments.

In 1996, through discussions between Chris Foe, Bill Croyle, Jerry Bruns and myself, I became aware of the problem and the interest of the Resources Agency Delta Levee and Habitat Advisory Committee members in addressing the problem. In 1997, I began to attend the monthly meetings of this Committee. Also in July 1997 I submitted a CALFED Category III proposal to assist CALFED in helping to formulate an approach that would bring together a panel of experts who could advise CALFED, the regulatory agencies and others on appropriate management of contaminants in dredged sediments associated with their use in levee enhancement and shallow water habitat development. I was involved with the Corps of Engineers in the 1970s in conducting over \$1 million in research as part of the Dredged Material Research Program that was specifically directed to develop dredged sediment disposal criteria for open water disposal of contaminated sediments. Many of the approaches which were addressed in this research have become standard practice and are currently being used today by the US EPA and the Corps of Engineers in regulating contaminated dredged sediment. Through the work that was done by my graduate students and myself as well as others in the 1970s, we demonstrated that the mechanical application of worst-case water quality criteria to dredged sediment management situations readily resulted in gross over-regulation of many of the chemical constituents in dredged sediments and therefore significantly impeded the beneficial uses of dredged sediments. The situation with respect to dredging in the Delta has evolved to one of where the Central Valley Regional Water Quality Control Board has a severe resources limitation in being able to develop and apply more appropriate dredged sediment management approaches to Delta dredging projects.

It was my proposal that a panel of experts could work with CALFED, the CVRWQCB and State Water Resources Control Board, the Resources Agency, Fish and Game, Fish and Wildlife Service, National Marine Fisheries, Department of Water Resources, etc. in developing guidance on Delta dredging, levee enhancement and shallow water habitat development projects that would be protective but yet not be sufficiently overly-protective of Delta water quality and aquatic resources so as to impede appropriate use of contaminated sediments in Delta shallow water habitat and levee enhancement projects.

In November 1997, I made a presentation to the Resources Agency's Delta Levee and Habitat Advisory Committee on the potential impacts of the California Toxics Rule on Delta dredging projects. A copy of the slides used during my presentation is available as , "Review of the Potential Impacts of the California Toxics Rule on Dredging of the Sacramento River, the Sacramento River Deep Water Ship Channel, and the Port of Stockton Deep Water Channel and Beneficial Uses of Dredged Sediment for Delta Levee Enhancement and Shallow Water Habitat Development," from Dr. Jones-Lee's and my web site. It summarizes the key issues that need to be considered in developing a more appropriate regulatory approach to protect Delta resources from chemical constituents in dredged sediments in Delta dredging projects as well as the use of dredged sediments obtained from within the Delta and from outside of the Delta for shallow water habitat development and Delta levee enhancement projects. The primary recommendation from

my presentation was that there was need for CALFED to support the development of an expert panel who would guide CALFED and others in the studies needed to specifically address the under- and over-regulation of contaminants in Delta dredged sediments as they are used for levee enhancement and shallow water habitat development.

My Category III proposal submitted in July 1997 was not funded; in fact, it was ranked sufficiently low as to not even make the first cut, evidently because it was not directed to work on specific fish species. Last winter CALFED made available to the Resources Agency \$500,000 of funding to implement a program designed to address the problems of the use of contaminated sediments for Delta shallow water habitat development and levee enhancement. The Resources Agency Delta Levee and Habitat Advisory Committee has recommended to CALFED that these funds be used to appoint an expert panel who would provide guidance along the lines that I originally suggested which would include a critical review of existing regulatory requirements, discussion of potential modification of these requirements to enhance protection where under-regulation occurs and to reduce the over-regulation that is occurring in managing contaminated sediments in Delta projects. This effort would include one or more demonstration projects where through intensive monitoring of the actual impacts of contaminants associated with dredged sediments that are used for levee enhancement and/or shallow water habitat development, it would be possible to fine tune the regulatory requirements to be protective without being overly-protective. As planned by the Resources Agency now, the \$500,000 would not be used to actually conduct studies, but would be designed to provide for expert panel activities and the consultant to assist the panel in formulating and implementing guidance on these issues. It is my understanding that at this time that the Resources Agency Delta Levee and Habitat Advisory Committee is awaiting CALFED funding to initiate this activity.

While the proposed program that I have outlined addresses contaminated sediments in the Delta issues, it is distinctly different from the CALFED-supported Delta Levee and Habitat Advisory Committee activities concerned with facilitating Delta dredging and beneficial use of dredged sediments for levee enhancement and shallow water habitat development. The two programs will strongly complement each other; they are both needed. The Resources Agency Committee activities will, if properly implemented, be highly directed to a narrow range of issues associated with dredging and dredged sediment management. It will not address the issues of the overall significance of contaminants in Delta sediments. That is a much larger issue that must be addressed separately. The two activities, however, should be closely coordinated.

My role in this effort can be that of a interested party who provides assistance as time and resources permit to one of providing active leadership where if funds are available, I would be willing to devote substantial time helping to develop, coordinate and implement this program through the expert panel. My work would be that of a technical leader where I would be willing to work on this effort at substantial reduction in my normal consulting fees.

If you or other members of the PWT have questions or comments or wish further information on any aspect of these issues, please contact me.

Fred

Reference as: "Lee, G.F., 'CALFED Water Quality Technical Group Heavy Metals Control Strategy: Heavy Metal-Caused Water Column Toxicity Control, Sediment Toxicity Control Programs,' submitted to CALFED Water Quality Task Group, Sacramento, CA, July (1998)."

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