<u>**Appendix K**</u>

Scientific Peer Review

Chollas Creek Metals Total Maximum Daily Load

California Regional Water Quality Control Board, San Diego Region

March 9, 2007

Scientific Peer Review:
"Technical Report for Copper, Lead and Zinc Total Maximum Daily Loads for Chollas Creek, San Diego, Tributary to San Diego Bay"

Garrison Sposito and Jasquelin Peña
Department of Civil and Environmental Engineering
University of California at Berkeley

The draft report under review provides technical information related to the establishment of Total Maximum Daily Loads (TMDLs) for Chollas Creek, an intermittent stream that drains a highly urbanized watershed through two major tributaries in the San Diego area. Outflow from the creek, whose lower reach (see photo of the North Fork, below, taken by J. Peña, March 2005) has impaired water quality, is into San Diego Bay. (Note, however, that the introductory statements on page 4 of the draft report appear to be contradictory in respect to the documentation of impaired water quality, implying that National Toxics Rule criteria are more often exceeded than California Toxics Rule criteria, while calling the latter "more stringent".) The TMDLs discussed in the report are for the metals, copper, lead, and zinc. As noted in the Introduction of the draft report, TMDLs are load allocations (mass per day) of pollutants to a waterbody, considering both point sources and nonpoint sources, such that the assimilative capacity of the waterbody in respect to applicable water quality objectives is not exceeded.

The methodology followed in the draft report for the three metals of concern is to apply the USEPA- California Toxics Rule (USEPA-CTR) to obtain numeric targets for dissolved metals in Chollas Creek. The dissolved mconcentrations are calculated for both acute (one-hour average) and chronic (four-day average) conditions from USEPA-CTR statistical regression equations that include factors for site-specific toxicity effects, total-to-dissolved metal concentrations, and direct hardness effects (Table 3.1 in the draft report). Hardness data for the waterbody will be required in order to implement these equations. It is possible to include direct effects of temperature and pH in the equations, but this was not done in the draft report. Site-specific toxicity effects also were not considered [i.e. Water Effects Ratio (WER) = 1.0 in the regression equations] and the total-to-dissolved metal concentrations ratio for each metal was set equal to a fixed constant for all conditions using the default USEPA-CTR values.

Although the draft report states that the numeric targets set by using the USEPA-CTR equations are a function of hardness, it does not justify why this choice is appropriate for Chollas Creek, other than its legal applicability in California for inland surface waters (draft report, page 11). Reference to CFR 40 Part 131 provides the following guiding commentary on the toxicological significance of hardness-based USEPA-CTR equations:

f. Hardness
Freshwater aquatic life criteria for certain metals are expressed as a function of hardness because hardness and/or water quality characteristics that are usually correlated with hardness can reduce or increase the toxicities of some metals. Hardness is used as a surrogate for a number of water quality characteristics which affect the toxicity of metals in a variety of ways. Increasing hardness has the effect of decreasing the toxicity of metals. Water quality criteria to protect aquatic life may be calculated at different concentrations of hardness, measured in milligrams per liter as calcium carbonate.

Given the importance accorded in the draft report (page 14) to hardness sampling as part of compliance testing, it would be very useful to have more detailed discussion on the relevance of the above paragraph to water quality criteria for the three metals of concern in Chollas Creek.

Although the choice of WER = 1.0 in the draft report is a conservative one, procedures are available from USEPA for evaluating site-specific toxicity effects and modifying the Water Effects Ratio accordingly. This additional information may be of special value in respect to copper because of its strong tendency to form toxicity-reducing soluble complexes with dissolved organic matter. Similarly, the use of a constant total-to-dissolved metal concentrations ratio as given by USEPA is problematic, since the chemical forms of copper, lead, and zinc are likely to vary both spatially and temporally depending on streamflow variation and the changing composition of streamwaters, including suspended load. In the draft report, the assumption is made that the USEPA-CTR default values for the three metals are upper limits of the actual values in Chollas Creek, the implication being that actual total-to-dissolved metal concentrations are always larger than the default values used in the USEPA-CTR regression equations. Since toxicity effect should vary inversely with total-to-dissolved metal concentration, this assumption amounts to an implicit Margin of Safety imposed on the recommended dissolved metal concentrations. An alternative approach would be to evaluate total-to-dissolved metal concentrations as a function of turbidity and include turbidity sampling as a part of compliance testing.

In the usual development of TMDLs for a waterbody, hydrologic data and pollutant source analyses are combined with the numeric targets to calculate waste load and load allocations. However, in the draft report under review, although spatial hydrologic modeling and a very thorough metal source analysis are presented, they are used only to determine TMDL Critical Conditions (Appendix D, Section 2.2). It appears that most of the data used to develop the TMDLs was collected during stormflows. Additional monitoring during low flow should be implemented since pools of slow-moving or standing water (see photo of Chollas Creek, below, taken by J. Peña) will have very different dynamics—and metal sources—from those associated with high-flow storm events. It is also possible that dissolved metal concentrations during low flow are greater than in the wet season because metal inputs are not diluted by large volumes of rainwater. Also, standing water can undergo evaporation, leading to the concentration of metals in sediments. Some additional minor points to consider in respect to the discussion of metal sources:

- Page 32, Section 4.4.5. In the last sentence, the reader should be reminded that this summary applies strictly to the Santa Clara Valley study.
- Page 33, Section 4.4.5.2. Quantify the difference between the "back of the envelope calculation" given here and the model results.
- Page 37, Section 4.5.4. The percentage of copper contained in each pesticide should be included in Table 4.10.

Because waste load and load allocations were not made, the linkage analysis in the draft report (page 39) consists of identification of the most important metal sources and streamflows to be considered when sampling metal concentration and hardness for assessing compliance with the recommended dissolved metal concentrations. The final recommendations for the three metals are dissolved concentrations equal to 90 % of the dissolved concentrations (i.e. 10 % Margin of Safety) calculated using the USEPA-CTR hardness-based regression equations. These recommended concentrations are compared illustratively to measured concentrations in Appendix G of the draft report. The results in this appendix indicate that maximum observed concentrations of the three metals are significantly greater than the concentrations required to meet water quality objectives, with the discrepancies being much larger at lower hardness values.

The use of dissolved metal concentrations as numeric targets presupposes that the metals do not increase in concentration at higher trophic levels (i.e. no biomagnification) and that they do not accumulate in sediments. Biomagnification of copper, lead, and zinc in test organisms (e.g. daphnia) has not been observed in laboratory studies, insofar as the reviewers are aware, nor is it expected. Biomagnification is associated with hydrophobic pollutants and hydrophobic chemical forms of pollutants (e.g. methyl mercury), whereas most toxic metals have hydrophilic chemical forms in aquatic ecosystems. It is possible that lead could take on a hydrophobic chemical form under anaerobic conditions because it can be methylated by microorganisms, but this is very unlikely in well-aerated waterbodies. Accumulation in freshwater sediments is well established for the three metals of concern, which have strong sorption affinities for natural particles, especially those with organic matter content. The case is made in the draft report that metal concentrations in the creek sediments are typically below levels of probable toxic effect and that particle-bound metals are flushed from the creek within one year by winter flows. These conjectures are not unreasonable, but no database currently exists with which to evaluate them, bringing to mind the important possibility that particle-bound metals transported to San Diego Bay may pose a potential toxicity threat, thus making Chollas Creek a source of this threat.

In summary, the principal points made in this peer review of the draft report are:

Dissolved concentrations of copper, lead, and zinc for acute and chronic conditions calculated from USEPA-CTR regression equations dependent on water hardness are promulgated with a 10 % Margin of Safety instead of TMDLs, which typically combine allowable dissolved metal concentrations with hydrologic and metal source analyses to prescribe mass loadings that meet applicable water quality objectives.

Detailed scientific justification of the USEPA-CTR hardness-based equations for applicability to Chollas Creek waters in determining allowable metal concentrations is not provided. However, assumptions of no metal biomagnification or accumulation in sediments, which underlie the use of numeric targets based on dissolved concentrations, seem justified.

Compliance testing guided by TMDL Critical Conditions will require measurements of both metal concentrations and hardness (as calcium carbonate) for use with USEPA-CTR regression equations that, along with the 10 % Margin of Safety, define the numeric targets. Preliminary calculations indicate that current metal concentrations in Chollas Creek are in excess of these targets, particularly at low hardness values.

Hydrologic modeling and metal source analyses are used to select TMDL Critical Conditions for compliance testing. Hydrologic modeling is not explicitly used in metal load and wasteload allocations. All hydrologic and metal source effects are implicit in these allocations.

The current database for Chollas Creek can be improved by additional monitoring of both metal concentrations during lowflow periods and metal accumulation in creek sediments that may serve as a source of contamination for San Diego Bay. Additional laboratory toxicity testing using Chollas Creek waters would be useful in order to justify the Water Effects Ratio and to evaluate the accuracy of the default total-to-dissolved metal concentration factor assumed in the USEPA-CTR regression equations.

Peer Review Comments from Dr. Joseph Shaw
Dartmouth College

Response to: **Request for scientific peer review of the technical portion of the amendment incorporating the *copper, lead, and zinc total maximum daily loads for Chollas Creek* into the water control plan for the San Diego basin.**

I commend the California Regional Water Quality Control Board, San Diego Region for their efforts to reduce the loads of copper, lead, and zinc entering the Chollas Creek Watershed by ~50-70% (e.g., depending on metal). The technical report presents a conservative approach to establishing Total Maximum Daily Loads (TMDL) for the three metals that are required to meet the established water quality standards. Given the paucity of data in certain instances this conservative approach, which was based on concentrations derived from California Toxic Rule requirements (U.S. EPA, 2000) for these metals and source/land use models to predict load, was warranted. It should be noted that cautionary/critical statements in this review are provided as an aid to strengthen the scientific portion of the proposed rule. It is my opinion that the current draft of the technical plan far surpasses the status quo (i.e., not implementing the TMDL). Comments to specific questions are given below.

1) Biomagnification potential for copper, lead and zinc:

"Copper, lead and zinc may biomagnify in aquatic life in Chollas Creek. The California Regional Water Quality Board, San Diego Region (Regional Board) believes that these metals do not biomagnify. We would like to know if we have sufficiently justified this position and if there are substantive arguments to the contrary."

As stated in the TMDL, there is little evidence that copper, lead and zinc biomagnify in top-level feeders. However, I question whether one sentence in Section 2.4 (p.8) that cites a single 20 year old reference (Moore and Ramamoorthy, 1984) from a book on organic chemicals sufficiently justifies this position. Appropriate citations would include Timmermans et al., 1989; Suedel et al., 1994; Jarvinen and Ankley, 1999; and Besser et al., 2001. Also, there is growing evidence that zinc and to some extent copper can biomagnify within aquatic food webs (Quinn et al., 2003; Chen et al., 2000; Timmermans et al., 1989). However, these studies focused on lower food chain levels (i.e., phytoplankton, zooplankton, macro-invertebrates) and evidence extending these findings to higher trophic-level consumers (e.g., birds and mammals) is unfounded.

2) Copper, lead, and zinc accumulation in creek sediments:

"The Regional Board has reviewed the available data and concluded that copper, lead, and zinc are not a problem in the sediments of Chollas Creek. We would like to know if we have scientifically and sufficiently supported this claim."

Sediment accumulation of metals in Chollas Creek appears to be minor (Table 2.4; Appendix C). The PEL (probable effect level; more recently termed PEC, probable effects concentration, MacDonald et al., 2000) approach has been successfully used to screen sediments on both a regional and national basis (Ingersoll et al., 2001). However, there are a couple of points of caution to be made with interpreting data provided (Table 2.4, Appendix C). As indicated in the text, PELs represent concentrations where toxicity (adverse effects) is expected to occur frequently. The water quality objective *("All waters shall be maintained free of toxic substances in concentrations that are toxic to, or that produce detrimental physiological responses in human, plant, animal, or aquatic life."*) is more strict, seeking to protect against toxicity, not just frequent toxicity. With this in mind, cadmium although rarely detected (11 of 81 samples) and detected in excess of PEL (1.2%), has an average concentration that approaches PEL. Also, the one time it exceeded PELs it did so by over 6.5 fold. However, it is difficult to draw conclusions about this site, since it was only sampled once. In fact, the bulk of the sampling within the creek (sampling designated 978-270 to 978-337) occurred at a single time point and no temporal replication of these sites is shown. The data set that includes temporal replication contains three sites within San Diego Bay and only one site within the creek (location not provided). Given the short residence time of the sediments within the creek (~1 year as given in Section 2.5), a single grab from 1998 could be dramatically different from 2005. For the PEL screening approach to be successful the data being screened needs to adequately reflect that of the creek. Also, as pointed out in this document (section 2.4), metal toxicity has a strong relationship with speciation. Total sediment metal concentrations (just as measurements of total metal in the water column) have proven problematic in assessing toxicity. Typically sediment metal concentrations are discussed in context of sediment characteristics such as grain size, organic carbon, simultaneously extracted metal:acid volatile sulfides ratio, pH, etc.

3) Selection of Numeric Targets:

"Numeric Targets must be appropriately chosen to ensure the attainment of the Water Quality Standards (Water Quality Objectives, Beneficial Uses and Anti-degradation Policy) of the Creek. It is expected that the used of the CTR objectives as Numeric Targets will lead to the protection of the WARM and WILD beneficial uses of the creek. However, CTR may not be protective of all species protected under these two beneficial uses. The Regional Board would like to know if the choice of Numeric Targets to protect the beneficial uses is bases upon sound scientific knowledge, methods, and practices. The regional Board would also like to know if there are other objectives that are also/more appropriate."

CTR criteria are set to protect aquatic-life in California water bodies against both acute and chronic exposures to harmful contaminants. These include hardness corrections for ambient copper, lead, and zinc standards, an approach that has been incorporated in U.S. EPA ambient water quality criteria for the protection of aquatic-life for over 20 years (including updates). The hardness corrections account for the (generally) protective effect of the two components of hardness (i.e., calcium, magnesium) on the toxicity of these metals. In the absence of site specific water quality parameters and species inventory lists for Chollas Creek, such an approach represents the most conservative and scientifically defensible action. However, there are some points of caution with their application. Criteria are designed to protect 95% of the species that fall within the range of sensitivities of those that were tested as part of the criteria development process. For acute criteria, these are generally robust and although a species inventory is not provided for Chollas Creek such targets would be expected to be protective of most species present. However, chronic criteria are established using a much smaller range of species through the development of acute to chronic ratios that are more broadly applied. For these reasons, chronic criteria would stand to be more impacted by site specific parameters. If data are present on the species residing in Chollas Creek it could really benefit application of CTR standards. Also, it is surprising that hardness data, while admittedly variable, are not provided. I agree that because of the temporal/seasonal variability of Chollas Creek that it is appropriate to present hardness dependent standards. However, information on hardness would be a useful addition to the Technical Report as a means of determining the current status of Chollas Creek. Also, these standards are less predictive at the lower and higher extremes for hardness (Gensemer et al., 2002), where other water quality parameters can have a greater influence on toxicity. Finally, I would like to compliment the authors of this report for their inclusion of the newly proposed Biotic Ligand Model (Paquin et al., 2002) for copper and support their position of revisiting Numerical Targets if/when these are adopted. The BLM represents a fundamental change in the way metals criteria are calculated that models metal binding to critical biotic ligands, such as the fish gill, and relates this metal burden to detrimental effects on the organism. While they are more inclusive of mitigating water quality parameters, they are more data intensive (e.g., requiring simultaneous measurements of copper and many complexing anions and competing cations).

4) Sampling requirements to assess Loads and Waste Load Allocations:

"The Regional Board has designated sampling requirements to evaluate the Load and Waste Load Allocations and would like to know if they are sufficient, appropriate, and based upon sound scientific knowledge, methods, and practices. The question really deals with spatial and temporal scales. Given the size of the creek and the seasonal variability of its flow, it will be key to select measurement sites and frequencies that will allow assessment of the attainment of the Load and Waste Load Allocations through the year and throughout the entire creek system."

There is insufficient material available regarding the spatial and temporal aspects of the monitoring/sampling plan to comment on its usefulness in assessing Load and Waste Load allocations for the Chollas Creek Watershed. In the absence of designating sampling requirements, it would be appropriate and necessary at a minimum to provide guidance on the development of such a plan in the Technical Report.

5) Water Effects Ratio:

"A Water Effects Ratio (WER) is part of the CTR Equation for establishing water quality criteria for copper, lead, and zinc. However, sufficient data are not available to modify the default WER value of unity (with the proposed Numerical Target). The Regional Board would like the reviewer to comment on the state of use of WERs in the freshwater systems."

Water effects ratios provide a way to calibrate numerical targets to site-specific conditions. These include endogenous species and/or water quality parameters that may vary from those used to develop the standard in sensitivity and influence on toxicity, respectively. These are typically derived after extensive on-site testing and are usually initiated by regulated parties. This approach (*i.e., making unity the WER default and letting the regulated community establish site-specific conditions under the guidance of the Regional Board*) is reasonable, especially given that WER are often implemented to make conservative Numerical Targets less restrictive. As discussed above for numerical targets, acute criteria are influenced less by site specific conditions (i.e., WER close to unity; Cherry et al., 2002). Cherry et al. (2002) established a site specific CMC for copper in the Clinch River, VA. This required a battery of toxicity tests conducted using 17 genera native to or currently residing in the river that were not part of the derivation of the Final Acute Value (FAV) used in the current U.S. EPA regulations. They concluded that the site specific CMC was not substantially different than the national copper criteria. They suggested site-specific adjustments would be most meaningful for criteria developed to protect against chronic exposures and low-level impact. I could find no published reports detailing successful integration of site-specific numerical targets using a WER approach.

It should be noted that one additional source of site-specific variability could easily be incorporated into the TMDL. Direct measurements of dissolved metals can be influenced by a number of parameters and the use of conversion factors to translate total metal concentrations into dissolved is somewhat arbitrary and likely not reflective of the specific chemistries found within the watershed. It would seem reasonable to require that the monitoring plan require dissolved metals to be measured.

6) Source Analysis:

"The Regional Board must adequately estimate the sources of the metals to the creek. The Regional Board would like the reviewer to comment on the science, methods, and practices used to estimate the sources of copper, lead and zinc. The analysis of the sources is key to successful implementation of reduction schemes. Therefore, it is critical to address all sources of metals and to make some type of

estimate of their total load to the creek. This was accomplished through a model based upon land uses and build-up/wash-off coefficients. Other sources were identified by reference to available literature that identify metal sources in other urban areas."

The methods or literature used to determine that the majority of run-off entering Chollas Creek is via the storm water conveyance system (MS4s, Section 4, introduction, p. 15) are not clearly stated. It makes sense given that there are no other point sources, but the reader is left to make the assumption that direct run-off into the creek is negligible (i.e., both volume and source). This is a crucial point as it identifies/acknowledges the jurisdiction of NPDES WDR and I think a citation or further explanation of this determination is warranted, especially since it places the load responsibility on 20 sources identified through NPDES permit requirements (Section 4.1, pp. 15-16). It would seem a mass accounting of volume entering via storm water conveyances and exciting the creek was used, but this was not mentioned.   This conclusion also makes since empirically because a direct link between stormwater discharges and creek toxicity has already been established (Schiff, 2001). Given that stormwater is the major source of load input for Chollas Creek, the paradigm of identifying sources and modeling land-use specific loads for MS4s is reasonable. Additional comments on load estimates and source identification are given below (Questions 7-10).

7) Land Use Model:

"The Regional Board would like the reviewer to comment on the adequacy of the Source Analysis model description found in Appendix D. The model provides the basis of the Source analysis and was run by Tetra Tech, Inc. The Regional Board merged the Tetra Tech document with literature from the U.S. EPA (BASINs manual) and other sources in an effort to create a document (Appendix D) more accessible to the layperson. Please comment on the adequacy of Appendix E in its description of the model."

As a non-modeler I found the model description in Appendix D accessible. It did a great job explaining the process of data acquisition, populating model parameters, calibration, and independent validation, which are critical for model development. It also was effective in conveying the strengths, weaknesses, and limitations of the models, especially with regards to data gaps/needs and appropriate/inappropriate applications.

8) Model Interpretation:

"The Regional Board would like the reviewer to comment on the scientific basis of the interpretation of the model results and deficiencies. Since the model was produced by an outside consultant, the Regional Board would appreciate the reviewer's opinion on the findings and limitations of the model used as the basis for the Source Analysis."

The immediate deficiencies are obvious; lack of input data (especially water quality measurements during dry weather conditions). Given these limitations it is difficult to assess the models performance. While it has potential to estimate metal concentrations in the Creek or support load allocations across varying condition, these identified deficiencies limited its application to identifying potential sources to target for load reductions. While this is useful it has less direct bearing on the derivation of the TMDL. As noted in Section 4, when data are sufficient they could be readily incorporated into the model.

9) Source Analysis Literature:

"The Regional Board would like the reviewer to comment on the scientific basis of applying results from studies of other urban areas to the Chollas Creek watershed. There are no known peer-reviewed studies describing sources of metals to Chollas Creek, nor is there much information about metal sources in the

greater Sand Diego area. Therefore, studies detailing metals sources in other urban areas served as the basis for part of the Source Analysis discussion. Some of the studies come from other highly populated cities in California, while others come from urban centers in other pars of the world. While certain land use practices are similar between all these areas, other controlling factors (climate, geology, local ordinances, social attitudes, etc) are likely to be much different. Therefore, these studies must be referenced in a conservative manner and not over extrapolated. Please comment on whether or not this boundary has not been breached."

The application of results from other studies to Chollas Creek is no different than most any discussion section found in a peer-reviewed article where the objective is to discuss results (strengths and weaknesses) in context of the body of existing literature. In this sense, such an approach seems not only warranted, but also mandated. I found the literature selections for comparisons justified in terms of similarities (i.e., the most similar studies were selected). Similarities included geographical proximity, population size, land-use, policy, etc. However, in all cases differences and their potential to influence interpretations were highlighted. The only reference I question is the inclusion of Brown and Caldwell, (1984), which was used in section 4.4.2, p. 31. While its limits were clearly noted, the inclusion of lead loading data prior to the CAA ban of lead and lead additives in gasoline provides little area for comparison.

10) Data Deficiencies:

"The available data for Chollas Creek is not as complete as desired. The Regional Board would like the reviewer to comment on whether or not data gaps have been adequately identified, particularly in the Source Analysis and in the Linkage Analysis sections. In particular, the model lacked site-specific flow data for validation and sufficient dry weather information for even a model run. These data gaps must be thoroughly discussed to ensure transparency of the document and to identify necessary monitoring areas under the Implementation Plan. Additionally, data gaps may weaken the connection between the allocations and the attainment of the Water Quality Standards."

The largest data gap I have found for the entire document deals with the lack of information pertaining to a monitoring plan. This is critical to fulfill one of the necessary requirements of Linkage Analysis (i.e., providing the quantitative link between the TMDL and attainment of WQSs) and does not seem to be appropriately identified (SEE RESPONSE TO QUESTION 4). Another unidentified gap appears in Section 5 (Linkage Analysis, p. 39) which states that the technical report is required to "estimate the total assimilative capacity (loading capacity) of Chollas Creek for the metals and *describe the relationship between Numeric Targets and identified metal sources*." I found no description of the later in this section. Also, as stated above it is a little unclear the role the model is serving (i.e., how it will be applied) in the TMDL development. Perhaps, I'm missing something, but it seems a little anticlimactic after reading section 4 and Appendix D that describe the model to get to the Linkage Analysis Section only to discover it has little application to TMDL development.

11) Synergistic Toxicity:

"The Regional Board is not aware of any synergistic toxicity effects associates with dissolved copper, lead, and zinc in the water column and has written this TMDL accordingly. Please comment on the scientific basis for this approach. If all three metals are present at just under their allowable CTR concentration, the water may still not be safe for aquatic life. It is possible that these three metals could work together to form a toxic condition…The Regional Board would like the reviewer to comment on the scientific basis for the potential for a synergistic effect with another chemical pollutant. If an interaction is likely, please comment on the scientific impacts to the Load and Waste Load Allocations. If the metals

Cu, Pb, and Zn are synergistic in their toxic effect on freshwater organisms, perhaps an additional margin of safety should be considered."

There is evidence for synergistic (i.e., greater than additive) and additive (which could also produce scenarios described above) effects of binary mixtures of copper and zinc and lead and zinc (Kraak et al., 1993; Franklin et al., 2002; Utgikar et al., 2004). However, published reports include laboratory studies that have focused on lower trophic levels (i.e., bacteria, phytoplankton, zooplankton). None of these studies investigated concentration ranges applicable to chronic effects and for the most part they focused on binary rather than more complex mixtures. It should be noted that mixture toxicity can be difficult to assess even in the laboratory as results (i.e., antagonism, additive effects, synergism) can vary with species, strain, concentration, and other parameters (Franklin et al., 2002, Borgmann et al., 2003, and numerous others). For example, Martinez et al. (2004) in studies with *Chironomous tentans* found lead and zinc to interact antagonistically to produce sub-chronic/population level effects (i.e., mouth part deformities), which is opposite from the studies cited above. This question could be pertinent, but does not appear to have been addressed in the de-listing of cadmium. There are numerous studies detailing interactive effects of cadmium combined with zinc, lead, and copper. Again, observed effects range from synergism to antagonism, but evidence exists for the scenario raised above where metals are present below the CTR concentrations and interact in a synergeistic (or depending on concentration in an additive) manner to produce toxicity (Beisenger et al., 1986; Kraak et al., 1993; Jak et al., 1996; Barata et al., 2002; Franklin et al., 2002). The CTR Numerical Targets are derived for individual chemicals and do not account for mixtures. However, given the variability in the nature of interactions reported for these metals, interactions would be difficult to regulate in the absence of site-specific data. In summary, I would conclude that while some evidence for metal interactions exists, appropriate determinations of effects would need to include site specific variables in order to be scientifically defensible. The BLM if/when it is adopted could eventually provide a means of dealing with metal mixtures (Paquin et al., 2002; Niyogi and Wood, 2004; Playle, 2004).

12) Linkage Analysis:

"The Linkage Analysis must adequately establish the link between the Load and Waste Load Allocations and the attainment of Water Quality Standards. Please comment on the scientific basis for the linkage provided in this TMDL. This is similar to number 3 above. The ultimate goal of the TMDL is to restore and protect the Water Quality Standards of Chollas Creek that are being degraded by Cu, Pb, and Zn. The Load and Waste Load Allocations must be calculated to achieve this goal. Therefore, they are the critical component of the technical discussion and must be thoroughly scrutinized. Furthermore, the Linkage Analysis must sufficiently establish this connection."

The Waste Load and Load allocations are directly linked to Water Quality Standards defined by the numerical limits, as they are identical. The decision was made by the Board to take a conservative (i.e., from the protection standpoint) approach and set load allocations based on concentration rather than mass. In other words, it is not the relative amounts (i.e., mass) of metals, but rather their respective concentrations that determine load and load reductions will be based on maintaining concentrations of metals at or below these concentration based targets (the exact concentration is fluid and depends on the water hardness). This approach seems reasonable given the dynamic nature of the system. There is one peer-reviewed study and at least one technical report that link effects of storm water drainage and more specifically the metal component of this drainage to toxicity in aquatic-life in Chollas Creek and the portions of San Diego Bay it enters (Schiff et al, 2001; 2003). Since the load allocations are identical to the numerical limits my response to question 3 is also applicable here.

13) Margin of Safety:

“The Margin of Safety (MOS), both implicit and explicit, incorporated in the TMDL should be of a reasonable magnitude to account for uncertainty. Please comment on the scientific foundations and adequacy of the Margin of Safety incorporated into this TMSL. A MOS is a required component of the allocations. It is designed to account for any uncertainty in the calculations supporting the Load and Waste Load allocations. Please comment on the scientific foundations and adequacy of the Margin of Safety incorporated into this TMDL.”

The explicit 10% MOS incorporated into the TMDL represents a commonly employed safety factor. The 10% load correction is to guard against the uncertainty inherent in the Source Analysis and Linkage Analysis; differences between total and converted dissolved metal concentrations; and site-specific differences in CTR derived Numerical Targets. It is difficult to comment on the appropriateness (or scientific validity) of the 10% correction. There was greater than 10% variability in measured metal concentrations (Table 2.1). Some explanation for the rationale behind the 10% MOS would be helpful. In addition, there are implicit MOS that stem from using measured rather than estimated hardness values to calculate the TMDL. Likewise, as discussed below, the CTR values incorporate 50% correction.

I didn’t understand the argument provided in the last paragraph of section 6 (p. 41). Metal interactions were discussed in question 11 above. There are numerous explanations for interactive effects, which have been observed for copper, lead, and zinc. For example, common uptake routes (e.g., calcium channels for cadmium and zinc) or distributions and detoxications could account for interactive effects. While speciation affects toxicity, biological processes have also been shown to influence interactions during laboratory tests conducted under identical water chemistries. Perhaps chemical interactions refers to complexation with anions and negatively charged sites on particulates, which would reduce bioavailability. Anyway, this paragraph/point could use clarification.

14) California Toxics Rule Inherent Margin of Safety:

“The California Toxics Rule formulas provide conservative water quality criteria that are protective of aquatic life. However, since the equations are based upon available laboratory data, they may not be protective of all aquatic life in Chollas Creek and an additional MOS has been added to the TMDL. Please Comment on the scientific basis of this approach…Criteria are based only upon available toxicity testing that may not be available for all taxonomic groups. Does this danger warrant the need for an additional10% MOS as addressed in number 12 above?

As stated above, the one peer-reviewed manuscript that described formulating site-specific CMC for copper concluded that including over 17 sensitive site-specific species to calculate the FAV did not significantly lower the CMC (Cherry et al., 2002). Also, the CTR are based on national ambient water quality criteria, for which the science has been validated through several updates over 20 years. It wasn’t until recently that new approaches (i.e., BLM) gained favor. Given the defensibility and robustness of this approach coupled with the lack of evidence for extreme site-specific sensitivities another 10% MOS does not seem warranted.

15) Critical Conditions:

"The Regional Board has addressed seasonal variations and critical conditions by the use of the CTR formulas that incorporate site and time-specific hardness and metal concentration data. Please comment on the scientific basis and adequacy of this approach. This TMDL is designed to be protective of the creek in all weather and flow conditions during all times of the year. It is believed that the use of the CTR equations will adequately apply the Load and Waste Load Allocations on a temporal and spatial specificity to ensure this protection at all times. By comparing each instream metal concentration against it's appropriate criteria calculated from the hardness measured at the same time and location, the Load and Waste Load Allocations will be a moving target that accounts for ecosystem variability."

The use of a concentration (mass/volume) based TMDL negates effects of variable flow on load allocations, since regardless of the amount (mass) of metals that are present, it is the CTR derived concentrations that must be maintained. Concentration based criteria have a long history of use and even the newly proposed BLM, which relate an amount of metal bound to a critical biotic ligand to toxicity, are still expressed as concentrations. The use of concentrations is an appropriate approach for Chollas Creek given the limited data available for Land Use Models and other methods used to estimate the metal load entering during wet and dry periods. Likewise, the use of CMC and CCC targets ensure critical exposure conditions (acute, chronic) are incorporated. Furthermore, the inclusion of measured rather than estimated hardness concentrations reduce seasonal variability, especially during critical conditions. Provisions are also made to revisit other stream chemistry parameters that were not included in this TMDL if/when the BLM for copper is adopted. Collectively, these measures stabilize the TMDL even over extreme/critical conditions that could be occurred within the basin.

16) Overarching issues:

"Reviewers are not limited to addressing only the specific issues presented above, and are asked to contemplate the following "big picture" concerns.

a. *In regarding the staff technical report and proposed implementation language, there may be additional scientific issues that are part of the scientific basis of the proposed rule that are not described above. If so, please comment with respect to the statute language given above.*

B. *Taken as a whole, please comment on the scientific knowledge, methods, and practices that constitute the scientific portion of the proposed rule.*

Reviewers should also note that some proposed actions may rely significantly on professional judgment where available scientific data are not as extensive as desired to support the statue requirements for absolute scientific rigor. In these situations, the proposed course of action is favored over no action."

With regards to additional scientific issues relating to the Technical Report, there was little mention of specific methods, especially for metal sampling and analysis. Most every question in this reviews asked the reviewer to comment on the scientific methods, so it would appear to be information useful this review. Inclusion of methods could be done in the form of references, but I think their inclusion in necessary to ensure appropriate sampling/measurement techniques are employed and thus, TMDLs are meaningful.

Specific comments regarding the Technical report are as follows:

Attachment 1, p. 1, second paragraph- There are more appropriate references than More and Ramamoorthy, 1984).

Technical Analysis, p.1, 1st paragraph, 1st sentence- insert ‘and a’ between County and tributary.

“ “, p. 1, 1st paragraph, with regards to de-listing Cd, see question regarding synergistic effects above.

Problem statement, p. 2, in the 1st paragraph inconsistencies with the use of lower and lowest.

“ “, same paragraph- Ceriodaphnia is misspelled.

“ “, same paragraph- not exactly clear on the use of the sea urchin. I assume this is from test of Bay water? Also, in general toxicity data were not presented in clearly.

Section 2.3, p. 8, 2nd paragraph, last sentence; it states that compliance shall be evaluated using a 96-hr acute bioassay. The Daphnia tests mentioned are 48-h tests.

Section 2.4., p. 8, 1st paragraph, poor reference for biomagnification of metals.

“ “, toxins are natural compounds (i.e., snake venom, ammonia); toxicants is the appropriate word here.

“ “. Next sentence; …same locations more commonly found at higher concentrations in ….

“ “. P. 9, Better references than Buffle, 1989.

“ “. P. 9. 2nd paragraph, last sentence, Unclear what is being referred to where the implementation plan is located?

Section 2.6. p. 10. In reference to the monitoring site, it is stated that this sampling station is representative of the entire watershed. How was this determination made?

“ “, next paragraph. Replace 1994.95 with 1994-95.

“ “. Same paragraph. Provide methods for toxicity tests.

“ “. Same paragraph. Sentence that states, “Reproduction of the water fleas was generally note impaired, even in individuals that died later in the test.” Is not clear.

Section 3, Numeric Targets, 1st paragraph. Reference the EPAs Metal Translator or whatever the source of the conversion factors was.

“ “. Same page, last paragraph, States that the targets given in table 3.1 were derived to be protective of marine aquatic life from toxicity. Should it read ‘freshwater’ aquatic life?

“ “ p. 12, Equation 3.2; Where: make sure subscripts agree with acute target. I think they should be A instead of C. This also needs correcting in the descriptive sentence to follow.

Section 3.2, Water Effects Ratios. 1st paragraph, 1st sentence, delete more

“ “. Last sentence. I would remove reference to the appendix if it will not be included.

Section 3.6. last sentence. Replace biochemical with biotic. (the gill is not a biochemical stie)

Section 4.2.1.1. add period between next to last and last sentence.

Section 4.3. p. 28. 2nd paragraph. Replace Creeks with Creek

Section 4.3.2. p. 31. 1st paragraph. I don’t think the argument is strengthened with the inclusion of the 1984 lead reference (SEE Comments above.).

Section 4.4.3. p. 31. second sentence. Replace do with low.
In addition, there are a number of mis-labelings in the appendices

References

Barata, C., Markich, S.J., Baird, D.J., Taylor, G. and Soares, A.M.V.M., 2002. Genetic variability in sublethal tolerance to mixtures of cadmium and zinc in clones of *Daphnia magna* Straus. *Aquat. Toxicol.* **60**, pp. 85–99.

K.F. Biesinger, G.M. Christensen, J.T. Fiandt. Effects of metal salt mixtures on Daphnia magna reproduction. *Ecotoxicol Environ Saf,* **11** (1986), pp. 9-14.

J.M. Besser, W.G. Brumbaugh, T.W. May, S.E. Church and B.A. Kimball, Bioavailability of metals in stream food webs and hazards to brook trout (*Salvelinus fontinalis*) in the Upper Animas River Watershed, Colorado. *Arch Environ Contam Toxicol* **40** (2001), pp. 48–59.

W.P., Borgmann, U., Dixon, D.G. and Wallace, A., 2003. Effects of metal mixtures on aquatic biota: a review of observations and methods. *Human and Ecological Risk Assessment* **9**, pp. 795–811.

C.Y. Chen, R.S. Stemberger, B. Klaue, J.D. Blum, P.C. Pickhardt and C.L. Folt, Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol Oceanogr* **45** (2000), pp. 1525–1536.

D.S. Cherry, J.H. Van Hassel, J.L. Farris, D.J. Soucek, R.J. Neves, Site-specific derivation of the acute copper criteria for the Clinch River, Virginia. *Human Ecolog Risk Assess* **8** (2002), pp. 591-601.

N.M. Franklin, J.L. Stauber, R.P. Lim, P. Petocz. Toxicity of metal mixtures to a tropical freshwater alga (Chlorella sp): the effect of interactions between copper, cadmium, and zinc on metal cell binding and uptake. *Environ Toxicol Chem.* **21** (2002), pp. 2412-22.

A. Jarvinen and G. Ankley, editors, *Linkage of Effects to Tissue Residues: Development of a Comprehensive Database for Aquatic Organisms Exposed to Inorganic and Organic Chemicals.* (1999), SETAC press, Pensacola, FL. pp. 364.

M.H.S. Kraak, H. Schoon, W.H.M. Peeters and N.M. van Straalen, Chronic ecotoxicity of mixtures of Cu, Zn, and Cd to the zebra mussel *Dreissena polymorpha*. *Ecotoxicol. Environ. Saf.* **25** (1993), pp. 315–327.

D.D. MacDonald, C.G. Ingersoll, T. Berger. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* **39** (2000), pp. 20-31.

Gensemer, R.B. Naddy, W.A. Stubblefield, J.R. Hockett, R. Santore and P. Paquin, Evaluating the role of ion composition on the toxicity of copper to *Ceriodaphnia dubia* in very hard waters, *Comp. Biochem. Physiol.* **133C** (2002), pp. 87–97.

P.R., Gorsuch, J.W., Apte, S., Batley, G., Bowles, K., Campbell, P., Delos, C., DiToro, D., Dwyer, R., Galvez, F., Gensemer, R., Goss, G., Hogstrand, C., Janssen, C., McGeer, J., Naddy, R., Playle, R., Santore, R., Schneider, U., Stubblefield, W., Wood, C.M. and Wu, K., 2002. The biotic ligand model: a historical overview. *Comp. Biochem. Physiol.* **133C**, pp. 3–35.

R.G. Jak, J.L. Maas, M.C.Th. Scholten, Evaluation of laboratory derived toxic effect concentrations of a mixture of metals by testing fresh water plankton communities in exposures, *Water Res* **30** (1996), pp. 1215–1227.

E.A. Martinex, B.C. Moore, J. Schaumloffel, N. Dasgupta. Effects of exposure to a combination of zinc- and lead-spiked sediments on mouthpart development and growth in Chironomus tentans, *Environ Toxicol Chem*, **23** (2004) pp. 662-667.

S. Niyogi, C.M. Wood, Biotic ligand model, a flexible tool for developing site-specific water quality guidelines for metals, *Environ Sci Technol*, **38**(2004), pp. 6177-6192.

R.C. Playle, Using multiple metal-gill binding models and the toxic unit concept to help reconcile multiple-metal toxicity results. *Aquat Toxicol*, **67**(2004), 359-370.

M. R. Quinn, X. Feng, C.L. Folt and C.P. Chamberlain, Analyzing trophic transfer of metals in stream food webs using nitrogen isotopes, *The Science of The Total Environment* **317** (2003), pp. 73–89

K. Schiff, S. Bay, D. Diehl, Stormwater Toxicity in Chollas Creek and San Diego Bay, California, *Environ Monit Assess*, **81** (2003), pp. 119-32.

B.C. Suedel, J.A. Boraczek, R.K. Peddicord, P.A. Clifford and T.M. Dillon, Trophic transfer and biomagnification potential of contaminants in aquatic ecosystems. *Rev Environ Contam Toxicol* **136** (1994), pp. 21–89.

Timmermans, K. R., van Hattum, B., Kraak, M. H. S. & Davids, C. Trace metals in a littoral foodweb: Concentrations in organisms, sediment and water. *Sci. of the Total Environ* **87-88** (1989), pp. 477-494.

V.P. Utgikar, N. Chaudhary, A. Koeniger, H. Tabah, J.R. Haines, R. Govind. Toxicity of metals and metal mixtures: analysis of concentration and time dependence for zinc and copper, *Water Res* **38** (2004), pp. 3651-8.