<u>Appendix L</u>

Response to Peer Review Comments

Chollas Creek Metals Total Maximum Daily Load

California Regional Water Quality Control Board, San Diego Region

May 30, 2007

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RESPONSE TO PEER REVIEW COMMENTS

Response to Peer Review Comments from Dr. Joseph Shaw

Overall Assessment by Dr. Shaw

Comment

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).

Response

Comment noted.

Biomagnification of Metals

Comment

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.*

Response

Our intention was not to justify the conclusion that copper lead and zinc do not bioaccumulate in Chollas Creek based on the Moore and Ramamoorthy reference. Section 3.4 (formerly 2.4) of the Technical Report states: "*Copper, lead and zinc may bioaccumulate within lower organisms, yet they do not biomagnify up the food chain as do mercury and selenium …*". This sentence implies that mercury and selenium have a higher potential for biomagnification over copper, lead, or zinc. The technical report does not state that copper, lead, or zinc will not bioaccumulate but rather the potential for biomagnification is more likely for mercury and selenium when compared against the other three metals.

There are no site-specific studies on Chollas Creek to verify whether metals are bioaccumulating into higher trophic level consumers. However, studies have been completed on marine sediments at the mouths of Chollas and Paleta Creek where they enter into San Diego Bay. Laboratory bioaccumulation sediment studies were conducted at 7 locations in the Chollas Creek channel and 7 locations in the Paleta Creek channel using the clam *Macoma nasuta*. The results from the 28-day bioaccumulation tests indicate a slightly higher bioaccumulation potential for copper and lead when compared to the reference mean tissue concentrations (RWQCB 2004).[1] Mean tissue concentrations for mercury and zinc were comparable to the tissue levels observed in the reference tissue.

Assuming Chollas Creek discharge contributes to the metals found in the sediment in the Chollas Creek channel, the preliminary study indicates a potential might exist for some metals that originated in the creek to reach higher trophic level consumers.

An additional reference has been included in the Technical Report to further support the position that copper, lead and zinc are not expected to biomagnify. Furthermore, the first paragraph of section 3.4 has been changed to:

> Copper and zinc are essential elements for all living organisms, but elevated levels may cause adverse effects in all biological species. Lead is presumed to be a non-essential element for life; more importantly, even at extremely low environmental concentrations this element may create adverse impacts on biota. Dissolved forms of these metals are directly taken up by bacteria, algae, plants and planktonic and benthic organisms. Dissolved metals can also adsorb to particulate matter in the water column and enter aquatic organisms through various routes. Copper, lead and zinc may bioaccumulate within lower organisms, yet they are not expected to biomagnify up the food chain as do mercury and selenium (Moore and Ramamoorthy, 1984). The issue of biomagnification is still being debated among the scientific community (Besser, et al, 200) and cannot be assessed in Chollas Creek with the available information. Of all of these metals, copper is considered the most potent toxicant at environmentally relevant aqueous concentrations. Copper is more commonly found at higher concentrations in herbivorous fish than carnivorous fish from the same location (USF&W, 1998). Copper is used as an aquatic herbicide to reduce algae growth in reservoirs and also applied (via antifouling paints) to boat hulls in marinas.

Creek Sediment

Comment

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

[1] RWQCB 2004. Sediment Assessment Study for the Mouths of Chollas and Paleta Creek, San Diego. Phase 1 Draft Report. Southern California Coastal Water Research Project and Space and Naval Warfare Systems Center San Diego, United States Navy – San Diego. September 2004.

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.

Response
The text in section 3.5 has been updated to include the Probable Effect Concentration (PEC) and references the 2000 paper by MacDonald et al.

The Regional Board agrees with Dr. Shaw that a sediment metal concentration at or below the PEL or PEC could be interpreted to be in violation of the more stringent water quality objective for toxicity (see Section 3.3). However, the toxicity objective is more appropriately applied to the water column. Unfortunately, neither the State of California nor the United Sates Environmental Protection Agency (USEPA) have objectives nor standards that are directly applicable to freshwater sediment metal concentrations. Until such criteria are promulgated, the interpretation of sediment metal concentrations must rely on screening values or some statistically based threshold, such at the PEL or PEC.

The average sediment concentration of cadmium in Chollas Creek is approximately 2.1 mg/kg (dry weight). This is approximately 40 percent below the PEL of 3.53 kg/mg (dry weight). Furthermore, cadmium sediment concentrations only exceeded the PEL in one out of 81 samples over a 7-year period and only 11 of those 81 samples even had detectable cadmium concentrations. While mean and median sediment cadmium concentrations are much closer to the PEL than copper, lead or zinc, cadmium still warrants removal from the Clean Water Act 303(d) List of Water Quality Limited Segments (see the response to Comment 12 for further discussion on the delisting).

If subsequent information indicates that sediment may be a contributor to water column toxicity, the Regional Board will consider revising the monitoring requirements to include cadmium, grain size, organic carbon, simultaneously extracted metal to volatile sulfide ratios and pH.

Numeric Targets

Comment

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).

Response

A comprehensive study to determine the species living in the riparian zone of Chollas Creek has not been conducted. When and if such information becomes available, it will be reviewed to ensure that the most sensitive and/or endangered and threatened species are being protected by this TMDL.

Hardness data is presented in Appendix A. Hardness ranges from 35 to 3,200 mg/L $CaCO_3$, with an average of 198 and a median of 91 mg/L $CaCO_3$. These higher hardness concentrations certainly represent the extreme upper end. However, for all applications of CTR formulas, hardness will be capped at 400 mg/L $CaCO_3$. As additional toxicity information becomes available, the protective ability of this TMDL at extreme low and high hardness concentrations will be reviewed. We hope that this additional information will include the data necessary to populate the Biotic Ligand Model.

Sampling Requirements

Comment

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.

Response

The cities of San Diego, Lemon Grove, and La Mesa, the County of San Diego, and the San Diego Unified Port District are conducting a metals monitoring and reporting program under order of the Regional Board (Order No. R9-2004-0227). The order stipulates that all sampling will be conducted using appropriate methods and that analyses will use approved techniques and meet minimum detection levels. Sections 11 and 12 of the draft Technical Report provide further details and sufficient guidance for the responsible parties to develop a revised monitoring and reporting program as part of the TMDL Implementation Plan if required by the Regional Board.

Water-effect Ratio

Comment

Water-effect 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.

Response

The Regional Board appreciates Dr. Shaw's insights on the application of the water-effect ratio (WER) to freshwater systems. If and when a WER study is undertaken for Chollas Creek, the Regional Board will ensure that any sight specific chronic conditions are protective of the beneficial uses of the creek. The monitoring plan of Sections 11 and 12 of this report does require the sampling and analysis of dissolved metals. Furthermore, under the ongoing sampling plan, total metals are also being sampled.

Source Analysis

Comment

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 storm water discharges and creek toxicity has already been established (Schiff, 2001). Given that storm water 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).

Response
The end of the first paragraph of Section 5.1 has been modified to clarify any confusion over the source of water and over the persons responsible for the water in the creek. The following text has been added:

> The small size of the creek's riparian zone and the encroachment of development along the creek make the amount of run-off directly to the creek much smaller than that entering from storm drains. Furthermore, under the current MS4 WDRs, the creek itself is considered part of the storm drain system. Therefore, parties named in the Order are responsible for not only the run-off entering the creek, but also for the water in the creek itself.

Land Use Model

Comment
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.

Response
Comment noted.

Model Interpretation

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.

Response
Comment noted.

Source Analysis Literature

Comment
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.

Response
The inclusion of deposition rates from Fresno, California in 1984 in the Source Analysis of this TMDL illustrate the upper range of possible lead atmospheric deposition. The Clean Air Act has drastically reduced the amount of lead that can reach the atmosphere. Nevertheless, the depositional rate from Fresno remains in the technical report as an informational item. When and if a local atmospheric deposition study is conducted, a comparison of the lead rates with those estimated from the 1984 study will be interesting. Only then will evidence be available to test the reasonable assumption that a watershed of cars with unleaded fuel will lead to a lower rate of atmospheric lead deposition than that observed in Fresno in 1984.

Data Deficiencies

Comment
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.

Response
The details of the monitoring plan can be found in sections 11 and 12 of the of this report. Please see the response to comment no. 5 above for more information regarding the monitoring requirements of this TMDL.

The Regional Board agrees that the relationship between Numeric Targets and identified metal sources is not clearly explained in the Linkage Analysis Section. Therefore, the following text has been added as the new third paragraph of Section 6:

> These loading capacities, which are equal to the Numeric Targets, will apply to the entirety of Chollas Creek and during all times of the year. Each of the land uses identified in the Source Analysis portion of this TMDL will not be allowed to have runoff or in-stream waters in excess of these concentrations. Further more, all other sources of copper, lead and zinc to Chollas Creek will be expected to not cause the creek to exceed these loading capacities. Once these capacities are achieved, it is expected that Chollas Creek copper, lead and zinc concentrations will be protective of the creek's beneficial uses.

The model described in section 5 and in Appendix D was used to identify and quantify the relative sources of copper, lead and zinc to Chollas Creek for the Source Analysis. Once the data deficiencies are overcome, the model will be used to more accurately quantify the mass loads of these metals from the creek to San Diego Bay. At that point, the TMDLs for copper, lead and zinc in Chollas Creek will be revised to contain both a concentration limit applicable at all times and a mass load limit that is not to be exceeded on an annual basis. This model refinement is expected to take place as part of the development of the TMDLs for the Mouths of Chollas and Paleta Creek in San Diego Bay.

Synergistic Toxicity

Comment

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 synergistic (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).*

Response
The Regional Board agrees that synergistic effects among metals that are individually below CTR may produce toxicity and that these interactions would be difficult to regulate in the absence of site-specific data. Should this site-specific data become available at some future date, it could be incorporated into the TMDL.

Chollas Creek samples collected and analyzed between February 2000 and February 2004 indicated no (0 percent) exceedances of the CTR for dissolved cadmium. Applying the listing policy (SWRCB, 2004) to the available cadmium data confirms that cadmium should be delisted. Therefore the Regional Board is recommending that cadmium in Chollas Creek be removed from the Clean Water Act List of Water Quality Limited Segments. The Regional Board would reconsider the listing should data become available indicating that cadmium concentrations have increased above the CTR, or that cadmium in a synergistic interaction, is producing toxicity.

Linkage Analysis

Comment
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.

Response
Comment noted. Please see the response to comment no. 4 for a discussion of the Numeric Targets.

Margin of Safety

Comment

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.

Response

The explicit 10 percent Margin of Safety (MOS) was incorporated into the TMDL to account for any uncertainties in the analysis of metals. Therefore, an explicit MOS is warranted. The choice of ten percent is not based on the amount of error in the data, nor on any scientific study that establishes that the CTR formulas may have a 10 percent error. Rather, the 10 percent MOS is based upon the size of the MOS found in other similar TMDLs. Please see the TMDL for Selenium in the Lower San Joaquin River in Region 5, the Clear Lake TMDL for Mercury in Region 5 and the TMDL for Toxic Pollutants in San Diego Creek and Newport Bay, California by the USEPA.

The Regional Board agrees that the last paragraph of section 7 needed clarification. The entire paragraph has been changed to the following:

> Another implicit MOS was not allowing for metal interactions with anions and negatively charged sites on particulates when calculating the loading capacity and allocations. Theoretically, an increase in bioavailability from these types of chemical interactions in water would only take place in waters with low pH levels. The increased aqueous acidity (low pH levels) would yield higher levels of free metal ions and thereby increase bioavailability to aquatic organisms. Such low pH levels in ambient waters are more likely to be observed in areas of high acid rain; these low pH conditions are not likely in San Diego. Therefore, metal interactions with negatively charged anions and particles

within the water were assumed to only decrease bioavailability. Not allowing for this interaction makes the TMDL concentration more conservative.

California Toxics Rule Inherent Margin of Safety

Comment

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.

Response

The explicit 10 percent Margin of Safety (MOS) was incorporated into the TMDL to account for any uncertainties in the analysis of metals. The CTR 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. Therefore, the Regional Board believes that an explicit MOS is warranted.

Critical Conditions

Comment

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.

Response

Comment noted.

Monitoring Details

Comment

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.

Response

The details of the monitoring plan can be found in sections 11 and 12 of this report. Please see the response to comment no. 5 above for more information regarding the monitoring requirements of this TMDL.

Specific comments regarding the Technical report are as follows

Comment A

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

Response

Please see the response to comment no. 2 above for a discussion on biomagnification and for the changes made to this TMDL Report.

Comment B

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

Response

This correction has been made.

Comment C

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

Response

The Regional Board still believes that Cd should be removed from the Clean Water Act List of Water Quality Limited Segments. Please see the response to comment no. 12 for a more in-depth discussion.

Comment D

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

Response

Paragraph has been updated to use ‘lowest’ in both instances.

Comment E

“ “, same paragraph- Ceriodaphnia is misspelled.

Response

This correction has been made.

Comment F

“ “, 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.

Response

The sea urchin test was run to see if Chollas Creek stormwater could be negatively impacting San Diego Bay. To avoid any confusion over the details of the Toxicity Identification Evaluation (TIE), the last sentence of the first paragraph of section 3 has been deleted. The full citation for the TIE study can be found in the reference section.

Comment G

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.

Response

The italicized text in section 3.3 is taken verbatim from the Basin Plan. Therefore, we do not want to change this quotation as it appears in this TMDL Report. However, this correction will be considered during the drafting of the monitoring plan and during the next revision of the Basin Plan.

Comment H

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

Response

The following reference has been added to that section:

> Besser, J. M., 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.

Please see the response to the Comment A for further discussion.

Comment I

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

Response
This change has been made.

Comment J
" ". Next sentence; …same locations more commonly found at higher concentrations in ….

Response
This change has been made.

Comment K
" ". P. 9, Better references than Buffle, 1989.

Response
The Regional Board appreciates the additional support for concepts put forth in section 3.4 and will be working to track down these references.

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

Response
A reference to sections 11 and 12 has been added to this paragraph.

Comment M
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?

Response
This determination was based upon the similarities in land use between the watersheds of the two forks of Chollas Creek. The last sentence of the first paragraph of section 3.6 has been changed to:

> This station samples run-off that is representative of the entire watershed because the land use distribution in the north fork portion of the watershed is nearly identical to the land use distribution of the entire watershed as shown in Table 3.5 below.

Comment N
" ", next paragraph. Replace 1994.95 with 1994-95.

Response
This change has been made.

Comment O
" ". Same paragraph. Provide methods for toxicity tests.

Response

The methods for these toxicity tests can be found in the original Stormwater Reports for the various years. These documents can be viewed at the Regional Board office.

Comment P

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

Response

The part that reads "*even in individuals that died later in the test*" has been removed from the text. The Stormwater Reports containing these toxicity test results can be reviewed at the Regional Board office.

Comment Q

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

Response

References for the conversion factors are properly cited in section 4.3, where they are discussed in detail.

Comment R

" ". 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?

Response

This change has been made.

Comment S

" " 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.

Response

This change has been made.

Comment T

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

Response

This change has been made.

Comment U

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

Response
The reference has been maintained and the appendix will be included as part of the TMDL report.

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

Response
This change has been made.

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

Response
This change has been made.

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

Response
This change has been made.

Comment Y
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.).

Response
Please see response to comment no. 10 above.

Comment Z
Section 4.4.3. p. 31. second sentence. Replace do with low.

Response
This change has been made.

Comment AA
In addition, there are a number of mis-labelings in the appendices.

Response
These corrections have been made.

Additional references provided by Dr. Shaw.

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Response
The Regional Board appreciates these additional supporting references and will consider them as the need arises.

Response to Peer Review Comments from Dr. Garrison Sposito and Ms. Jasquelin Peña

Overall Summary

Comment

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.

Response

Comment noted.

National Toxics Rule vs California Toxics Rule

Comment

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."

Response

The Regional Board did not intend to imply that the water quality criteria contained in the CTR are more "stringent" or lower than the values contained in the NTR. Water quality criteria in the CTR are based on dissolved metal concentrations for copper, lead and zinc, unlike water quality criteria in the NTR, which are based on total copper concentrations. Therefore, it is possible to exceed values contained in the NTR but not exceed the water quality criteria in the CTR because they are measuring different aspects of a metal. In order to avoid further confusion, the text on page 4 at the beginning of the second sentence, "While exceeding NTR criteria" was deleted.

Definition of TMDL

Comment

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.

Response

Comment noted. For clarification purposes, in accordance with the applicable federal regulation [40 CFR 130.2(i)]: "TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measure." The TMDLs for metals in Chollas Creek are concentration-based.

Numeric Targets

Comment

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 metal concentrations 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.

Response

The Regional Board agrees that hardness data will be necessary to monitor for compliance with the TMDLs. Water quality criteria in the CTR are expressed as a function of hardness. The Regional Board will require the dischargers to collect hardness data in addition to metals concentrations as part of the monitoring required to comply with the TMDLs. Please note that Table 3.1 is now labeled as Table 4.1.

Temperature and pH

Comment

It is possible to include direct effects of temperature and pH in the equations, but this was not done in the draft report.

Response

The equations in the CTR do not include the parameters of temperature or pH. The Regional Board will continue to use the equations defined in the CTR with the WER = 1.00 until it can be demonstrated that an alternative approach is appropriate based on further studies or information.

Site-Specific Objectives

Comment

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.

Response

The passage of the CTR in 2000 by USEPA established legally applicable numeric water quality objectives for priority toxic pollutants including copper, lead and zinc in California. Water quality criteria in the CTR are based on dissolved metal concentrations. In the absence of site-specific data, a WER equals one and a constant total-to-dissolved metal conversion factor set in the CTR is appropriate for use in the equations that define the CTR water quality criteria.

Until sufficient information is available to justify a change, using a WER equal to one in the CTR and a constant total-to-dissolved metal conversion factor will ensure protection of beneficial uses in Chollas Creek. However, the Regional Board supports the collection of data and information necessary to determine if a modified WER value or some other site-specific criteria is appropriate and/or to establish a site-specific conversion factor for total-to-dissolved metal concentrations. Once data are available to change the WER or total-to-dissolved metal conversion factor, the State has the discretion to interpret the CTR water quality criteria and modify the TMDLs based on site-specific studies and information for Chollas Creek

CTR as Numeric Target

Comment

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.

Response

The Regional Board agrees that a more detailed discussion regarding the role of hardness to the water quality criteria is important. The above text under *"f. Hardness"* was added to the end of the first paragraph of section 4.4.

Site-Specific Toxicity Evaluation

Comment

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.

Response

Implicit MOS are an allowable component of the TMDL process. TMDL design allows for limitless methodological and equation refinements that find their reasonable limit via best professional judgement. In this instance, the Regional Board will continue with the "WER = 1.0" approach until it can be demonstrated that an alternative approach significantly alters the final result

In addition, please see the response to comment no. 25 above.

Hydrologic Modeling

Comment

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).

Response

The model described in section 5 and in Appendix D was used to identify and quantify the relative sources of copper, lead and zinc to Chollas Creek for the Source

Analysis. Once the data deficiencies are overcome, the model will be used to more accurately quantify the mass loads of these metals from the creek to San Diego Bay. At that point, the TMDLs for copper, lead and zinc in Chollas Creek will be revised to contain both a concentration limit applicable at all times and a mass load limit that is not to be exceeded on an annual basis. This model refinement is expected to take place as part of the development of the TMDLs for the Mouths of Chollas and Paleta Creek in San Diego Bay.

Monitoring Needed

Comment
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.

Response
The Regional Board agrees that additional monitoring should be conducted during low flow periods to more accurately characterize metals loading to Chollas Creek. The Regional Board will require the dischargers to monitor during dry weather metals concentrations to comply with the TMDLs. Information gathered as a result of this monitoring will be incorporated into the TMDLs as appropriate.

Editorial Clarification

Comment
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.

Response
The draft Technical Report has been updated to reflect this change.

Treatment Plant Effluent

Comment
Page 33, Section 4.4.5.2. Quantify the difference between the "back of the envelope calculation" given here and the model results.

Response
As stated in the text, the quantities associated with the treatment plants have been determined to be insignificant because the treatment plants' effluents have little detectable copper, lead and zinc. Therefore no further analysis is necessary.

Pesticide Copper Concentrations

Comment

Page 37, Section 4.5.4. The percentage of copper contained in each pesticide should be included in Table 4.10.

Response

Comment noted. As stated in the text, only a percentage of the pesticide amount shown in Table 5.10 is actually copper or zinc and there is not enough information to quantify the actual amount of copper or zinc that would reach a water body in San Diego County.

Load and Waste Load Allcoations

Comment

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.

Response

Comment noted. For clarification, waste load and load allocations were made in the draft Technical Report. These allocations are concentration–based, in accordance with federal regulations [40 CFR 130.2(i)], which state: “TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measure.”

Biomagnification

Comment

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.*

Response
The existing data on sediment metals concentrations in Chollas Creek demonstrated that metals in the sediment are most likely not accumulating in Chollas Creek. Instead, metals adsorbed to particles in Chollas Creek are likely flushed out of the creek during wet weather events, acting as a source of metals loading to the mouth of Chollas Creek and San Diego Bay. A TMDL is currently under development for the mouth of Chollas Creek that will address this issue.

Concentration-based TMDL

Comment
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.

Response
The TMDL is the combination of a total wasteload allocation (WLA) that allocates loadings for point sources, a total load allocation (LA) that allocates loadings for nonpoint sources and background sources and a MOS. For clarification, waste load and load allocations were made in the draft Technical Report. These allocations are concentration–based, in accordance with federal regulations [40 CFR 130.2(i)], which state: “TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measure.”

Scientific Justification for Using CTR

Comment
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.

Response
The CTR hardness-based equations are legally and scientifically applicable to Chollas Creek. The legal applicability is established by federal regulation [40 CFR 131.38] and is sufficient to warrant the use of the CTR for this TMDL. In addition, Chollas Creek is a freshwater system, with variable physical parameters that make the use of the hardness-based equations to prevent toxic conditions scientifically reasonable.

The comment regarding biomagnification is noted.

Summary of Current Problem

Comment
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.

Response
The Regional Board agrees with this comment and is requiring hardness (as calcium carbonate) to be measured.

Hydrologic Modeling

Comment
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 waste load allocations. All hydrologic and metal source effects are implicit in these allocations.

Response
Compliance sampling will not be based upon the critical conditions identified in the hydrologic model used in the Source Analysis. Sampling details can be found in sections 11 and 12 of the draft Technical Report.

Additional Monitoring

Comment
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.

Response

The Regional Board agrees that additional data should be collected to fully characterize the contribution of metals during dry weather. Monitoring of metals concentrations during dry weather will be required of the dischargers in order to comply with the TMDLs. Further data would also be useful to characterize the contribution of metals in sediment to metals loading into San Diego Bay. The Regional Board will address this issue in a TMDL currently under development for the mouth of Chollas Creek.

Additional Toxicity Testing

Comment

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.

Response

The Regional Board supports the collection of data and information necessary to determine if a modified WER value or some other site-specific criteria is appropriate and/or to establish a site-specific translator for total-to-dissolved metal concentrations. Unfortunately, the Regional Board does not have the resources to actively engage in these investigations. The current WER value of one is appropriate for use in the equations that define the CTR water quality criteria. Until sufficient information is available to justify a change, the value of one is appropriate for all CWA uses, including the SIYB TMDL. In the meantime, using a WER equal to one in the CTR copper objective will ensure protection of beneficial uses in the water column of SIYB. Once data are available to change the WER, the State has the discretion to interpret the CTR copper criteria based on a site-specific WER for Chollas Creek.