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August 31, 2016

Cynthia Gorham
Senior Environmental Scientist
Restoration and Protection Planning Unit
San Diego Regional Water Quality Control Board

RE: Peer Review of Site-Specific Water Quality Objectives for Trace Metals in Chollas Creek

Dear Ms. Gorham,

Please find below comments related to my peer review of documents related to Site-Specific Water Quality Objectives for Trace Metals in Chollas Creek, including the study entitled *Development of Site-Specific Water Quality Objectives for Trace Metals in Chollas Creek: Water-Effects Ratio Study for Copper and Zinc, and Recalculation for Lead* and the San Diego Regional Board's *Technical Report for Tentative Resolution No. R9-2016-0148*. Based on my review of the documents, and presuming my comments below are readily addressed, I find the proposed rule is based upon sound scientific knowledge, methods and practices. I also agree that adoption of site-specific WERs that are more representative of actual site conditions, while increasing water quality objectives for copper and zinc, will yield water quality objectives that will be protective of aquatic life.

1. Perhaps my most significant question is could you more precisely present the justification for basing the WER on the geometric mean of four sampling events in the context of the USEPA's 1994 *Interim Guidance on the Determination and Use of Water-Effects Ratios for Metals*? Much of the guidance document was couched in terms of point source pollution, design flows, and the assessment of toxicity in "effluent" combined with "upstream waters," thus making it difficult to clearly understand how the guidelines inform assessment of toxicity in a flowing creek that is integrating non-point pollution loading from throughout its watershed. The guidelines seem to state that more than three sampling events are needed to develop a WER, and that use of the geometric mean, rather than an arithmetic mean or use of a the maximum value from a set WERs, is appropriate in some cases. But a more detailed description of how you interpreted the guidance document to support your approach would be helpful. Can you also expand on the statement on page 19 of the 2014 WER development study that four monitoring events were "able to capture site-specific variability associated with temporal seasonality and flow"? The rainfall totals and intensities appeared to be fairly similar for the monitoring events, though there was some variability in hydrograph response and peak flows. In essence I am asking if the four sampling events provide enough data on which to confidently estimate WERs for the site.

2. A related question is the rationale for using flow-weighted composites as the method for assessing WERs. Was this an approach recommended in the 1994 WER USEPA guidance manual or an approach that has been used in California sites (e.g., Los Angeles River copper WER study)? Is there a concern that any toxicity associated with a first-flush associated with the rising arm of the hydrograph may be subsequently diluted as a storm event progresses? Is it enough of a rationale to say that sampling methods used to develop WERs should be consistent with compliance monitoring, which is also based on flow-weighted sampling?

3. As detailed in Tables 6-2 and 6-3 of the 2014 WER development study, the copper LC50 for *C. dubia* measured in dilute mineral water was an order of magnitude lower than USEPA species mean acute value, which was appropriately used to subsequently calculate WERs. Is this a common outcome in toxicity testing? How did the zinc LC50 for *C. dubia* measured in dilute mineral water compare to the USEPA species mean acute value, presuming there is a reported value for zinc? Why the difference in response between copper and zinc relative to USEPA species mean acute values, if any? Do the results for copper LC50 for *C. dubia* measured in dilute mineral water call into question the LC50 values measured for the creek water samples?

4. In Table ES-2 of the 2014 WER development study, there is a footnote stating that during dry weather the WERs are equal to 1. Is there a reason this seasonal overlay on the WERs is not a part of the recommended revisions to Table 7-21a. Is it reasonable to apply WERs developed for wet weather events between October and April to dry weather conditions? Is this considered a non-issue because of the very limited precipitation during the dry season? Is there direction in the 1994 USEPA WER guidance manual on how to handle this situation?

Thank you for this opportunity to provide peer review regarding the development and implementation of copper and zinc water-effect ratios for Chollas Creek. Please do not hesitate to contact me if you have any questions.

Sincerely,

Marc Beutel
Associate Professor
Environmental Engineering

September 12, 2016

Review of the Site Specific Water Quality Objectives for Copper and Zinc in Chollas Creek

1.1. The background chemical basis for the criteria for copper and zinc

The results found appear to fit with our understanding of the complexation of metals with inorganic ligands and natural organic matter in the environment, and with the knowledge of the stronger binding capacity of copper (Cu) compared to zinc (Zn) for dissolved ligands in solution. Also, the results are consistent with the known impact of the major cations in freshwater (calcium (Ca) and magnesium (Mg)) on the interaction of other cations with the tissues of organisms. For fish, as detailed in the Biotic Ligand Model (BLM), these cations (Ca^{2+} and Mg^{2+}) interact with the same sites on the membrane of fish gills, for example, as the toxic metals. Also, it is likely given the different chemistries of the cations, that Cu would interact more strongly with the surface sites on the organism's tissue than Zn would, and so would be more toxic. Thus, the consideration of hardness in toxicity estimations is for these two reasons: 1) that the concentration of the major cations effect the interaction of the toxic metal with the binding site on the organism's surface; and 2) that the presence of carbonate in solution, and the pH (i.e. H^+ concentration) influence the speciation of the metal and thus the free ion concentration, which is the form that is considered to be interacting with the tissue surface.

Overall, the differences in the interaction and bioavailability of Cu and Zn are because of their chemistry, which relates to their location next to each other in the periodic table. While Cu has an unfilled d orbital, Zn has a filled d orbital and this affects their reactivity and chemistry. Zinc is essentially found as a +2 cation in the natural environment, and is mostly present in environmental solutions as the free ion (Zn^{2+}), with substantial complexation only occurring at higher concentrations of the ligands in solution to which it binds most strongly (Cl^-, sulfide, natural organic matter (NOM)) or at higher pH. In the absence of organic ligands, Cu, in its +2 oxidation state (Cu can also exist as a +1 cation but is dominantly as a +2 cation in oxic waters), forms relatively strong complexes with carbonate species and with hydroxide at higher pH. The relatively strong complexation of Cu with carbonate is thought to reduce the toxicity of Cu in the environment and is an additional reason for including a parameterization that includes hardness (a measure of alkalinity and therefore reflective of the concentration of carbonate and bicarbonate, the relative amount of which depends on pH) besides that related to the competition affect of the major cations. This realization has allowed for the incorporation of detailed metal chemistry into the understanding of toxicity – it is not the total dissolved concentration that matters, but the bioavailable fraction, which depends on complexation. The impact of hardness for Zn speciation is less than for Cu, but can be important at relatively high alkalinity. For

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example, at a pH of 7, there would need to be a very high alkalinity (>3 meq/L; ~300 mg/L hardness) for more than half the Zn to be complexed by carbonate and bicarbonate ligands (based on the equilibrium constants in the computer thermodynamic program MINEQL+).

Considering typical water conditions and a near neutral pH, as is the creek water, even in the absence of organic matter, a much larger fraction of the Cu would be complexed compared that of Zn, which would be mostly present as the free ion. For example, thermodynamic equilibrium calculations indicate that at pH 7 and with hardness representative of what is found in the creek, Zn would be mostly as the free ion while Cu would be mostly as carbonate complex, ranging from ~20% complexed at low hardness (20 mg/L) to greater than 60% for the higher range of values found in the creek water, with correspondingly decreasing free ion concentration. So, depending on the actual hardness of the water, the fraction of the metal present as a free ion is would be very different for the two metals.

To date, most water quality criteria only account for the inorganic speciation of the metal while it is well known that many metals in solution are strongly bound to NOM. Copper is one of the metals that is bound very strongly by NOM, and, in many environments, nearly all (>90%) of the metal is bound to organic matter (Morel and Hering, 1993; Mason, 2013), and the most important inorganic ligand is carbonate, depending on the pH. This, therefore is the most likely chemical explanation for the higher values determined for the WER in the studies reported for Chollas Creek. It is also known that Cu is more toxic than Zn and the higher toxicity of Cu relative to Zn is established and reflected in the equations used for the water quality criteria – overall Cu is about 10 times more toxic in the creek water based on the calculated total concentration using the previously derived equations in Table 8-1 of the Site Specific Criterial Report (see Table 1) even though Zn is present as a free ion at much higher relative concentrations.

Table 1: Calculated toxic concentrations for copper and zinc using the equations presented in the report

Metal	*Hardness (mg/L) 20*	*50*	*100*	*200*	*300*
Cu (µg/L)	2.65	6.29	12.10	23.24	34.05
Zn (µg/L)	25.91	55.32	101.33	182.30	257.03

However, even given the higher complexation of Cu, the effect of hardness is different for the two metals and this reflects the fact that changing the hardness has a much larger impact on the speciation of Cu compared to Zn. For Zn, the effect of hardness is mostly related to the increased competition for the binding sites by the major cations while for Cu there is the combined effect of the increased cation concentrations and the changes in speciation. The ratio of the toxic concentrations for a hardness of 100 relative to 20 mg/L (a factor of 5 increase in

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hardness) is 3.9 for Zn and 4.6 for Cu. So, for both metals, the increasing hardness mitigates the effect of the metals on toxicity in a non-linear manner, and leads to a higher concentration required for toxicity for both metals. Overall, the rate of change in concentration is different, with the effect of hardness having more impact for Cu. This makes sense based on the known chemistry of Cu and Zn in freshwaters in the presence of carbonate species.

Based on the potential effect of NOM on the relative complexation of Cu compared to Zn, I examined various model outcomes and evaluations reported in the literature, as well as making my own calculations using the MINEQL+ program. Overall, these indicate that the impact of NOM on the relative toxicity of Cu would be much greater than on Zn, and this is what the revised criteria essentially indicate. Again, the relative change appears to be consistent with biogeochemical understanding Morel and Hering, 1993; Mason, 2013). Based on published papers in the literature, and my own calculations using MINEQL+, it can be concluded that the impact of the levels of NOM documented in the creek (4-30 mg/L) would be to decrease the concentration of Cu^{2+} dramatically, and this would impact the toxicity assuming that Cu^{2+} is the most bioavailable species of Cu, which reflects scientific consensus. Based on the literature and my calculations, the relative ratio of the various models is that the complexation of Cu to carbonate relative to NOM, at the levels found in the creek, would be about 1:8 for the medium values of hardness reported in Table 6-1, and the higher levels of NOM reported (i.e. the DOC concentrations). In other words, the complexation of Cu to NOM could reduce the toxicity by a substantial amount relative to that which would be found in the presence of only inorganic chemicals in solution. Clearly, this relative decrease in toxicity is comparable to the value derived from the toxicity tests, and promulgated in the equations, as this would result in a calculated WER value that would be very similar to the value that is promulgated based on the toxicity tests of ~7 for Cu.

Also, based on thermodynamic modeling it would be concluded that the impact of NOM on Zn would be much less than that for Cu, and around a factor of 2 decrease in the toxicity under the median conditions of the creek, based on thermodynamic equilibrium equations, and this is again similar to the value suggested in the report of 1.7. So, overall, based on the known chemistry of these metals and the conditions in the creek, the initial WER values are not inconsistent with the notion of the previous criteria, which were based on the known inorganic chemistry of the waters and the chemistry of Cu and Zn in solution in natural waters, in the absence of NOM. However, these initial criteria ignored the potential impact of NOM, and the new criteria appear to reflect the relative impact of NOM complexation on Cu and Zn toxicity, based on the results of chemical thermodynamic modeling and the understanding of the chemistry of these two metals. While this was not included in any of my modeling calculations, there is also the possibility that the NOM would complex some of the major cations (Ca and Mg) and this would reduce their relative competition for the binding although the effect would likely be small at the concentrations in the creek water.

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Overall, the revised values for the WERs with an addition of a factor of ~7 increase in the toxicity concentration for Cu and a 1.7 increase in the toxicity concentration for Zn is consistent with the known effect of the complexation chemistry of NOM on Cu and Zn, and the fact that the presence of NOM would have a much more substantial impact on the toxicity of Cu relative to Zn. The final WER values recommended in the report (Table 6-8 and pg 62) are the lower average values obtained for one of the two sites in the creek where the water quality tests were done (6.998 for Cu and 1.711 for Zn). This is a good approach to take the more protective value for application to the whole creek. However, there were lower values reported in some of the tests, with the lowest value being 4.951 for Cu and 1.18 for Zn. Perhaps the consideration could be made that the proposed WER values be the lowest determined value, which would be more protective. It seems that even if these lower values (column 3 in Table 2) were adopted the creek would remain in compliance as most of the dissolved Cu measurements are below 20 µg/L and most Zn concentrations below 200 µg/L (Fig. 6-1) – as most of the hardness concentrations are below 200 mg/L.

Table 2: Calculated values for the CMC Acute using the formula in Table 8-1 for various values of water hardness.

CMC Acute		**WER**	
Hardness	**Original**	**Proposed**	**Lowest value**
Cu	*1*	*6.998*	*4.951*
20	2.65	18.58	13.14
50	6.29	44.05	31.17
100	12.10	84.64	59.88
200	23.24	162.64	115.06
300	34.05	238.30	168.60
Zn	*1*	*1.711*	*1.183*
20	25.91	44.33	30.65
50	56.32	96.36	66.63
100	101.33	173.37	119.87
200	182.30	311.92	215.66
300	257.03	439.79	304.07

Another reason for considering a lower WER value is the fact that the relative variability in the four tests for each site are quite high. The relative standard deviation (RSD) for the WER for Cu at SD8(1) is 51% while that for DPR2 is 32%. This is a high variability in the response and suggests that the average value is perhaps not the best value to use, although the value

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suggested in the final conclusion is the lower value based on the DPR2 site, which has the lowest RSD. The RSDs for the Zn tests are lower for both sites, between 25 and 30%.

1.2 The overall method and testing

From reading the report, it is concluded that the approaches used and the quality assurance/methods appear to follow the EPA guidelines properly and therefore the toxicity tests are adequate for the determination of the WER values for Cu and Zn. As detailed in Section 6.2.1 and discussed in details in the previous review reports and responses in the appendix (Appendix A) there was a potential bias because of the impact of low values for the LC50s for the control animals in “laboratory water” (DMW) for Cu. This appeared as a potential concern in the initial review of the report by the TAC but the documentation in the appendix satisfied this concern and it appears that this issue has been adequately addressed in the final report as detailed in this section. Instead of using these determined values a more conservative approach was used as detailed in Tables 6-2 and 6-3. This is an acceptable solution to the problem. The WER values that would have been determined using the DMW would have been unrealistic.

As noted in Appendix H, the values reported for the WER are comparable to the results obtained using the BLM even though the BLM results are not used to set these targets. As discussed above, this is consistent with the chemistry of the metals in solution and the role of hardness and NOM in moderating their toxicity. This provides further confidence and support for the values that are recommended in the report. Additionally, the results obtained with the secondary species appear to confirm that the WER values that have been determined are protective as the lowest WER values with the secondary species are higher than those which were chosen as the overall creek WER for both metals. Also, the results with the combined metals do not show any synergistic effects but in fact confirm that the toxicity of Cu is greater than that of Zn, as expected.

Overall, it can be concluded that the approach and methodology for determining the WER values for Cu and Zn follow the criteria and approach outlined by EPA and are consistent with their guidelines. Furthermore, the basin amendment plan that clarifies the adoption of the new WER values will be not less protective of aquatic life as the rationale for using the higher WER values is consistent with the expected impact of organic complexation of the metals in the water on their toxicity, as such complexation reduces the metals’ bioavailability. The impact is larger for Cu than for Zn, and this is reflected in the new values.

Please let me know if you have any questions or comments concerning my review.

Sincerely,

Robert P Mason, Professor

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ADDITIONAL EXTERNAL PEER REVIEW COMMENTS

From Dr. Robert Mason (October 7, 2016)

My evaluation of the documentation in terms of the statements there is no downstream impact of the new WER criteria is that these statements represent a scientifically defensible position as they are based on the impact of the water quality on the bioavailability of the metals and this will not change downstream at the mouth given that these are determined by water hardness – more specifically its role on complexation of the metals as well as the impact of the major cations on interactions of the metals with biological surfaces. The criteria will remain valid downstream given the expected changes on water hardness and pH would not lead to any substantial difference in the metals' bioavailability.

The role of sediment toxicity is not an issue as explained in the documentation as the major cause of this toxicity has been shown to be organic contamination and not metals, and indeed it seems that the metal levels reflect background conditions. It is also indicated, however, that this will be further evaluated and if found to be different, then there could be further amendments in the future, But the role of sediment toxicity is a different issue and will not impact the outcome that is a consequence of the changes in the WERs on the downstream regions. As indicated as well, given the nature of the system and its "flashiness" in flow, any downstream impacts would be short-lived due to rapid mixing and dilution. While this is not a justification for allowing the new WER in lieu of other scientific validation, it represents an additional level of safety as this would potentially mitigate any effects.

Overall, based on my reading of the documents, I conclude that the statements about the lack of any downstream impacts are scientifically valid.

From Dr. Marc Beutel (October 9, 2016)

I have reviewed the CEQA checklist and the Board's response letter to comments from the San Diego Coastkeeper and US FWS dated February 5, 2016. I also reviewed key supporting documents including the executive summaries of the 2011 SCWRRP sediment toxicity study and the 2005 Navy sediment assessment. I did not find any significant areas of concern related to the scientific rationale used to support the CEQA checklist or the contention that adopting the site-specific WERs for copper and zinc will be protective of downstream water quality. The 2011 SCWRRP study clearly found that sediment toxicity was associated with exposure to organic compounds. As noted in the study, PAH concentrations in Chollas Creek mouth sediments were "greater than most other locations in southern California." In contrast, metals were not a substantial source of toxicity since "bioavailability of divalent metal contaminates in sediment and pore water was very low." The 2005 Navy study reported that sediment toxicity to aquatic-dependent life was likely associated with PAHs, PCBs, chlordane and DDT. Based on these sediment studies, it is clear that adopting site-specific WERs for copper and zinc will not substantially exacerbate toxicity in downstream sediments located at the mouth of Chollas Creek.

In addition, I agree with the Board's assessment that adopting site-specific WERs for copper and zinc is protective of downstream water quality. Since the WERs were developed based on storm water collected in the creek, they are reasonably representative of water quality conditions throughout Chollas Creek. And since metals have been show to not drive toxicity in sediment at the creek's mouth, the settling out of copper and zinc in the mouth is not a significant toxicity concern. As noted in the Board's February 6, 2016 letter and detailed in the WER study, even with the adoption of the WERs, the loading of copper and zinc into Chollas Creek is expected to decrease. And over the long term this will result in a decreases in metals concentration in the water column, sediments and sediment pore water in the creek and creek mouth.

Note that my comments above should be considered in the context of my original peer review summary letter dated September 31, 2016, which details a number of comments related to the WER study and proposed Basin Plan amendment.