December 17, 2010

Becca Conklin
Water Quality Standards Coordinator
Washington State Department of Ecology
1822 E. Highway 54, Suite 120
P.O. Box 47600
Olympia, WA 98504-7600

Subject: **Comments on the Washington State Triennial Review: Recommendation for Updating the Aquatic Life Criteria for Zinc**

Dear Ms. Conklin:

As requested by the Washington State Department of Ecology (Ecology), this letter provides comments for the current triennial review (TR) of surface water quality standards (WQS) in the State of Washington. The comments provided here are primarily related to the numeric zinc criteria for protection of aquatic life. These comments are being provided jointly by the International Zinc Association (IZA) and Windward Environmental. The IZA is a non-profit industry association dedicated to the global market for zinc and the role of zinc in sustainable development. As such, the IZA actively supports research programs on the fate and effects of zinc in the environment and supports the adoption of regulatory standards for zinc that reflect the current state-of-the-science. Windward Environmental is a consulting firm consisting of environmental scientists and engineers who support the IZA on zinc research projects and work with the regulated community in complying with water quality standards for zinc and other metals.

The following section first provides a brief summary of our recommendation with regard to updated aquatic life criteria for zinc in WA State, with subsequent sections providing additional background and details used as the basis of our recommendation.

Summary of Recommendations for Updated Aquatic Life Zinc Criteria in WA State

The hardness-based zinc criteria for protection of freshwater aquatic life in WA State are now over 23 years old. Research conducted since the 1987 criteria were released has added a substantial amount of data on the toxicity of zinc to a number of freshwater species. The data from these studies can be used to provide a substantial update to hardness-based zinc criteria. In addition to hardness, it is now well understood that several water chemistry variables influence the bioavailability and, hence, toxicity of zinc. The biotic ligand model (BLM) is a tool to predict the toxicity of zinc, and other metals, to aquatic life over a range of water chemistry conditions (and not just over a range of hardness conditions). The EPA recommended BLM-based copper criteria for freshwater aquatic life in 2007. Draft BLM-based zinc criteria were submitted by the International Lead Zinc Research Organization (ILZRO) to the EPA in 2006, but have not been released by the EPA for public comment. Although we recommend that Ecology ultimately adopt the BLM as the basis for numeric zinc criteria in WA State, the current status of BLM-based zinc criteria within EPA may complicate statewide adoption of BLM-based zinc criteria during the current triennial review. Accordingly, we recommend that Ecology consider an update to the aquatic life criteria for zinc as follows:

1. *Update the hardness-based zinc criteria using the substantial body of zinc toxicity data published in the last 23+ years; and*
2. *allow use of the BLM to derive site-specific zinc criteria.*

In addition, relevant to #2, we recommend that Ecology restore language in the Permit Writer's Manual concerning guidance for the use of water effect ratios (WERs) for deriving site-specific water quality standards and their appropriate use in National Pollution Discharge Elimination System (NPDES) permits. Furthermore, footnote dd to the numeric criteria Table 240(3) should be revised as needed to facilitate the use of WERs as intended in longstanding EPA policy.

INTRODUCTION

The current WA State WQS include aquatic life criteria that have not been updated for many years, in some cases more than two decades. These criteria include the priority pollutant metals arsenic, cadmium, chromium, copper, lead, nickel, selenium, silver, and zinc. In the period since WA State last updated the aquatic life criteria, the Environmental Protection Agency (EPA), other states, and various organizations have updated criteria for many of these metals and other non-priority pollutant metals, such as aluminum. These updated criteria are based on more current scientific information and were developed following the EPA's criteria update procedures, and in many cases are already EPA approved. It is the EPA's policy to update criteria as new scientific information becomes available, especially that which could significantly affect environmental management decisions. Therefore, these updates give WA State an opportunity to bring their state WQS up-to-date and provide more appropriate policy and more accurate tools for regulating and managing water quality in WA State.

The WA State WQS contain the current aquatic life criteria for zinc in Section 173-201A-240 of the Washington Administrative Code (WAC). The current WA State acute and chronic zinc criteria are calculated as a function of water hardness, and are based on the 1987 EPA criteria for zinc (EPA 1987). A more recently developed tool for deriving water quality criteria for several metals, including zinc, is the biotic ligand model (BLM). The BLM accounts for several factors that influence metal bioavailability. Another set of comments submitted to Ecology on behalf of the Copper Development Association (CDA) and International Copper Association (ICA) has recommended that Ecology consider updating the freshwater aquatic life criteria for copper using the BLM.

For copper, the EPA recently released aquatic life criteria based on the BLM (EPA 2007a). The BLM represents a significant step forward in the best available science of not only copper, but several other metals, including zinc. A few states have recently adopted the EPA's BLM-based copper criteria in their WQS, but to-date mostly as a tool for deriving site-specific WQS rather than as the default basis for statewide numeric criteria. Draft BLM-based zinc criteria were submitted to the EPA in 2006, but the EPA has yet to review and release the draft BLM-based zinc criteria for public comment. While EPA review and issuance of nationwide criteria is a principal pathway for states to update their own criteria, it is not the only means of doing so. States can provide their own updates following EPA guidance and procedures and these can be approved by EPA, as required. Many states have decided not to wait for EPA and have already developed and adopted their own updated criteria for metals such as zinc, cadmium and aluminum (such as Colorado and New Mexico this past year). We strongly encourage use of the BLM-based criteria for copper and other metals and its adoption in standards as more states undergo their WQS triennial reviews.

The BLM is easy to use and the data required to run the BLM are a marginal increase in costs for data already needed to calculate hardness-dependent criteria. The BLM generates instantaneous acute and chronic criteria using 10 water quality input parameters that typically cost less than $200 per sample. These 10 input parameters are: temperature, pH, and concentrations of dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. The BLM software is publicly available, sanctioned by EPA, and requires only brief training to generate rapid and useable output. The BLM for zinc can be readily obtained and uses the same input data set as the copper BLM.

Washington's current zinc criteria, like most states' criteria, only take into account hardness as a factor that modifies toxicity. Using only hardness as a modifying factor for metals criteria is an outdated approach that does not take into account a substantial body of science. The peer-reviewed scientific literature demonstrates that additional modifying factors can and should be incorporated into regulatory benchmarks or standards, while providing the same level of aquatic life protection (EPA 1985, 1994, 2001). Zinc toxicity is a function of its bioavailability, which in addition to being controlled by hardness, is also strongly related to other important factors such as pH and DOC. The key strength of the BLM is that it accounts for multiple factors—in addition to hardness—that influence the amount of zinc that is bioavailable to aquatic life and, hence, potentially toxic. Therefore, the BLM-based criteria can provide more accurate levels of aquatic life protection across a broad range of water quality conditions than the outdated hardness-based criteria.

In WA State there are well over 1,000 National Pollution Discharge Elimination System (NPDES) permittees subject to compliance based on the EPA's outdated 1987 zinc criteria. NPDES permits are the principle regulatory vehicle for Clean Water Act implementation to protect and restore water quality. NPDES permits rely on state WQS and criteria for setting appropriate compliance levels. Water quality criteria drive permit compliance decisions and can lead to significant capital expenditures. Water quality criteria also drive the 303(d) and TMDL process for identifying and cleaning up impaired water bodies. Using outdated criteria for NPDES, 303(d), and TMDL purposes could lead to wasted resources on unnecessary listings (i.e., false positives). Using outdated criteria may also result in under-protection of aquatic life (i.e., false negatives).

The EPA has always intended criteria to be updated as new toxicity data become available and has specific guidance for developing and updating criteria. These criteria updates can be performed by the EPA or by the states, and the triennial review process is the means for adoption. Zinc toxicity has continued to be extensively researched since 1987. As a result, new freshwater zinc criteria were recently adopted by the State of New Mexico (NM). These 2010 NM zinc criteria are based on a nationwide update of the zinc toxicity data set, which contains toxicity data for approximately twice as many species as in the data set used in the 1987 criteria. Similarly, recent State of Colorado zinc criteria updates have used this same process. Consequently, these other states' precedents give Washington a robust starting point for adopting updated hardness-based zinc criteria.

Therefore, given these opportunities to use more effective criteria, WA State at a minimum should consider updating its hardness-based zinc criteria to reflect the 23+ years of research conducted since the EPA's zinc criteria were released in 1987. Ideally, WA State should consider adoption of BLM-based zinc criteria in order to reflect the state-of-the-science with regard to zinc toxicity to freshwater aquatic life, or at least recognize the option of using the BLM as a tool for developing site-specific WQS for zinc.

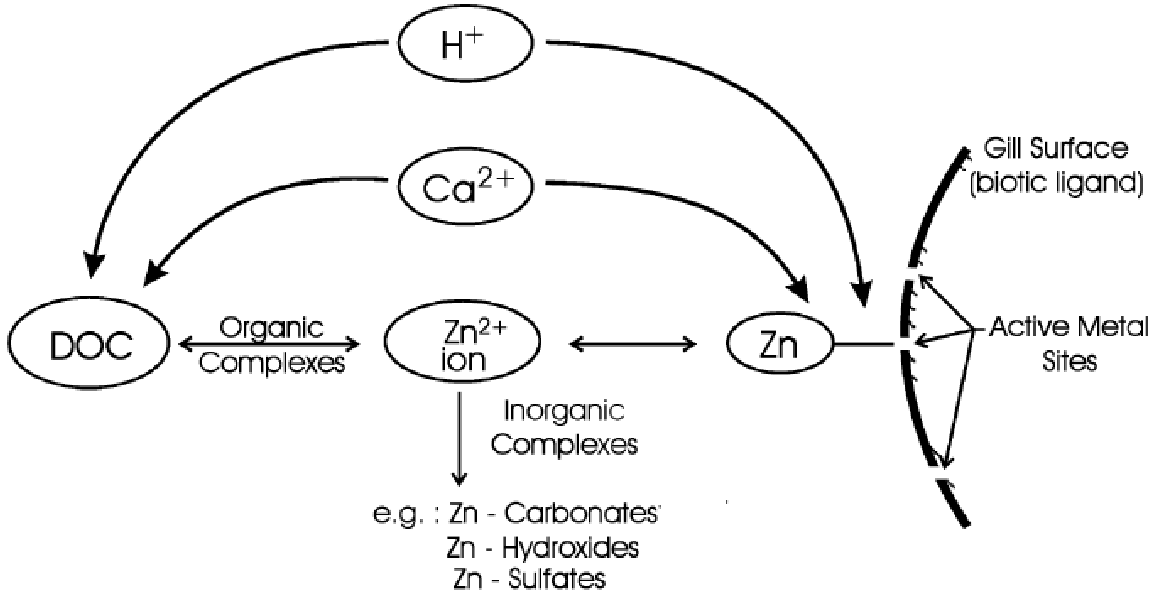
TECHNICAL BASIS OF THE ZINC BLM

Like the copper BLM recommended by the EPA for copper criteria development, the zinc BLM is a computational model that incorporates chemical reaction equations to evaluate the amount of metal that would bind to organism tissues (termed the "biotic ligand", such as a fish gill) and thus be ultimately responsible for causing toxicity. By incorporating chemical equilibria, the BLM better represents the complex chemical factors that influence zinc bioavailability, more so than the simple hardness-based approach (Di Toro et al. 2001, Heijerick et al. 2002). Unlike the hardness-based equation for zinc criteria, the BLM explicitly accounts for more of the important water quality variables that determine zinc bioavailability, and the BLM is not limited to a particular correlation between toxicity and these variables.

The mechanistic principles underlying the BLM follow general trends of zinc toxicity as related to individual water quality variables and their combinations. The basic premise of the BLM is that changes in water quality will cause a corresponding change in the concentrations of toxic forms of zinc (primarily Zn^{2+}) that can potentially bind to biological surfaces (i.e., the "biotic ligand"; Di Toro et al. 2001). Zinc bioavailability is also affected by competitive chemical binding interactions at the biotic ligand (e.g., fish gill) with calcium, in particular (Santore et al. 2002). The interactions between zinc, other ions, dissolved organic carbon (DOC), and the biotic ligand are shown in Figure 1. Each of the dissolved chemical species, with which the biotic ligand reacts, is represented by characteristic binding site densities and conditional stability constants (Playle et al. 1993). In turn, each of the chemical species can be predicted as a function of inorganic and organic equilibrium reactions. The thermodynamic constants used to simulate these equilibrium reactions are empirically derived and do not change for simulations involving different organisms.

Predictions of zinc toxicity are based on the relationships between the dissolved zinc LC50 and a critical level of zinc accumulation at the biotic ligand. This critical accumulation is called the median-lethal biotic ligand accumulation concentration, or LA50. While LA50 values can vary based on differential species sensitivity (i.e., more or less zinc-gill accumulation required to exert a similar toxic response), they are assumed to be constant within individual species regardless of water quality (Meyer et al. 1999). Overall, increases in hardness and natural organic matter tend to decrease zinc bioavailability, while changes in pH may have a variable influence on Zn bioavailability (Santore et al. 2002; Clifford and McGeer 2009).

Figure 1. Conceptual Diagram of the Biotic Ligand Model for Zinc



Source: Santore et al. (2002)

The draft BLM-based zinc criteria submitted to EPA in 2006 were ultimately developed using an approach that is analogous to EPA metals criteria derivation methods that are based on normalizing available toxicity data to a similar hardness (EPA 1985). The zinc BLM was used to normalize LC50 values to a single reference exposure condition that includes all of the BLM water quality parameters. Although not all historical studies reported concentrations of parameters needed for the BLM, the dataset was supplemented by new data from current research. Once the data were normalized to the BLM parameters for this reference exposure condition, criteria derivation procedures followed EPA guidance (EPA 1985). Accordingly, the acute criterion was estimated from a ranked distribution of BLM-normalized genus-mean acute values from which the 5th percentile of sensitivity (i.e., the final acute value) was divided by two to calculate the acute criterion. Insufficient data were available to explicitly derive a separate BLM-based chronic criterion. Thus, according to the EPA guidance, the BLM-normalized acute criterion was divided by the final acute-chronic ratio to derive a chronic criterion.

Use of the BLM represents a significant improvement upon the current hardness-based zinc criteria. The BLM has been adequately validated for a wide range of water quality conditions, and therefore provides more accurate and scientifically-defensible water quality criteria. Validation studies have shown that over a very wide range of water quality characteristics (e.g., hardness, alkalinity, and ion composition), the BLM provides criteria concentrations that are more accurate and consistently protective of even the most acutely sensitive aquatic organisms (e.g., De Schamphelaere et al. 2005).

APPLICATION OF THE BLM TO WATER QUALITY CRITERIA

It is important to note that both the hardness-based and BLM-based zinc criteria rely on "models" to calculate criteria. For hardness-based metals criteria, a simple equation, which is in essence a "model," mathematically relates the criterion concentration to a single variable, in this case hardness (hardness is an aggregate measure of calcium and magnesium cations). For the BLM-based zinc criteria, a computer model mathematically relates multiple water quality characteristics, including hardness cations, to the final criterion concentration. While the BLM itself is mathematically more complex, it is mechanistically more realistic than the hardness-based approach.

Like any policy, changes to a regulatory criterion should consider implementation needs and how they will be different from the status quo. Most states have guidance documents for implementing water quality criteria in assessments and regulatory needs, such as Ecology's Water Quality Program Permit Writer's Manual (Ecology 2010) and other guidance documents. Guidance documents like these can be a more appropriate place to provide the necessary details for implementation than the WQS language, especially given that rulemaking considerations affect only the standards (i.e., guidance documents are not rules). Accordingly, Ecology should thoroughly evaluate their related guidance and policy documents so they are effective and up-to-date with best practices and EPA guidance.

In terms of data needs for implementation, for determining zinc criteria under either the hardness- or BLM-based approach, measurements of Ca^{2+} and Mg^{2+} are needed (assuming the hardness-based criterion would employ the more accurate method for determining hardness by calculating hardness from the Ca and Mg ion concentrations per SM2340B). Therefore, the difference between data needs for the hardness-based and BLM-based criteria are the remaining eight BLM parameters: temperature, pH, alkalinity, DOC, sodium, potassium, chloride, and sulfate. Temperature and pH data must be field collected, which is a straight forward process using handheld meters or simpler means. For the remaining additional parameters, the costs for analyses by accredited laboratories are typically less than $100. Furthermore, samples for these analyses are as easily collected as the samples for hardness data needs for hardness-based criteria. Note that DOC samples must be filtered shortly after collection, which is also needed for evaluating metals criteria compliance based on a dissolved (filtered) metals sample. Therefore, the added cost and field effort for BLM data needs are minimal.

The next criteria implementation need would address the number and location of water quality samples that need to be collected to adequately characterize a particular water body for applying the criterion. General guidance is available from EPA which provides several suggested sampling strategies depending on the type of water body and the anticipated seasonal or spatial variation anticipated in BLM parameters (EPA 2007b). This potential issue of variability over time and space would be important to address for both BLM-based and the current hardness-based criteria. It is important to note that any criterion based on an instantaneous or short-term reading such as a hardness would be susceptible to certain time-variability considerations. Therefore, this situation is not unique to the BLM, as noted in the EPA's BLM-based copper criteria (EPA 2007a):

> *With regard to BLM-derived freshwater criteria, to develop a site-specific criterion for a stream reach, one is faced with determining what single criterion is appropriate even though a BLM criterion calculated for the event corresponding to the input water chemistry conditions will be time-variable. This is not a new problem unique to the BLM—hardness-dependent metals criteria are also time-variable values. Although the variability of hardness over time can be characterized, EPA has not provided guidance on how to calculate site-specific criteria considering this variability. Multiple input parameters for the BLM could complicate the calculation of site-specific criteria because of their combined effects on variability. Another problem arises from potential scarcity of data from small stream reaches with small dischargers.*

EPA has also provided general guidance as to the various regulatory options that could be used to encourage states and tribes to implement copper BLM-based criteria in their water quality standards programs (EPA 2007c). This guidance emphasizes that considerable flexibility exists in implementing BLM-based copper criteria, with suggested implementation options being full statewide implementation of the BLM-based criteria, or the incremental approach of using the BLM for certain water bodies (i.e. TMDLs) on a site-specific basis.

OTHER ISSUES-GUIDANCE DOCUMENTS

Ecology's Water Quality Program Permit Writer's Manual (Ecology 2008) and related standards language should be updated to clarify and re-institute the apparently defunct water effect ratio (WER) provisions and guidance in Washington. Footnote "dd" to table 240(3) in the standards clearly allows WER implementation to derive and set appropriately protective site- specific aquatic life criteria for a number of metals. However, the 2008 version of the manual excised the detailed WER guidance provided in the 2006 version of the manual (Ecology 2006; see pages 60-72 in Appendix 6). The recent update has not restored the WER guidance (Ecology 2010). Earlier versions of this manual have provided WER guidance also (Ecology 2001). There are at least several NPDES permittees in WA state that have implemented WERs for copper, zinc or silver. We have heard that there may have been some technical issues with how the EPA reviewed and approved footnote dd in past WQS.

In the last update of WA State WQS, EPA's 2008 approval letter, with enclosure, did not deny the WER provision in footnote dd. In fact, EPA stated that the 2006 Permit Writer's Manual WER guidance in "Chapter 5 of Appendix 6 is based on scientifically defensible methods and is appropriate in providing guidance in developing WERs and based on our evaluation would be as protective as EPA's guidance for developing WERs." Somehow, subsequent to this 2008 EPA approval, Ecology decided to excise this WER guidance. As a result, we have heard that Ecology will not entertain WER proposals.

This situation should be rectified and appropriately vetted by EPA as needed to allow WERs to continue to be implemented. The use of a WER is an existing standards provision that should be allowed, irrespective of the decision to update statewide numeric criteria such as via the EPA 2007 copper BLM. The EPA has approved many WER implementations nationwide for copper, zinc and other metals and provides comprehensive WER guidance documents (EPA 1994, 2001). The EPA's policy has allowed WERs for several decades. Other states have implemented WERs as needed in specific listings in their WQS, such as Texas, a procedure intended by EPA. Denying permittees or TMDLs the utility of an appropriately derived WER is regressive and could lead to unnecessary capital expenditures or liabilities related to metals that do not present a real water quality standards issue.

PROPOSED CHANGES TO CHAPTER 173-201A-240 WAC

In summary, the IZA and Windward Environmental encourage Ecology at a minimum to update the hardness-based zinc criteria based on 23+ years of additional toxicity data. We also recommend consideration of the zinc BLM as an option for deriving site-specific zinc criteria in 173-201A-240 WAC. Use of the BLM to derive zinc criteria is based on the most current science and has been recommended by the EPA for copper (EPA 2007a) and adopted in several states. However, we believe that statewide implementation of BLM-based zinc criteria should be the ultimate goal of Ecology. Using the BLM would allow Ecology to more effectively assess and manage waters where the hardness-based criteria could be over- or under-protective of aquatic life.

Thank you for the opportunity to provide these comments for consideration by Ecology during the WA State triennial review process. Please let us know if you have any questions or if you would like to discuss this further.

Sincerely,

Eric Van Genderen, Ph.D.
Assistant Manager, Environment
International Zinc Association

Scott Tobiason
Sr. Environmental Engineer
Windward Environmental

David DeForest
Sr. Environmental Toxicologist
Windward Environmental

REFERENCES

Clifford M, McGeer JC. 2009. Development of a biotic ligand model for the acute toxicity of zinc to *Daphnia pulex* in soft waters. Aquat Toxicol 91:26-32.

De Schamphelaere KAC, Lofts S, Janssen CR. 2005. Bioavailability models for predicting acute and chronic toxicity of zinc to algae, daphnids, and fish in natural surface waters. Environ Toxicol Chem 24:1190-1197.

Di Toro DM, Allen HE, Bergman HL, Meyer JS, Paquin PR, Santore RC. 2001. Biotic ligand model of the acute toxicity of metals. 1. Technical basis. Environ Toxicol Chem 20:2382-2396.

Ecology 2001. Water Quality Program Permit Writer's Manual. Publication No. 92-109. Washington State Department of Ecology. Revised January 2001.

Ecology 2006. Water Quality Program Permit Writer's Manual. Publication No. 92-109. Washington State Department of Ecology. Revised July 2006.

Ecology 2008, Water Quality Program Permit Writer's Manual. Publication No. 92-109. Washington State Department of Ecology. Revised July 2008.

Ecology 2010, Water Quality Program Permit Writer's Manual. Publication No. 92-109. Washington State Department of Ecology. Revised November 2010

EPA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. U.S. Environmental Protection Agency, Washington, D.C. PB85-227049.

EPA. 1987. Ambient aquatic life water quality criteria for zinc. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-87-003.

EPA. 1994. Interim guidance on determination and use of water-effect ratios for metals. U.S. Environmental Protection Agency, Washington, D.C. EPA-823-B-94-001.

EPA. 2001. Streamlined water-effect ratio procedure for discharges of copper. U.S. Environmental Protection Agency, Washington, D.C. EPA-822-R001-005.

EPA. 2007a. Aquatic life ambient freshwater quality criteria - Copper. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. EPA-822-R-07-001.

EPA. 2007b. Training materials on copper BLM: Data requirements. U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2007c. Training materials on copper BLM: Implementation. U.S. Environmental Protection Agency, Washington, D.C.

Heijerick DG, De Schamphelaere KAC, Janssen CR. 2002. Predicting acute zinc toxicity for *Daphnia magna* as a function of key water chemistry characteristics: Development and validation of a biotic ligand model. Environ Toxicol Chem 21:1309-1315.

Meyer JS, Santore RC, Bobbitt JP, Debrey LD, Boese CJ, Paquin PR, Allen HE, Bergman HL, Di Toro DM. 1999. Binding of nickel and copper to fish gills predicts toxicity when water hardness varies, but free ion activity does not. Environ Sci Technol 33:913-916.

Playle RC, Dixon DG, Burnison K. 1993. Copper and cadmium binding to fish gills: Estimates of metal-gill stability constants and modelling of metal accumulation. Can J Fish Aquat Sci 50:2678-2687.

Santore RC, Mathew R, Paquin PR, Di Toro DM. 2002. Application of the biotic ligand model to predicting zinc toxicity to rainbow trout, fathead minnow, and *Daphnia magna*. Comp Biochem Physiol Part C 133:271-285.