May 8, 2013

Ms. Clem
Arkansas Department of Environmental Quality
5301 Northshore Drive
North Little Rock, AR 72118

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

Dear Ms. Clem:

This letter provides comments for the current triennial review of water quality standards (WQS) in Arkansas. The comments provided here are primarily related to the numeric zinc criteria for protection of freshwater aquatic life and, specifically, use of a tool called the biotic ligand model (BLM) that allows for derivation of freshwater criteria based on site-specific water chemistry parameters. These comments are being provided jointly by the International Zinc Association (IZA, Durham, NC) and Windward Environmental (Seattle, WA).

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 Arkansas, with subsequent sections briefly providing additional background used as the basis of our recommendation (we included technical details in the appendix to this letter).

Summary of Recommendations for Updated Freshwater Aquatic Life Zinc Criteria in Arkansas

The hardness-based zinc criteria for protection of freshwater aquatic life in Arkansas were last updated in 1987. Accordingly, Arkansas's current zinc criteria are now essentially 26 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. In addition to hardness, it is now well understood that several other 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). Recognizing the importance of this new tool, in 2007 the EPA provided nationally recommended BLM-based copper criteria for freshwater aquatic life (EPA 2007). Draft BLM-based zinc criteria were submitted to the EPA in 2006 by the International Lead Zinc Research Organization (ILZRO), but these criteria have not been released by the EPA for public comment. In addition, an updated evaluation of BLM-based criteria for zinc, including development of BLM-based acute and chronic criteria following the EPA guidelines for criteria development (EPA 1985), has recently been published in the peer-reviewed journal Environmental Toxicology and Chemistry (DeForest and Van Genderen 2012). Notably, chronic BLM-based zinc criteria derived using the expanded ecotoxicity database demonstrated that several of the most sensitive genera were not protected using the current hardness-based criteria.

Given the opportunity to provide more accurate water quality protection, we strongly recommend that the ADEQ adopt the BLM as the basis for freshwater zinc criteria in Arkansas. However, 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, as an interim step, we recommend that the ADEQ consider updating Reg. 2.308 to specifically allow for use of the BLM to derive site-specific zinc criteria.

INTRODUCTION

The current Arkansas WQS provide freshwater aquatic life criteria based on nationally recommended EPA criteria that have not been updated for many years, in some cases for more than two decades. These criteria include the priority pollutant metals arsenic, chromium, copper, lead, nickel, selenium, silver, and zinc. It is the EPA's policy to update criteria as new scientific information becomes available, especially that which could significantly affect environmental management decisions. However, EPA criteria updates have not kept pace with the state of the science. As long as they follow accepted EPA guidance, states are free to provide their own criteria updates and not wait for EPA to provide criteria documents. Given the current state of the science as explained below, the ADEQ has an opportunity to use the current triennial review to bring their state WQS up-to-date with the best science and provide more appropriate policy and more accurate tools for regulating and managing water quality in the state.

LIMITATIONS WITH ARKANSAS'S CURRENT ZINC CRITERIA

The Arkansas WQS currently include acute and chronic zinc criteria that are calculated as a function of water hardness. These criteria are based on the 1987 EPA criteria updates. 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 and, hence, toxicity. For example, in addition to hardness, zinc toxicity is also strongly related to other important factors such as pH and dissolved organic carbon (DOC), which are accounted for in the BLM (see Appendix A for a more detailed discussion of the BLM and derivation of BLM-based criteria).

The BLM-based criteria, therefore, can provide more accurate levels of freshwater aquatic life protection across a broad range of water quality conditions than the outdated hardness-based criteria. In fact, the recent evaluation of DeForest and Van Genderen (2012) determined that chronic hardness-based zinc criteria do not meet the desired level of protection in certain water bodies (several most sensitive genera not protected), while the chronic BLM-based criteria do.

PRECEDENT FOR BLM-BASED CRITERIA

For copper, the EPA recently released aquatic life criteria based on the BLM (EPA 2007). The BLM represents a significant step forward for developing criteria based on the best available science for not only copper, but several other metals, including zinc. 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. In addition, as previously noted, an updated evaluation of BLM-based criteria for zinc, including development of BLM-based acute and chronic criteria following the EPA guidelines for criteria development (EPA 1985), has been recently published in the peer-reviewed journal *Environmental Toxicology and Chemistry* (DeForest and Van Genderen 2012).

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 the EPA, as required. Many states have decided not to wait for EPA criteria updates and have already developed and adopted their own updated criteria for metals such as zinc, cadmium and aluminum (e.g., Colorado and New Mexico in 2010-2011).

IMPLEMENTATION OF BLM-BASED CRITERIA

Some commonly expressed concerns with implementing BLM-based criteria are that there are too many water quality parameters to measure, that the parameter measurements are time varying, that the model is too complex, or that state-wide implementation is premature. However, some of these concerns are misperceptions or are germane to any water quality criterion, while there are existing procedures for simplifying implementation.

- First, in terms of the number of water quality parameters required, the BLM generates instantaneous acute and chronic criteria using 10 water quality input parameters that typically cost less than $200 per sample (temperature, pH, and concentrations of DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity). However, several of these measurements are routinely measured (e.g., temperature and pH, and calcium and magnesium in support of hardness-based criteria). Accordingly, the added cost and field effort for these remaining BLM data needs are minimal. In addition, not all of the parameters are equally important in the BLM and may be estimated from concentrations of other parameters, such as using calcium concentrations to estimate concentrations of other ions (Peters et al. 2011).

- Second, the concern with time varying water chemistry is not an issue unique to the BLM as this also applies to hardness when implementing hardness-based metals criteria. There are existing approaches, such as the fixed monitoring benchmark (FMB) approach (current BLM-based implementation approach being reviewed by the EPA), which is a probability-based method that incorporates time variability in BLM-predicted instantaneous water quality criteria and in-stream metal concentrations.

- Third, in terms of the perception that the BLM is too complex, the BLM software is publicly available, sanctioned by EPA, and requires only brief training to generate rapid and useable output (the user interface looks like an Excel® spreadsheet). The model has built in features to guide the user and prevent errors, such as using inconsistent units or using input parameters beyond calibration ranges.

- Fourth, state-wide implementation can be incremental or deferred while site-specific BLM criteria are implemented. New Mexico is an example of one state that has elected this approach for the EPA's 2007 copper BLM-based criteria (NMED 2011).

IMPORTANCE OF UPDATED BLM-BASED ZINC CRITERIA

In Arkansas, numerous permittees covered by National Pollution Discharge Elimination System (NPDES) permits would be subject to compliance based on the EPA's outdated zinc criteria. These permits are the principle regulatory vehicle for Clean Water Act implementation to protect and restore water quality. The NPDES

permits rely on state WQS and criteria for setting appropriate effluent limits or performance benchmarks. 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 regulatory 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.

PROPOSED CHANGES TO ADEQ'S NUMERIC CRITERIA FOR ZINC

In summary, the IZA and Windward Environmental encourage the ADEQ to adopt BLM-based zinc criteria as the default basis for development of state-wide zinc criteria or, at a minimum, as an explicit option for deriving site-specific zinc criteria. 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 2007) and adopted in several states. However, we believe that statewide implementation of BLM-based zinc criteria should be the ultimate goal of the ADEQ. Using the BLM would allow the ADEQ to more effectively assess and manage waters where the hardness-based criteria could be over- or under-protective of aquatic life and correspondingly result in over- or under-regulating permittees. The evaluation of DeForest and Van Genderen (2012) indicated that for most waters the existing hardness-based acute zinc criteria are over-protective and that the chronic zinc criteria are under-protective.

The IZA and Windward Environmental believe that adoption of BLM-based water quality criteria for metals represents a fundamental advancement to achieve appropriate environmental protection and regulation. To this end, comments being submitted to the ADEQ on behalf of the Copper Development Association (CDA) and International Copper Association (ICA) are also recommending that the ADEQ consider updating the freshwater aquatic life criteria for copper using the BLM.

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

Sincerely,

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APPENDIX A

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
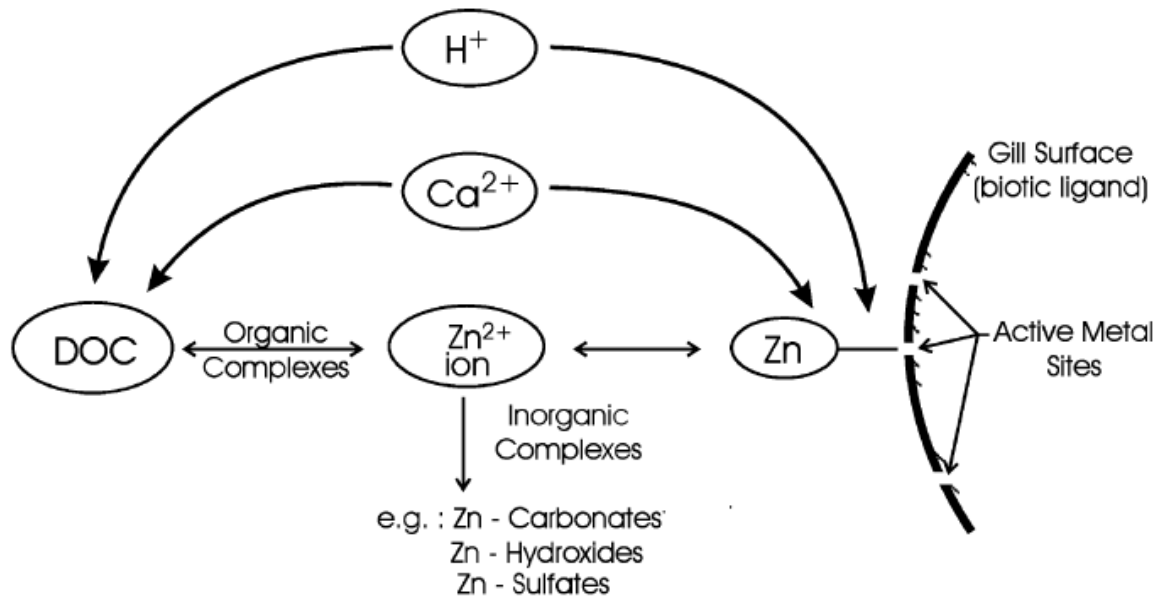
Source: Santore et al. (2002)

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.

As discussed above, updated BLM-based zinc criteria have recently been updated and developed following EPA guidelines (DeForest and Van Genderen 2012). This included an update of acute and chronic zinc toxicity data, parameterization of a single BLM that accurately predicts acute and chronic zinc toxicity as a function of varying water chemistry (i.e., varying DOC, hardness, pH, etc.), and development of BLM-based acute and chronic criteria. The chronic BLM-based zinc criteria developed in DeForest and Van Genderen (2012) are based on empirical chronic toxicity data and preclude the use of an ACR. This evaluation found that the existing hardness-based chronic criteria for zinc may be under-protective in several water types.

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 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, the ADEQ 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.

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