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December 17, 2010

Becca Conklin
Water Quality Standards Coordinator
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

Re: Washington State Triennial Review: Recommendation to Incorporate the Biotic Ligand Model for Copper into Aquatic Life Criteria

Dear Ms. Conklin:

Attached to this letter, please find our comments as requested by the Washington State Department of Ecology (Ecology) for the current triennial review (TR) of surface water quality standards in the State of Washington.

We appreciate the opportunity to provide you these comments. Please feel free to contact me if you have any questions. We look forward to discussing our recommendations with you.

Sincerely,

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WASHINGTON STATE TRIENNIAL REVIEW:

RECOMMENDATION TO INCORPORATE THE BIOTIC LIGAND MODEL FOR COPPER INTO AQUATIC LIFE CRITERIA

Submitted to:

Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

Submitted by:

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New York, NY

December 2010

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Executive Summary

This report provides comments as requested by the Washington State Department of Ecology (Ecology) for the current triennial review of surface water quality standards in the State of Washington. These comments are presented by GEI Consultants Inc. (GEI) and Windward Environmental consultants on behalf of the Copper Development Association (CDA) and International Copper Association (ICA). The CDA is the market development, engineering, and information services arm of the copper industry. The CDA and ICA played a significant role in sponsoring scientific research used in development of the freshwater Biotic Ligand Model (BLM) for copper. In early 2007, the Environmental Protection Agency (EPA) released revised national aquatic life ambient water quality criteria for copper in freshwater, which are based on the BLM (EPA 2007a). Since EPA published the BLM-based criteria, further evaluations have shown the BLM is also appropriately protective against olfactory impairment in juvenile salmon. Given the opportunity and main goal of triennial reviews, the CDA and ICA are interested in encouraging states and tribes to incorporate these latest recommended EPA national criteria for copper into their water quality standards programs.

It is our understanding that the State of Washington has initiated the triennial review process and that you are currently accepting written comments, which are due by December 17, 2010. Thus, the purpose of this report is to urge Ecology to consider updating its aquatic life criteria for copper by allowing the use of the BLM, as recommended by the EPA. This proposal outlines our rationale, the technical basis for the BLM, recommendations with respect to application of the BLM criteria, and proposed changes to Washington's freshwater aquatic life standards for copper.

1.0 Introduction

The current Washington State water quality standards include aquatic life water quality 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 Washington State last updated their aquatic life criteria, the EPA, other states, and various organizations have updated criteria for many of these metals and other non-priority pollutant metals, such as aluminum. These updates encompass more current scientific information and have used the EPA procedures for updating criteria, 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 Washington State an opportunity to bring their state water quality standards up to-date and provide more appropriate policy and more accurate tools for regulating and managing water quality.

The Washington State water quality standards contain the current aquatic life criteria for copper in Section 173-201A-240 of the Washington Administrative Code (WAC). The current Washington State acute and chronic copper criteria are calculated as a function of water hardness and are based on the 1984 EPA criteria for copper (EPA 1985a). However, the BLM is the most current basis for copper criteria as recommended by the EPA to establish freshwater copper criteria (EPA 2007a). The BLM represents a significant step forward in the best available science of copper toxicity and derivation of criteria that are appropriately protective of freshwater organisms, including olfactory effects in juvenile salmon (DeForest et al., In Press). Seven states have recently adopted the EPA's BLM-based copper criteria in their water quality standards, but to-date, most have adopted the BLM as a tool for deriving site-specific standards rather than as the default state-wide standard.

The BLM generates instantaneous criteria (acute and chronic) 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.

Washington State's current aquatic life copper 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 1985b, 1994, 2001, 2007a). Copper 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 DOC, alkalinity, pH, and temperature. The key strength of the BLM is that it accounts for multiple factors—in addition to hardness—that influence the amount of copper 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 Washington State, there are well over 1000 National Pollution Discharge Elimination System (NPDES) permittees subject to compliance based on the outdated 1985 EPA copper criteria. NPDES permits are the principle regulatory vehicle for Clean Water Act implementation to protect and restore water quality. NPDES permits rely on state water quality standards 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). Therefore, Washington State should consider adopting the most current EPA criteria for protection of freshwater aquatic life, which for copper are the 2007 BLM-based criteria.

2.0 Technical Basis of the Copper BLM

The copper 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 copper bioavailability, more so than the simple hardness-based approach (Di Toro et al. 2001, De Schamphelaere and Janssen 2002). Unlike the hardness-based equation for copper criteria, the BLM explicitly accounts for more of the important water quality variables that determine 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 copper 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 copper (primarily $Cu^{2+}$and $CuOH^{-}$ to a lesser degree) that can potentially bind to biological surfaces (i.e., the "biotic ligand"; Di Toro et al. 2001, EPA 2007a). For example, increases in pH, alkalinity, or natural organic matter would all tend to decrease copper bioavailability, and hence decrease toxicity, which would result in increased median-lethal concentrations (LC_{50}) for copper (Erickson et al. 1996).

Copper bioavailability is also affected by competitive chemical binding interactions at the biotic ligand (e.g., fish gill) with calcium and sodium, which are important for metabolic and ion regulatory activities in the gill, thereby reducing toxicity (i.e., increasing copper LC_{50} values; Erickson et al. 1996). The interactions between the biotic ligand (e.g., the fish gill) 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 copper toxicity are based on the relationships between the dissolved copper LC_{50} and a critical level of copper accumulation at the biotic ligand. This critical accumulation is called the median-lethal biotic ligand accumulation concentration, or LA_{50}. While LA_{50} values can vary based on differential species sensitivity (i.e., more or less copper-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). For example, although binding constants for copper and other cations were derived using fathead minnows, the values apply to invertebrates and other fish (Santore et al. 2001).

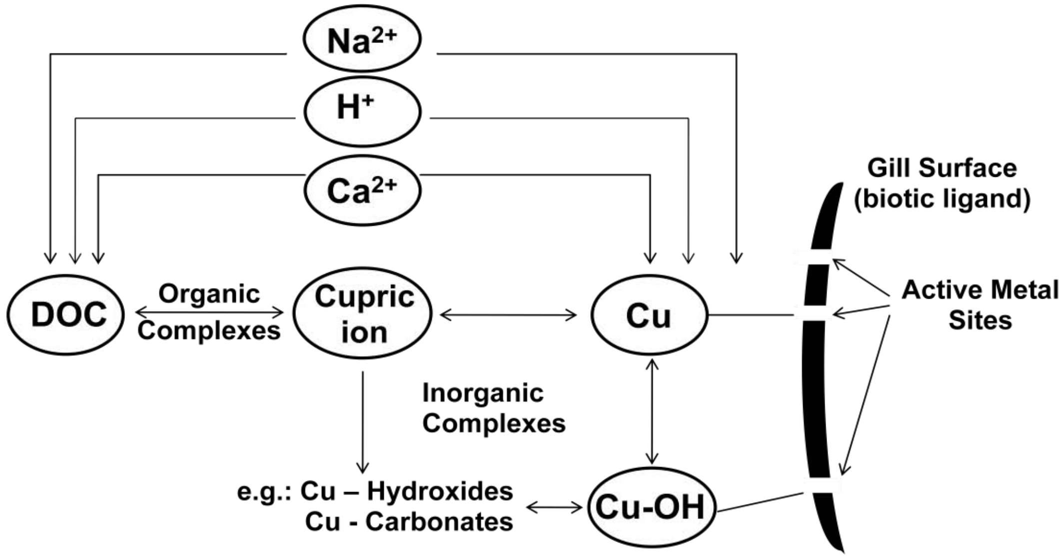

Figure 1: Conceptual diagram of the Biotic Ligand Model for copper. Source: Adapted from EPA 2007a.

The BLM-based copper criteria 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 1985a). In the 2007 recommended water quality criteria (EPA 2007a), the BLM was used to normalize LC_{50} values to a single reference exposure condition that includes all of the water quality parameters included in the BLM. 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 1985b). 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 EPA guidance, the BLM-normalized acute criterion was divided by the Final Acute-Chronic Ratio to derive a chronic criterion (EPA 2007a).

Use of the BLM represents a significant improvement upon the current hardness-based copper 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 (Gensemer et al. 2002, Van Genderen et al. 2007), including protection against olfactory impairment in fish, as discussed further below.

3.0 Protection Against Olfactory Impairment in Fish

Recent studies by the National Oceanic and Atmospheric Administration (NOAA) and others have demonstrated that short-term laboratory exposures to low copper concentrations (e.g., <20 µg/L) in synthetic laboratory waters can cause olfactory impairment in fish, which may limit the ability of fish to detect and avoid predators (e.g., Hansen et al. 1999, McIntyre et al. 2008, Green et al. 2010). The ability of low copper concentrations to result in olfactory impairment is of particular concern in the Pacific Northwest (PNW) region of the United States due to the presence of Pacific salmon (*Oncorhynchus* spp.), many populations of which are listed as threatened or endangered species under the Endangered Species Act. Some recent papers, such as McIntyre et al. (2008), suggest that existing copper criteria may not be protective against olfactory impairment in juvenile salmon. However, as discussed below, this position does not appear to be supported, particularly when considering BLM-based copper criteria.

The EPA's ambient water quality criteria for protection of aquatic life are derived primarily using endpoints of survival for acute criteria and survival, growth, and reproduction for chronic criteria. However, other sub-lethal endpoints can be considered if they are ecologically important or can be reliably linked to these traditional acute or chronic criteria endpoints. Therefore, the copper concentrations shown to result in olfactory impairment in juvenile salmon and other fish should be compared to both the acute and chronic hardness- or BLM-based copper criteria.

Based on these comparisons, new studies indicate that the BLM-based copper criteria (EPA 2007a) would be protective of olfactory impairment, while hardness-based copper criteria are usually, but not always, protective across a broad range of water quality conditions representative of the PNW (Meyer and Adams 2010, DeForest et al., In Press). The protectiveness of the BLM-based copper criteria, and to a lesser degree the hardness-based criteria, is largely because of the greater sensitivity of some invertebrates to copper relative to fish. In other words, although olfactory impairment resulting from short-term copper exposures can be a more sensitive endpoint in fish than lethality, the greater sensitivity of invertebrates ultimately results in copper criteria that are protective of olfactory impairment in fish.

Meyer and Adams (2010) compiled copper studies that evaluated olfactory impairment, based either on electro-encephalogram (EEG) or electro-olfactogram (EOG) responses to a natural odorant, or avoidance behavior, and where sufficient water chemistry data were available to derive BLM-based copper criteria. IC_{20} values (20% impairment concentrations) were calculated for olfactory impairment and avoidance in 16 different tests encompassing varying water chemistry and test species. Meyer and Adams (2010) concluded that chronic

BLM-based copper criteria were protective of the olfactory response and avoidance IC_{20} values in all 16 waters and acute BLM-based criteria were protective in all but two waters. Meyer and Adams (2010) also parameterized an olfactory-based BLM that can be used to estimate olfactory-based copper IC_{20} values for waters with varying chemistry. In turn, DeForest et al. (In Press) used the olfactory-based BLM to estimate copper IC_{20} values for olfactory impairment based on water chemistry data sets for 133 western United States streams. In this work, the olfactory BLM-based copper criteria were always less than the predicted IC_{20} values for olfactory impairment, while the hardness-based criteria exceeded the IC20 values in some cases (Figure 2). These results show that the BLM based criteria are more consistently protective against olfactory impairment than the hardness-based criteria that are currently used in Washington. Furthermore, these studies show that the BLM can be adapted to endpoints other than the conventional acute and chronic criteria basis, which in this case is the olfactory response.

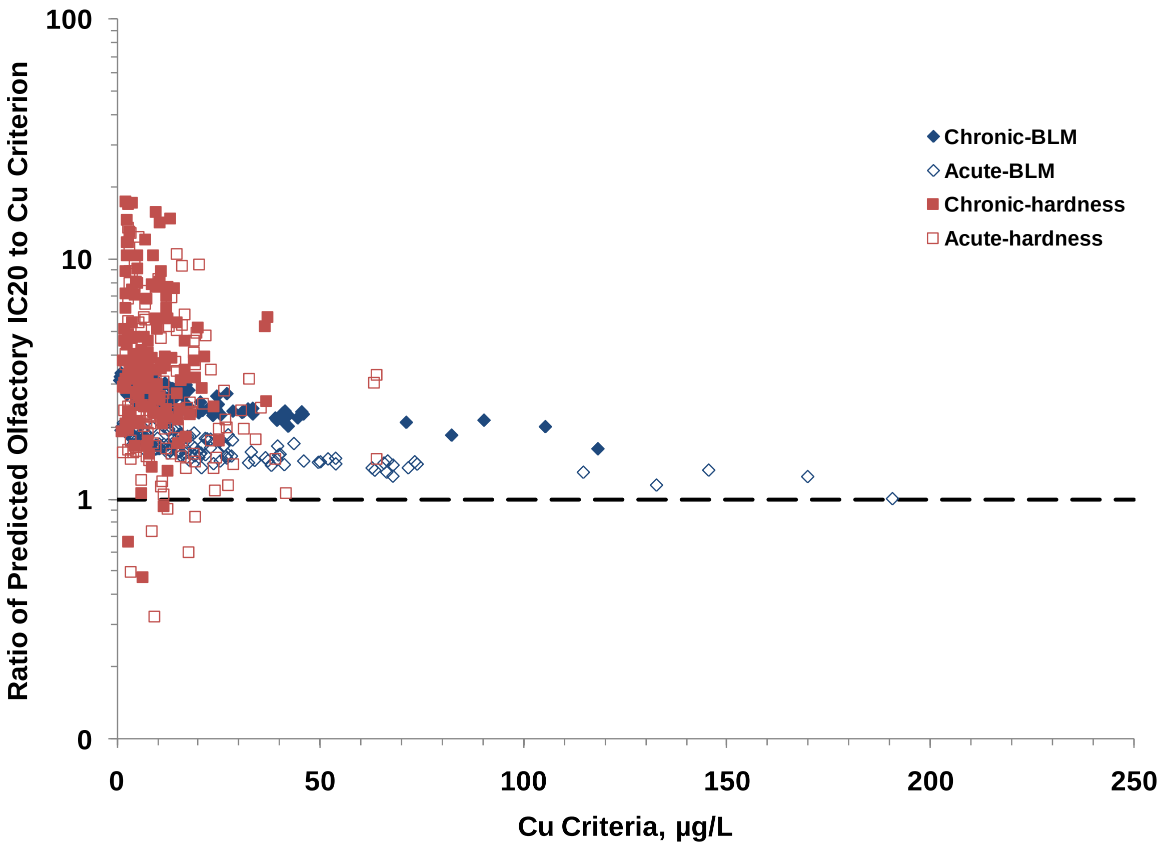

Figure 2: Ratios of predicted olfactory IC_{20} values to BLM-and hardness-based Cu criteria as a function of Cu concentrations. Source: DeForest et al., In Press.

Therefore, the BLM-based aquatic life criteria for copper are the most accurate regulatory tools for ensuring adequate levels of protection for fish against olfactory effects. In contrast, it appears that the current hardness-based aquatic life criteria would not consistently provide adequate protection against potential olfactory effects. This situation means that continued use of hardness-based copper criteria in Washington State surface waters could present reduced levels of protection for sensitive salmonid populations. The BLM-based copper criteria, therefore, present a means to more adequately regulate and manage water quality because they encompass current science and endpoints of regional significance.

4.0 Application of the BLM to Water Quality Criteria

It is important to note that both the hardness-based and BLM-based copper 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 copper criteria, a mechanistic computer model mathematically relates multiple water quality characteristics, including hardness cations, to the final criterion concentration. Hence, the National Criteria Statement in the 2007 criteria document (EPA 2007a) is as follows:

The available toxicity data, when evaluated using the procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" indicate that freshwater aquatic life should be protected if the 24-hour average and four-day average concentrations do not respectively exceed the acute and chronic criteria concentrations calculated by the Biotic Ligand Model.

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, 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 water quality standards language, especially given rulemaking considerations affect only the standards. 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.

For determining copper criteria under either 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, Na^{+}, K^{+}, Cl^{-}, and SO_4^{-}. 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-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 the BLM and the current hardness-based criterion. It is important to note that any criterion based on an instantaneous or short term measurement of a water quality variable such as hardness would be susceptible to certain time-variability considerations. Therefore, this situation is not unique to the BLM (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 BLM-based copper 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 state-wide 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. These two options outlined in EPA's general implementation guidance (EPA 2007c) are briefly summarized below:

1. Full statewide implementation

Under this approach, a state would implement the BLM-based criteria as a full replacement of the hardness-based criteria. In Washington State, the hardness-based criteria equations for copper referenced in footnotes "o" and "p" to table 240(3) in 173-201A-240 would be deleted and replaced with text citing the EPA 2007 criteria document. This approach would allow a state to use the BLM as a statewide standard. The new numeric criteria derived using the BLM would most likely begin to apply as new permits and TMDLs are developed or existing permits are renewed. This implementation approach would depend on the availability of sufficient water quality data for the 10 BLM input parameters in the waterbodies for which the new standards would apply. To-date, no state has fully replaced their hardness-based copper criteria with BLM-based criteria. Only one state (South Carolina) has adopted the BLM as an alternative to the hardness-based criteria for derivation of water quality criteria, but still stopped short of full statewide implementation.

2. Incremental implementation

A more incremental and practical approach would enable states and tribes to move as quickly as possible to adopt the BLM methods into water quality standards by allowing use of BLM-based copper criteria on a site-specific basis. Under this approach, the hardness-based criteria would continue to be the "default" basis of copper standards, except in waters where site-specific criteria are eventually derived using the BLM. EPA suggests that some of the higher priority sites for development of BLM-based criteria might be those waters in which hardness-based standards are likely to be significantly over-protective (e.g., waters with high concentrations of dissolved organic carbon) or significantly under-protective (e.g., waters with low pH or alkalinity). Thus, this approach would allow for the most rapid and efficient implementation of BLM-based criteria by focusing on water bodies in which they would have the most impact, and providing additional time and resources to collect the necessary data for full statewide implementation. Recently, six states have adopted the BLM using this approach as a site-specific criteria derivation tool (Maryland, New Hampshire, New Jersey, New Mexico, Pennsylvania, and Texas).

5.0 Proposed Changes to Chapter 173-201A-240 WAC

GEI, CDA, ICA, and Windward Environmental encourage Ecology to consider using the BLM as an alternative to the hardness-based approach for deriving copper water quality criteria in 173-201A-240 WAC. Use of the BLM to derive copper water quality criteria is based on the most current science and is recommended by the EPA (EPA 2007a). The costs for additional data needs and sampling effort are minimal compared with current approaches needed for hardness-based criteria. The most scientifically rigorous approach would be full statewide implementation of BLM-based criteria for copper. This approach would allow Washington State to use the latest available science to derive new or revised water quality standards that are more consistently protective against the effects of copper on aquatic life, including olfactory impairment in juvenile salmon, in all surface waters in Washington State.

Due to the BLM's increased precision and efficiency compared to the hardness-based criteria, cost effectiveness, availability to the public and technical simplicity, we recommend use of the BLM to calculate copper criteria in Washington State. We also recognize that it may be more practical to implement BLM-based criteria on a more incremental or site-specific basis until sufficient water quality data are available for derivation of state-wide criteria. This would also allow Ecology to apply the BLM to waters for which the hardness-based criteria are most likely to be over- or under-protective of aquatic life.

We appreciate the opportunity to provide you these comments. Please let us know if you have any questions. We look forward to discussing this with you further.

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