International Zinc Association

Thank You Ecology,

The International Zinc Association (IZA) has uploaded a comment letter.

Thanks,
Adam Ryan

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May 7, 2024

Marla Koberstein
Department of Ecology, Water Quality Program
PO Box 47600
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Subject: Comments on Proposed updates to Aquatic Life Toxics Criteria, WAC 173-201A-240: Technical Support Document

Dear Department of Ecology:

Thank you for the opportunity to provide input to the Department of Ecology (hereinafter, Ecology) on the "Proposed updates to Aquatic Life Toxics Criteria, WAC 173-201A-240: Technical Support Document", pertaining to "Chapter 173-201A WAC (Aquatic Life Toxics Criteria)". The International Zinc Association (IZA) is a non-profit industry association dedicated to supporting the global market for zinc and the role of zinc in sustainable development. 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.

This submittal provides high-level comments with reference to detailed data analyses pertaining to the technical basis and application of the proposed updates for Zinc (Zn) and Copper (Cu) aquatic life toxics criteria (hereinafter, criteria). Specifically, our comments highlight the need to properly account for metal bioavailability when deriving appropriately protective criteria, and to thoroughly examine the implications associated with applying the criteria models (e.g., hardness equations, multiple linear regression models [MLRs], or biotic ligand models [BLMs]) to surface waters in Washington and the whole of the United States. Additionally, we provide comments on the choice of models used to derive the Washington state criteria.

Our familiarity with this topic stems from the technical assistance that we have provided to the U.S. EPA (via the CRADA) and other states as they move towards development of bioavailability-based site-specific objectives for Zn and other metals, such as Cu. To help understand the technical challenges with applying MLR model- or BLM-based criteria, we have compiled a large nationwide database containing the necessary data to apply MLR models and BLMs. This database, assembled from publicly available data from the Water Quality Portal (WQP), also includes data for metal concentrations so that we can examine model behavior under widely varying surface water conditions, while also examining relative protectiveness of the different bioavailability models. Therefore, the breadth of our analysis and associated comments applies to Ecology's proposed criteria as well as to bioavailability model application nationwide.

Approach to Developing Washington State Copper Criteria

Firstly, we commend Ecology for considering a bioavailability-based approach for developing Cu criteria for the state of Washington. The work of Kevin Brix, David DeForest, Lucinda Tear, and others to develop MLR models has provided MLR models for several metals, including both Cu and Zn that follow sound scientific principles and the US EPA (1985) guidelines for deriving criteria. Further, the current nationally recommended Cu BLM-based criteria, and the Phase 1 CRADA report indicate that bioavailability considerations are important for Cu and several other metals. Available MLR models are certainly an improvement over the existing hardness equations, and they have been shown to be predictive of ecotoxicological data under finite sets of exposure conditions. However, MLR models – specifically those parameterized as separate acute and chronic models for criteria – have not been widely applied to natural surface waters. Whereas the Cu BLM (USEPA 2007) has been adopted by several states as statewide criteria (e.g., Idaho and Oregon) or as site-specific criteria (e.g., Colorado, Iowa, and several others).

As MLR models continue to be applied to US surface waters, their behavior in a wide range of natural surface waters (with widely varying combinations of toxicity modifying factors [TMFs]) will be thoroughly examined. Ecology has already recognized the issue associated with inversion of MLR model-based acute and chronic Cu criteria (i.e., where chronic criteria are higher than acute criteria) under certain circumstances and has proposed a simple remedy for that situation by applying a reverse acute-to-chronic ratio (ACR) on the chronic MLR model results. While this approach is simple, and it may be appropriate, what it emphasizes is that there appears to be a limit to the linearity assumption associated with MLR models (at least for some metals under some situations).

Using the nationwide database that we have assembled, we evaluated the frequency of occurrence of the inversion in acute and chronic MLR-based Cu criteria, and identified locations at which this situation occurs at least once (Figure 1). Prior to performing this evaluation, we constrained the dataset to surface water samples with pH between 5 and 9, hardness between 1 and 600 mg/L as $CaCO_3$, and dissolved organic carbon (DOC) concentrations between 0 and 50 mg/L. Of the 8,650 locations in the evaluation dataset, 4,261 locations (49%) had at least one sample that exhibited an inversion in the MLR-based acute and chronic criteria. Therefore, this is not a rare phenomenon, and indicates that almost half of the locations in the US with data sufficient to support MLR model calculations require the application of the reverse ACR to derive acute Cu criteria as proposed by Ecology. From Figure 1, it can be seen that this phenomenon occurs widely in Washington state. On a sample-specific basis (considering n = 107,282 samples), the inversion of acute and chronic criteria occurs nationwide in 40% of samples, and there is a clear effect of water hardness (Figure 2) and pH (not shown). This indicates that for 40% (or ~**43,000**) samples, the reverse ACR is needed to determine the acute Cu criteria. Importantly, this also indicates that for 40% of US samples, the approach that Ecology is proposing would result in acute criteria that do not correspond to the acute MLR-based bioavailability relationships described by the acute Cu criteria equation. In other words, the bioavailability relationships developed from ecotoxicological data no longer apply to 40% of the criteria estimates for US surface waters. This issue is difficult to ignore, and if other states follow Ecology's lead, the purported best MLR-based bioavailability models may fall short of properly incorporating bioavailability in their criteria determinations.

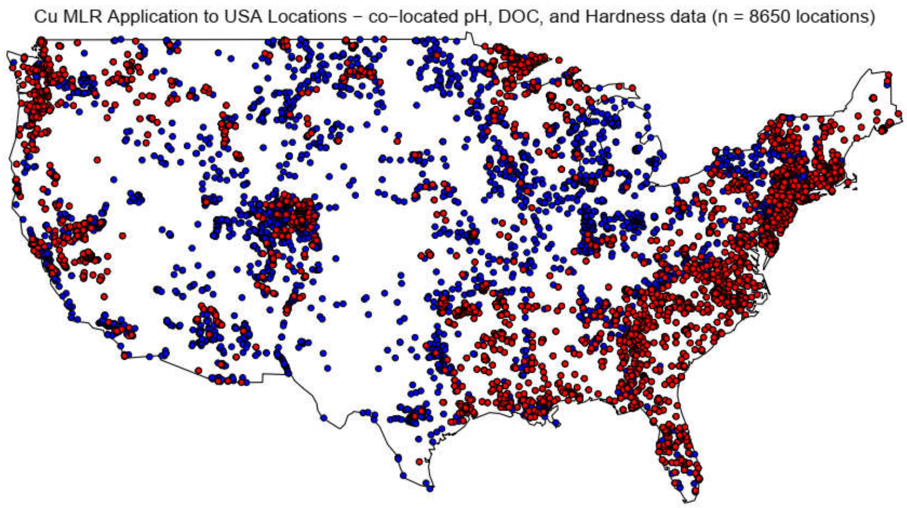

Figure 1. Monitoring locations with data to support MLR model calculations. Red symbols: locations with acute and chronic Cu criteria inversions. Blue symbols: no inversions.

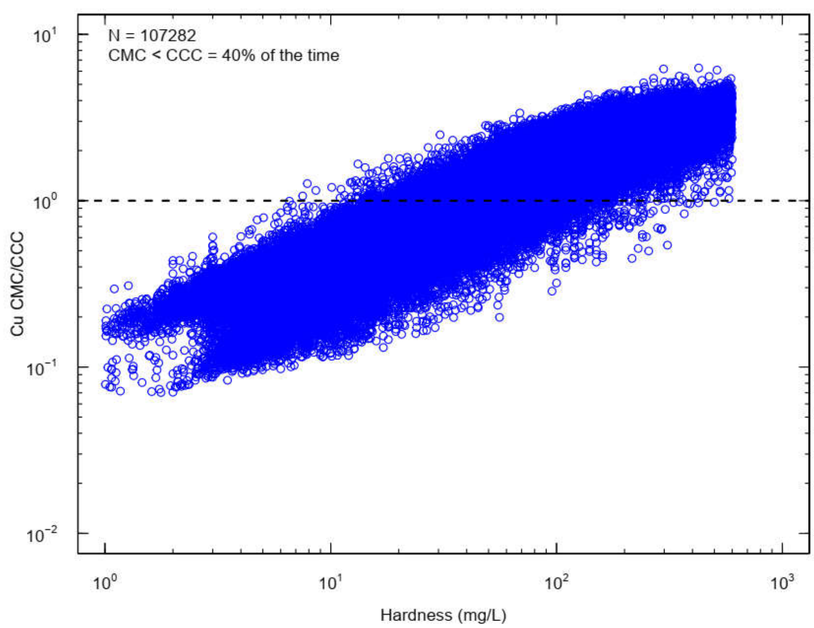

Figure 2. Ratio of acute and chronic MLR-based Cu criteria as a function of water hardness.

Making further use of our assembled dataset, we can further constrain the dataset to samples that can support Cu BLM (U.S. EPA 2007) calculations for the purpose of examining relative protectiveness of Ecology's proposed Cu MLR-based criteria vs. the nationally recommended Cu BLM-based criteria. This decreases the size of the dataset by ~10%. We also made a simplifying assumption regarding the BLM input for dissolved inorganic carbon (DIC) by assuming that it could be calculated from pH and atmospheric pCO_2 (i.e., where $pCO_2 = 10^{-3.42}$ atm). Note that alkalinity as a BLM input is also used to approximate DIC in the BLM software. This represents an alternative simplifying approach.

Figure 3 shows a comparison of BLM-based Cu acute criteria and Ecology's proposed MLR-based Cu acute criteria (making use of the reverse ACR where there is an inversion in acute and chronic criteria). With nearly 100,000 nationwide samples, Ecology's proposed acute MLR-based Cu criteria is higher than the nationally recommended acute BLM-based criteria in 59% of the samples. Therefore, it is not as protective as BLM-based criteria. A similar result can be seen with the comparison between Ecology's proposed chronic MLR-based criteria and the nationally recommended chronic BLM-based criteria (Figure 4), although the chronic MLR-based criteria exceed the chronic BLM criteria in 48% of the cases. However, it should be noted in Figure 4 that when chronic MLR-based criteria exceed chronic BLM-based criteria, they can exceed the criteria by up to 100-fold. When BLM-based criteria exceed MLR-based criteria, they tend to do so by less than 10-fold. In other words, when the MLR- and BLM-based criteria differ, the MLR-based criteria tend to be much higher (i.e., much less protective than the BLM-based criteria).

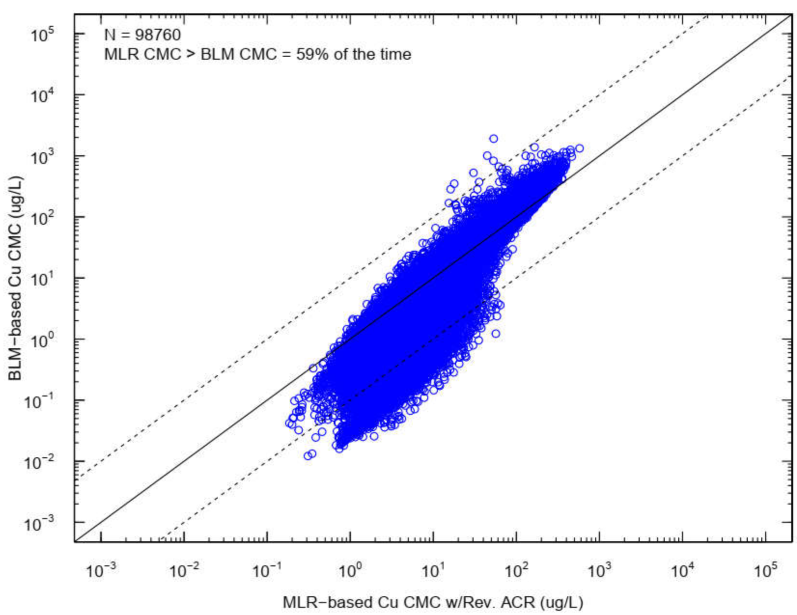

Figure 3. Comparison of nationally recommended BLM-based acute criteria (i.e., CMC) and Ecology's proposed MLR-based acute criteria when applied to a nationwide dataset.

Another way to look at the implications of this issue is to look at exceedance frequency of samples across the US. For this, we further constrain our dataset to samples that also have measured Cu concentrations. Figure 5 shows the acute hazard quotients (HQs), calculated as reported Cu concentration divided by calculated MLR- and BLM-based acute criteria. This summary indicates that MLR- and BLM-based criteria agree on 97% of samples, (13,430 of 13,829 samples below or above both MLR- and BLM-based criteria). However, the BLM-based criteria show exceedances for 325 samples, for which MLR-based criteria do not show exceedances, and the MLR-based criteria show exceedances for 74 samples for which BLM-based criteria do not show exceedances. In other words where MLR- and BLM-based criteria do not agree, the BLM-based criteria are more likely to identify exceedances than the MLR-based criteria. This indicates that the BLM is generally more protective than the MLR-based criteria. A similar result is evident for the chronic criteria (Figure 6).

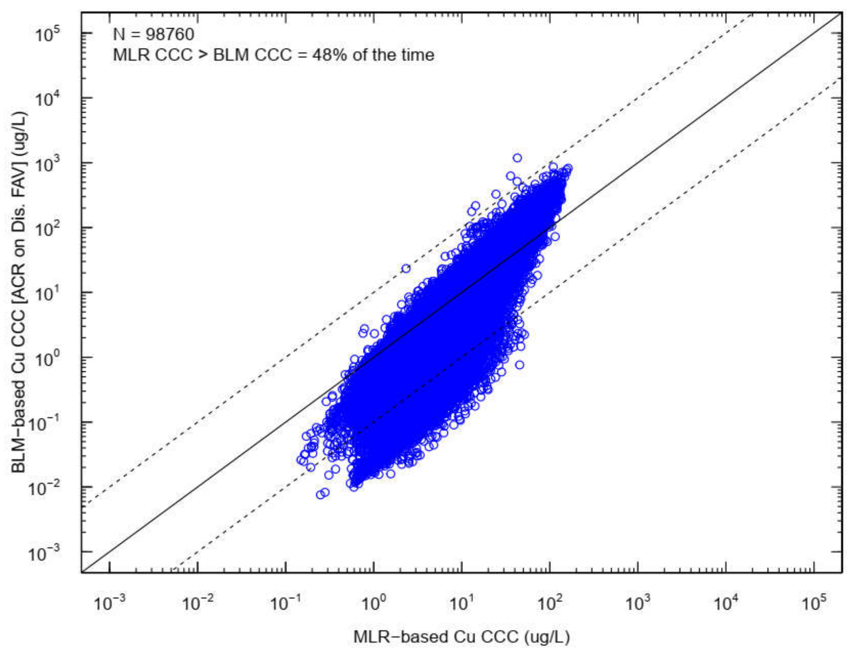

Figure 4. Comparison of nationally recommended BLM-based chronic criteria (i.e., CCC) and Ecology's proposed MLR-based chronic criteria when applied to a nationwide dataset.

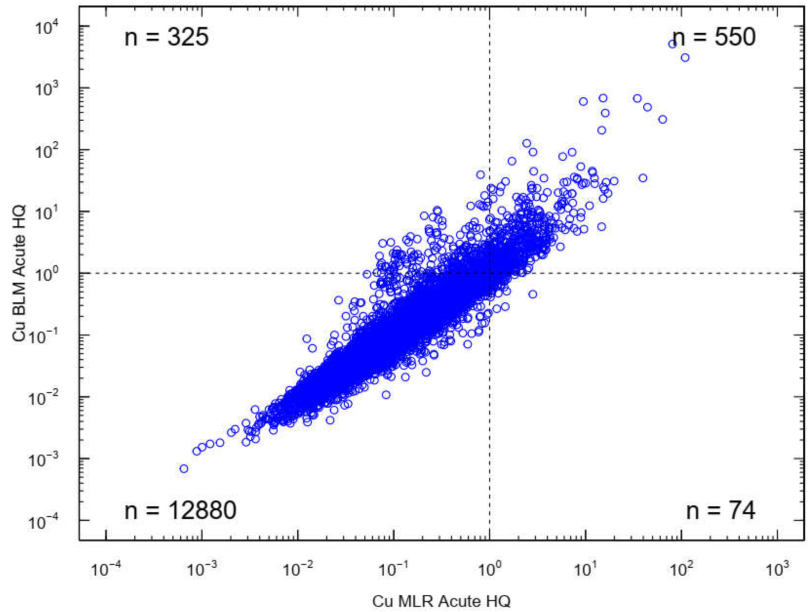

Figure 5. Comparison of acute BLM-based and MLR-based hazard quotients (HQs) using nationwide monitoring data. Dashed lines represent HQ = 1. When HQ > 1, acute criteria are exceeded by the reported copper concentration.

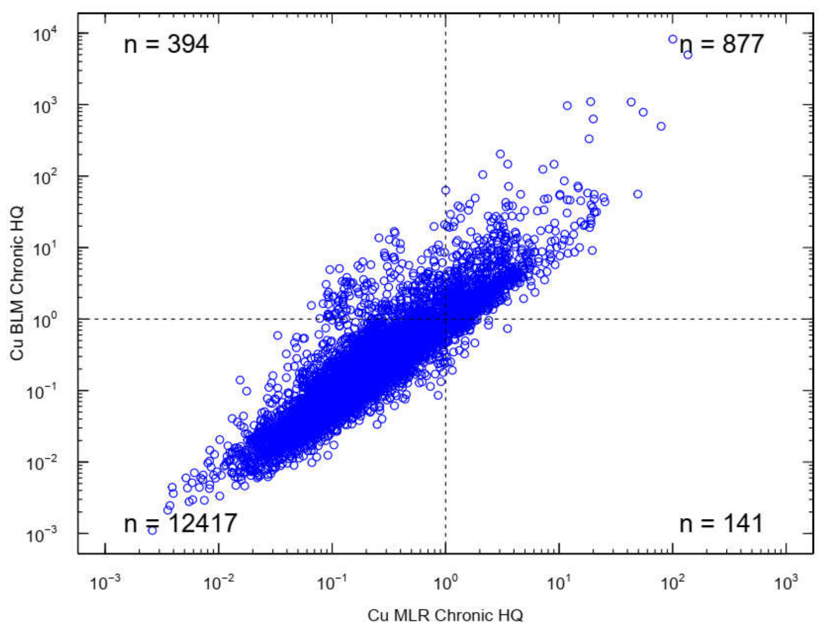

Figure 6. Comparison of chronic BLM-based and MLR-based hazard quotients (HQs) using nationwide monitoring data. Dashed lines represent HQ = 1. When HQ > 1, chronic criteria are exceeded by the reported copper concentration.

Given Ecology's references to the NMFS and USFWS biological opinions (BiOps) on Oregon's and Idaho's Cu criteria, the lower level of protectiveness of the Cu MLR-based criteria (compared to the BLM-based criteria) should be cause for concern. In fact, the path that Oregon and Idaho took to address the protectiveness concerns over the hardness equation was to adopt the nationally recommended Cu BLM. With the concerns raised here, we strongly recommend that Ecology follow a similar path as Oregon and Idaho on Cu criteria. If Ecology fails to do so, we predict that there will be future challenges from stakeholders on the lack of protectiveness and on the apparent departure from the best available science under some exposure scenarios. Furthermore, the proposed Cu criteria are different than the national recommendations and are likely different than any Cu criteria that will be recommended nationally by U.S. EPA in the future (i.e., U.S. EPA will develop their own MLR-based criteria). Therefore, the most appropriate pathway to incorporate bioavailability for Cu (at this time) is to use the nationally recommended Cu BLM (U.S. EPA 2007).

Approach to Developing Washington State Zinc Criteria

Since 1995, a substantial amount of data on the toxicity of Zn to several freshwater species has overwhelmingly demonstrated that multiple water chemistry characteristics, in addition to hardness, influence the bioavailability and toxicity of Zn. Therefore, Zn criteria should be updated to reflect Zn bioavailability more accurately in freshwaters.

As recognized by U.S. EPA (2007, 2022), BLMs and MLR models are appropriate tools for incorporating bioavailability into criteria. Currently, there are acute and chronic Zn MLR models (DeForest et al. 2023) and acute and chronic Zn BLMs (DeForest and Van Genderen 2012; DeForest et al. 2023) for characterizing Zn bioavailability in freshwaters. Further, both MLR models and BLMs have been applied in a manner consistent with U.S. EPA (1985) guidelines for criteria development (DeForest and Van Genderen 2012; DeForest et al. 2023), and the outcome of those applications represents technically robust alternatives to hardness-based Zn criteria. In fact, DeForest et al. (2023) demonstrated that Zn MLR models and BLMs performed similarly with available ecotoxicity data, and that both performed **substantially better than the hardness equation**. We recommend that Ecology take a closer look at DeForest et al. (2023), and avoid using the hardness equation.

Ecology's willingness to consider the Cu MLR models from Brix et al. (2021) suggests that Ecology would be willing to consider similar bioavailability-based models for other metals. Application of the acute and chronic pooled MLR models described in DeForest et al. (2023) indicates that the Zn MLR model results can suffer from the same acute-chronic inversion (Figure 7) that occurs with the Cu MLR models. However, it occurs for Zn in only approximately 5% of the samples in our nationwide dataset, and it tends to occur in softer waters (Figure 8). If the acute and chronic Zn BLMs were used, the inversion would occur in fewer than 0.02% of samples. So, we recommend that Ecology considers updating the bioavailability-basis for the Zn criteria (i.e., by using the Zn MLR models or BLMs), as well as the normalized sensitivity distributions. On both aspects, IZA is happy to provide technical assistance to Ecology, and we would be willing to share our ecotoxicological database with Ecology for update of the Zn sensitivity distributions.

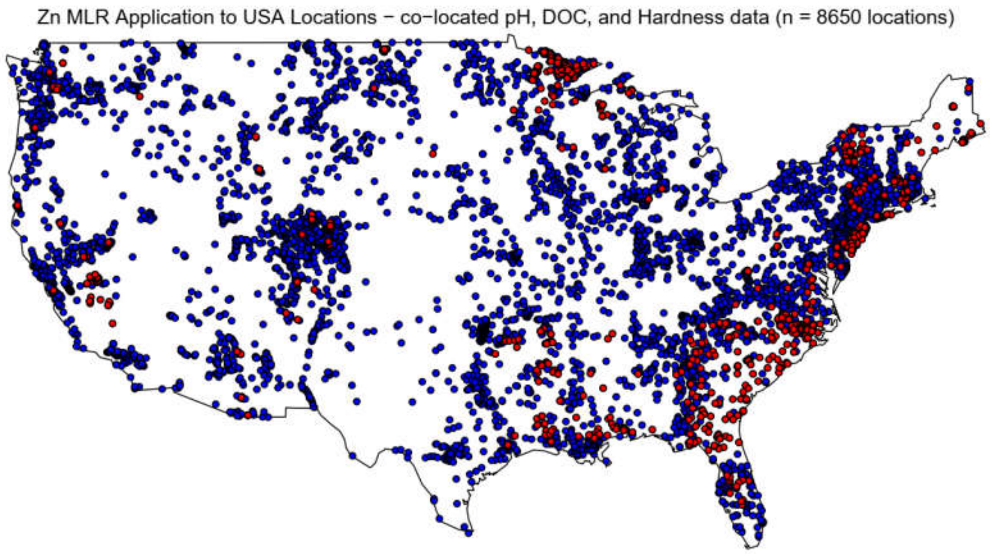

Figure 7. Monitoring locations with data to support MLR model calculations. Red symbols: locations with acute and chronic Zn criteria inversions. Blue symbols: no inversions.

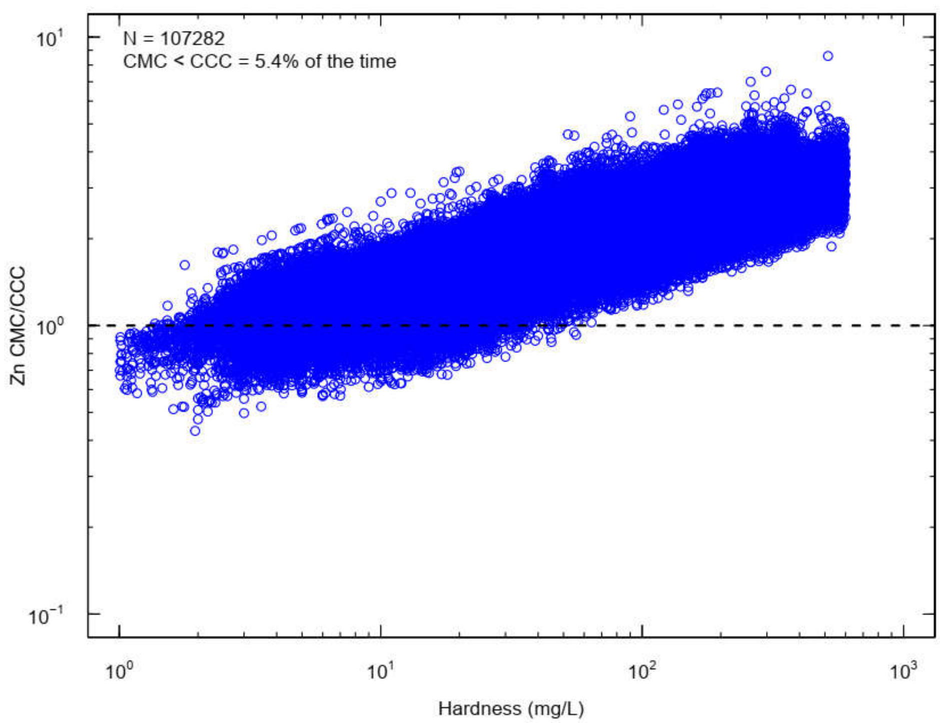

Figure 8. Ratio of acute and chronic MLR-based Zn criteria as a function of water hardness.

In summary, the IZA encourages Ecology to adopt bioavailability-based freshwater WQC for Zn (and other metals). Technically robust MLR model- and BLM-based approaches that are consistent with U.S. EPA guidelines for development of criteria are currently available. We believe that bioavailability-based criteria for Zn represent a fundamental advancement that will serve to achieve appropriate environmental protection and regulation.

However, our analyses have also demonstrated that application of different bioavailability models to natural surface waters can result in an acute-to-chronic criteria inversion. This occurs in up to 40% of U.S. samples and would affect samples in Washington. This phenomenon occurs with both Cu and Zn, though with much more likelihood for Cu. Also, this phenomenon is much more likely to occur with MLR models than with BLMs. So, while a quick reverse ACR approach might seem appropriate, it breaks the relationship between the criteria value and the bioavailability model(s). To avoid these scenarios, we recommend that Ecology consider using available BLMs for Zn and other metals.

We would like to stress that we are available as a technical resource as Ecology pursues bioavailability-based criteria. Please do not hesitate to contact us to discuss models and data.

Thank you for the opportunity to provide these recommendations for consideration during Ecology's public review process. Please let us know if you have any questions or if you would like to discuss these recommendations further.

Sincerely,

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References

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