Comparison of Hardness-Based and Biotic Ligand Model Water Quality Criteria for Copper and Zinc in Streams near Los Alamos National Laboratories

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Introduction

The Biotic Ligand Model (BLM) is based on a gill-site interaction conceptual model and predicts metal bioavailability and toxicity by incorporating metals speciation, complexation, and competing cations in solution (Figure 1). In 2007, the US Environmental Protection Agency (EPA) released nationally recommended copper water quality criteria (WQC) for aquatic life based on the BLM (EPA 2007). BLM-based WQC for zinc have been submitted to EPA. Although the New Mexico water quality standards allow for the use of the copper BLM on a site-specific basis, the hardness-based method to calculate copper WQC is the default statewide approach (NMWQCC 2010). The application of the BLM for zinc, cadmium, and aluminum WQC estimations is also under investigation, with promising results. Understanding metal bioavailability is critical to better understanding immediate complex environmental conditions. Using the BLM for copper is the current EPA policy and represents the current science.

Storm flow in typical ephemeral channel

Storm flow in upper Sandia Canyon

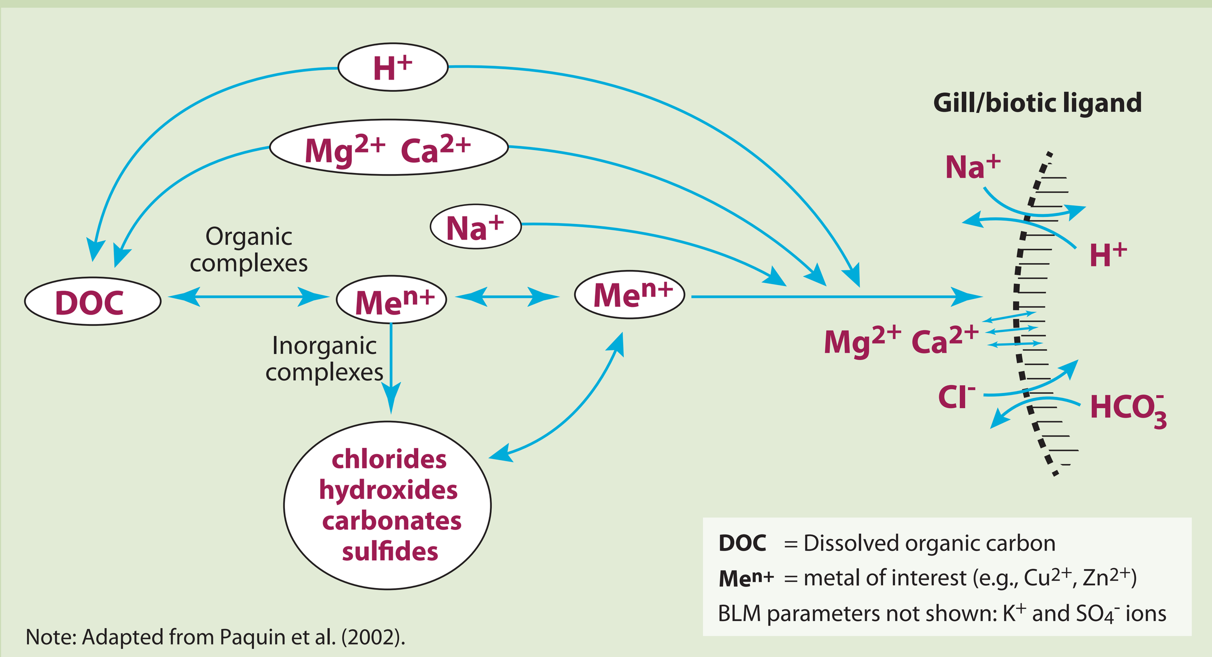

Figure 1. Schematic of processes governing metal bioavailability considered by the BLM, including the interaction of metals with dissolved organic matter, and principal anions and cations

Methods

In 2013, water quality samples were collected and analyzed, including for BLM constituents, from 19 ephemeral, intermittent, and perennial stream segments that cross Los Alamos National Laboratory (LANL) and are located within an area known as the Pajarito Plateau in north-central New Mexico (Figures 2 and 3). Chronic and acute copper instantaneous WQC (IWQC) were estimated and compared using the BLM (Version 2.2.3) and New Mexico hardness-based WQC. For zinc, EPA-recommended IWQC based on the BLM are not currently available so the BLM-based zinc "criteria" derived by (DeForest and Van Genderen 2012) were used. These "criteria" were derived following EPA guidelines and using the same method as that applied by EPA in deriving its recommended BLM-based copper criteria, but the criteria have not been officially reviewed by EPA. For both copper and zinc, the BLM IWQC were derived at 10 and 20 °C to bracket missing temperature data.

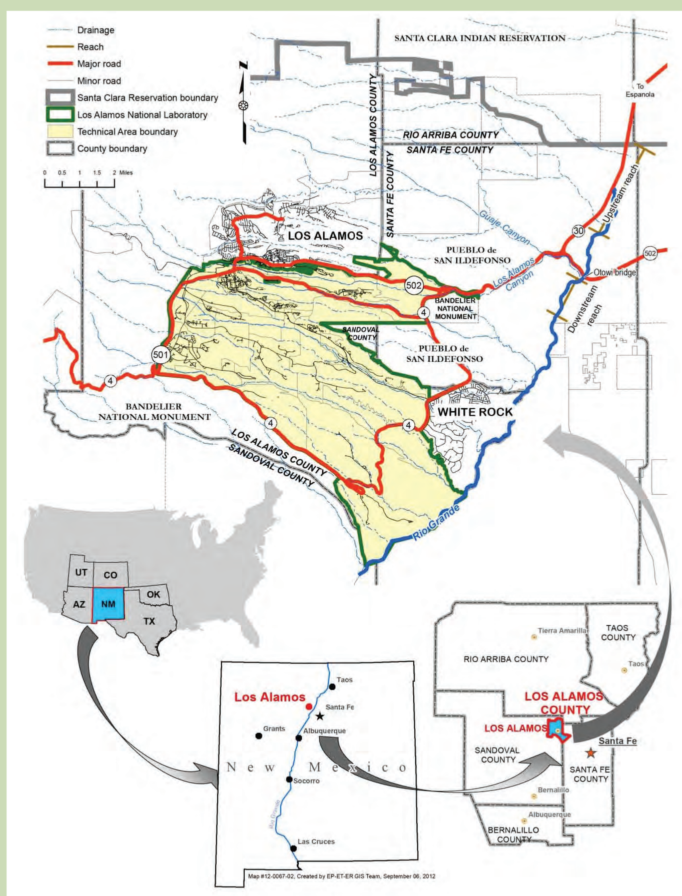

Figure 2. Location of the Pajarito Plateau

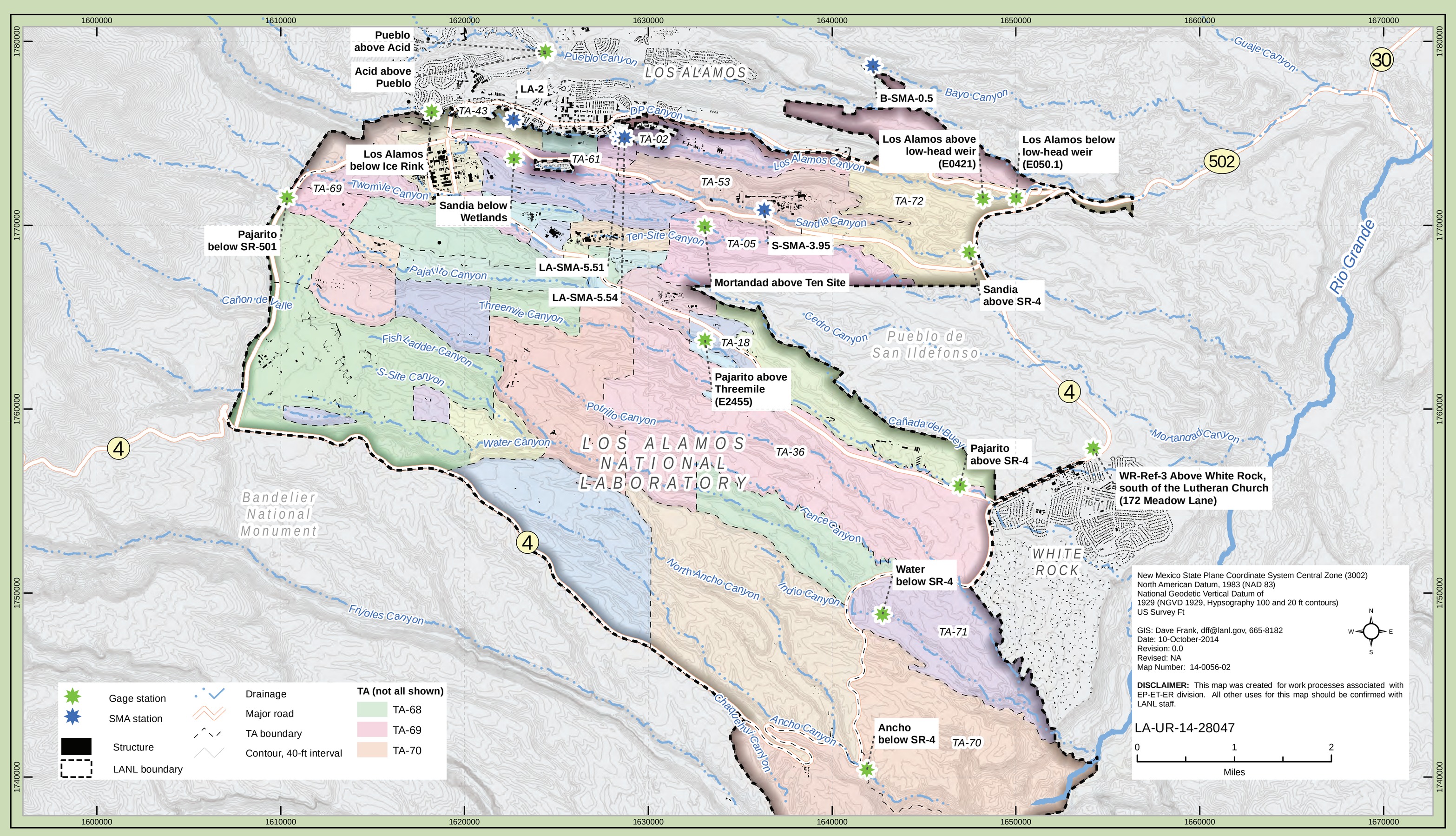

Figure 3. Locations of major watersheds and monitoring locations on the Pajarito Plateau

Stormwater sampling in upper Sandia Canyon

Results

Overall, BLM-based IWQC values (T = 10 °C) were 3- to 8-fold greater than hardness-based IWQC for copper and zinc (Figures 4 and 5). The BLM-based acute copper IWQC ranged from 3.4 to 361 µg/L, while the hardness-based IWQC ranged from 0.5 to 12.4 µg/L. Meanwhile, acute zinc BLM-based IWQC ranged from 167 to 1,138 µg/L, while hardness-based acute IWQC for zinc ranged from 6 to 149 µg/L. Running the BLM at 10 and 20 °C showed an average of only 3 to 4% relative difference between acute copper and zinc BLM-based IWQC. In all cases, the acute toxicity units (TUs), which equal observed copper or zinc concentrations divided by BLM acute IWQC, were < 1, indicating that observed copper and zinc concentrations did not exceed their respective BLM-based acute criteria levels (Figure 6). In the 36-sample dataset, 7 samples (19%) had acute copper TUs > 1 for hardness-based IWQC but not for BLM-based IWQC, and 1 sample had an acute zinc TU > 1 for hardness-based IWQC but not for BLM-based IWQC (Figure 6). These results (in the upper left quadrant of Figure 6) suggest a potential false positive rate in decisions made using the hardness-based IWQC instead of the BLM-based IWQC.

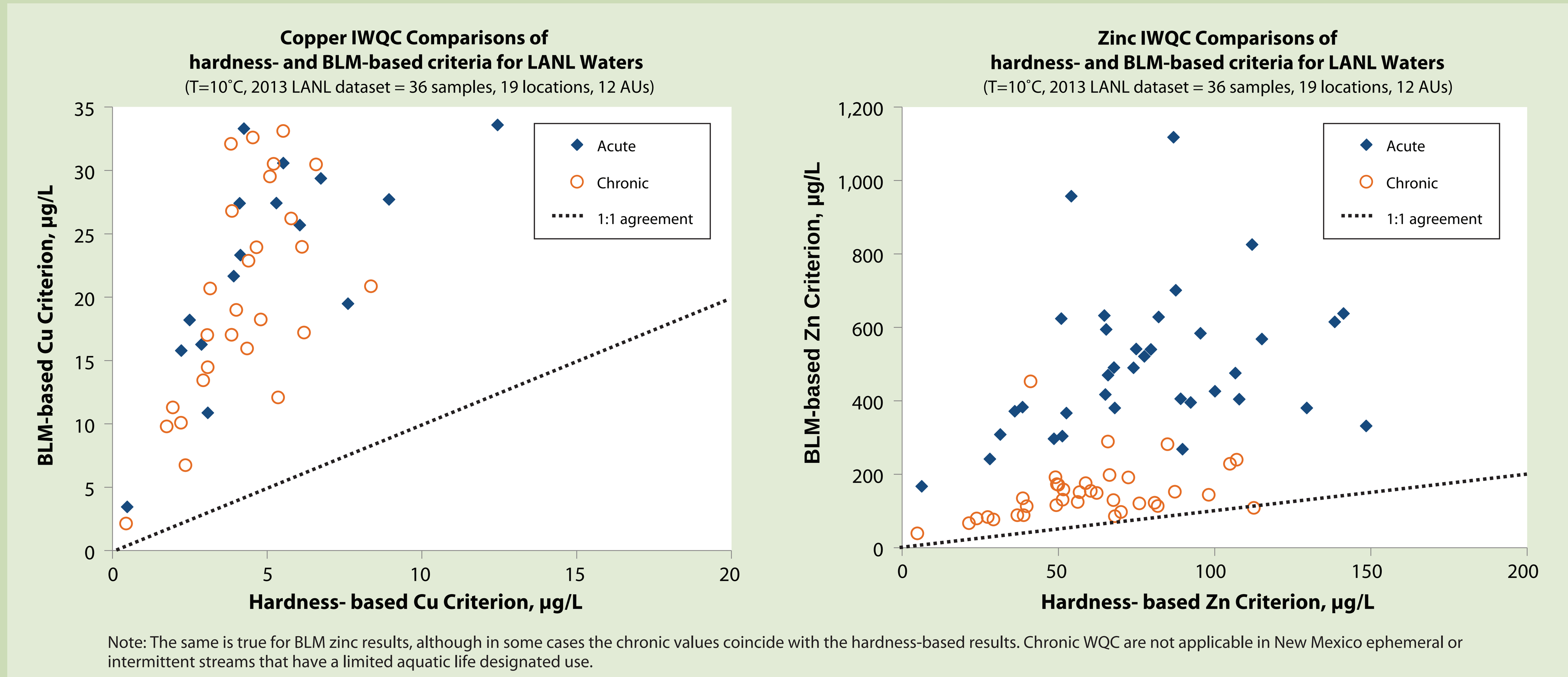

Figure 4. Comparison of copper (A) and zinc (B) acute and chronic WQC estimated using the hardness-based and BLM methods (T = 10 °C)

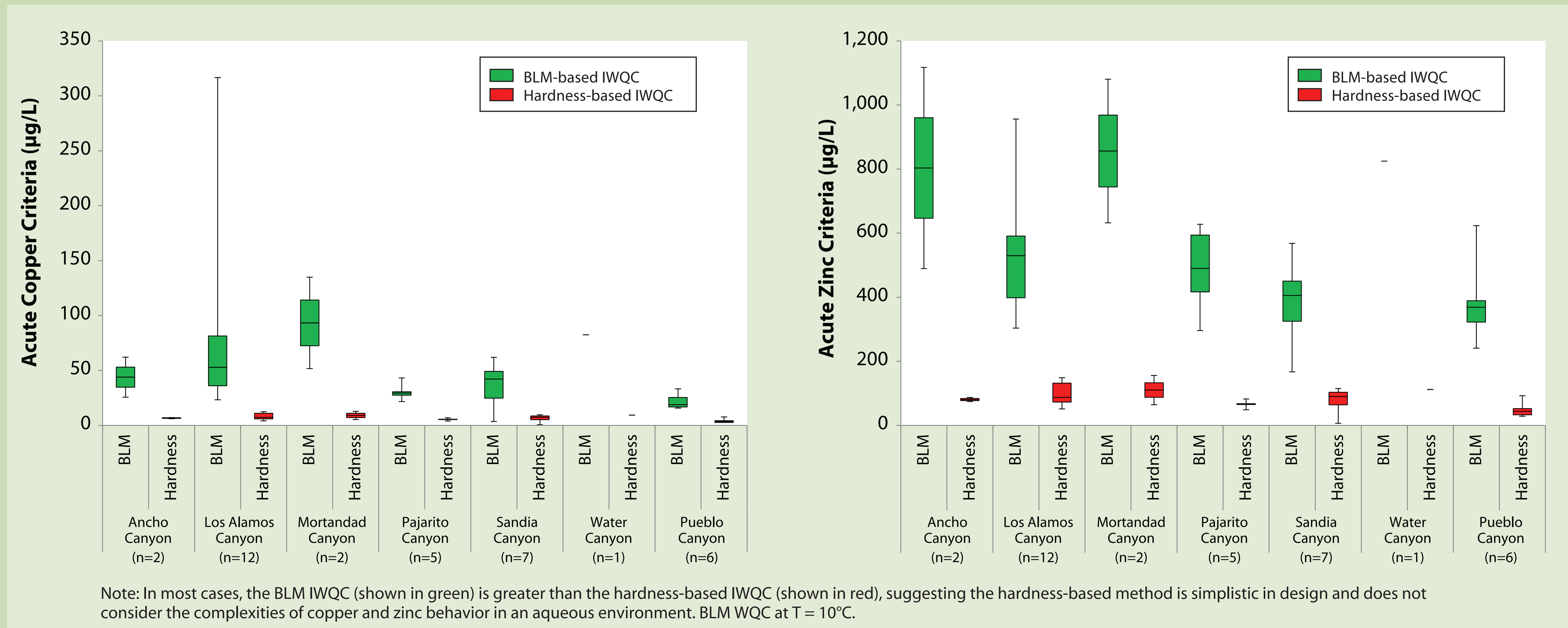

Figure 5. Box plots of acute (A) copper and (B) zinc IWQC by select watersheds on the Pajarito Plateau

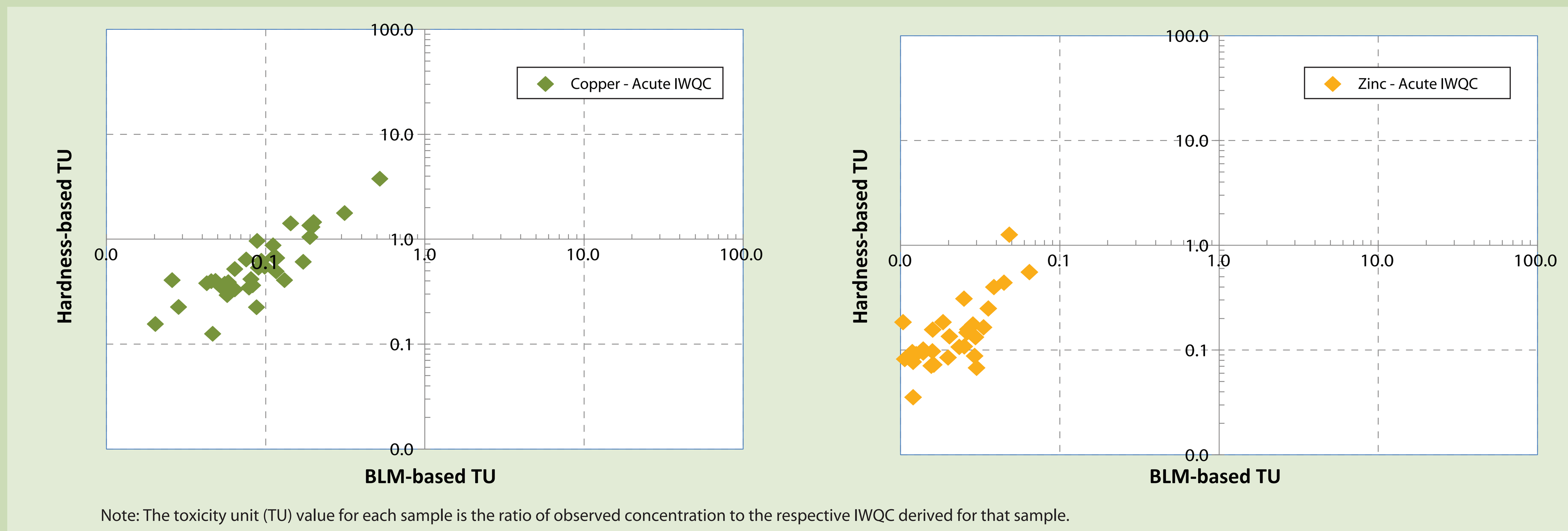

Figure 6. Comparison of acute toxicity units for (A) copper and (B) zinc based on BLM and hardness-based acute IWQC

Conclusion/Discussion

These findings indicate that bioavailable copper and zinc concentrations estimated by the BLM are much lower and more representative than those estimated using the hardness-based WQC. In addition, these results suggest that in many cases, the hardness-based WQC are overprotective of the environment, lacking the resolution inherent in the BLM to represent complex aquatic environmental conditions and diverse geochemistry. Consequently, the National Pollutant Discharge Elimination System (NPDES) permits and state water quality assessments affecting LANL that use hardness-based WQC (often assuming 30 mg/L hardness) would result in more accurate management actions if action levels were based on the BLM for copper and zinc.

Typical surface water monitoring gage station

References

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