# BLM-Based Ambient Water Quality Criteria and FMBs for Four Metals in Surface Waters of the Pajarito Plateau, New Mexico

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## Abstract

Potential aquatic life ambient water quality criteria (AWQC) for copper, lead, zinc, and aluminum based on the biotic ligand model (BLM) were generated for 48 locations representing surface waters of the Pajarito Plateau, a relatively high-altitude (~2000 m above sea level), arid region west of the Rio Grande in the vicinity of Los Alamos National Laboratory (LANL), New Mexico. Most waters there are ephemeral or intermittent and flow only in response to summer monsoonal thunderstorms and spring snowmelt; the few perennial waters are sourced to springs (e.g., in Bandelier National Monument) or effluent (permitted discharges). A total of 457 BLM-based instantaneous water quality criteria (IWQC) and various spatial scales of fixed monitoring benchmarks (FMBs) were generated for each metal based on LANL sample data collected largely from 2013 through 2017, with some data dating to 2005.

The copper, lead, and zinc BLM-based acute and chronic IWQC were often substantially greater than the hardness-dependent IWQC based on New Mexico water quality standards (WQS). Consequently, observed metal concentrations exceeded the BLM-based IWQC far less frequently in comparison with New Mexico hardness-based IWQC. Copper exceeded hardness-based acute IWQC in 36% of the samples wherein copper did not exceed BLM-based IWQC (i.e., using the BLM prevented 36% false positive conclusions). Furthermore, these results suggest that 12 waters 303(d) listed for copper in the LANL area should be reconsidered in light of the copper BLM-based AWQC. Similar rates of false positive exceedances of hardness-based chronic IWQC for copper, lead, and zinc further warrant adoption and implementation of BLM-based AWQC in New Mexico WQS.

For aluminum, BLM-based IWQC were also generally higher than New Mexico hardness-based IWQC, although each basis was substantially lower than US Environmental Protection Agency (EPA)-proposed aluminum AWQC (2017), which are computed from equations using three water quality variables (pH, dissolved organic carbon [DOC] and hardness). Compared with EPA (2017) AQWC, using New Mexico AWQC would result in false positive aluminum AWQC exceedances for 11% of the unfiltered samples (n=457), 41% of the samples pre-filtered using a 10-µm filter (n=149), 29% of the samples pre-filtered using a 1-µm filter (n=34), and 44% of the samples pre-filtered using a 0.45-µm filter (n=457). There is currently debate and related developments regarding the most appropriate sample preparation methods for aluminum in natural surface water samples (i.e., acidification and filtration, to restrict aluminosilicates while representing potentially toxic dissolved and precipitated forms of aluminum).

## Introduction

The biotic ligand model (BLM) is a recognized tool for evaluating the bioavailability and potential toxicity of various metals. The BLM can also be used to develop ambient water quality criteria (AWQC) for metals that are consistent with US Environmental Protection Agency (EPA) (1985) guidelines, such as those criteria EPA developed in its 2007 update of its nationally recommended copper AWQC. The states of Oregon and Idaho recently adopted BLM-based copper AWQC statewide to replace former EPA (1996) hardness-based AWQC for copper (ODEQ 2016; IDEQ 2017). The BLM improves hardness-based approaches for evaluating bioavailability or deriving AWQC by incorporating additional water quality variables, such as dissolved organic carbon (DOC), that can bind metals and thereby decrease bioavailable concentrations (see Figure 1).

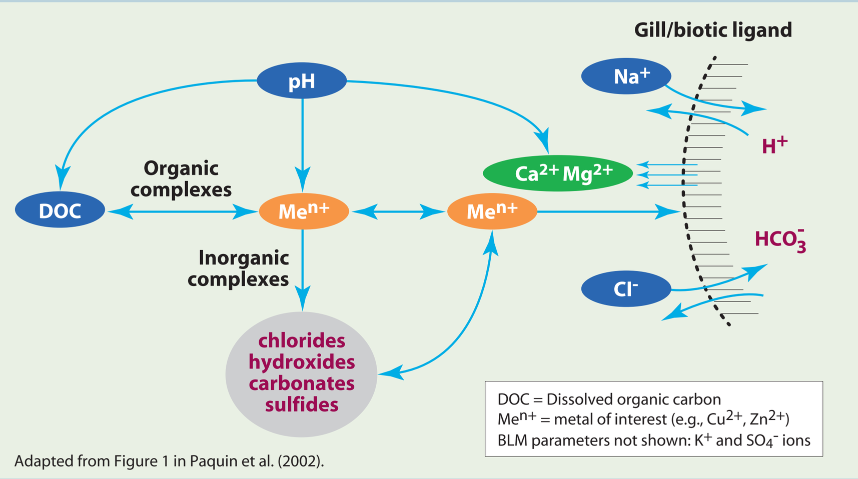


**Figure 1. Schematic of the BLM**

While other objectives were covered in the associated data quality objectives (DQOs) document (Windward 2018), the key study objectives covered in this poster include:

1. Generate hardness-based instantaneous water quality criteria (IWQC) consistent with New Mexico water quality standards, and generate BLM-based IWQC for copper, lead, zinc, and aluminum consistent with nationally recommended AWQC (EPA 2007), draft AWQC (EPA 2017), or EPA guidelines (EPA 1985) where national AWQC have yet to be established.
2. Compare observed dissolved metal concentrations with each IWQC outcome to evaluate relative differences in assessment outcomes between different AWQC.
3. Determine if area waters' assessment units (AUs) currently 303(d) listed for copper might be affected if re-assessed using BLM-based IWQC.
4. Determine how use of BLM-based acute IWQC could impact the target action levels (TALs) for dissolved copper, lead, and zinc in the 2015 draft individual National Pollutant Discharge Elimination System (NPDES) stormwater permit for Los Alamos National Laboratory (LANL).

## Methods and Dataset

- EPA's DQO process (EPA 2006) to define the dataset and establish guidance and evaluations appropriately (Windward 2018) was used.
- Available data for 457 sampling events across 13 years (2005–2017) and 48 surface water sampling locations were assembled (data from LANL's Intellus database):
  - Twelve reference watersheds represented "natural background" locations outside, or upstream of, LANL and the town of Los Alamos (see Figure 2).
  - Thirty-six locations were within surface waters downstream of LANL and/or the town of Los Alamos (see Figure 2).
  - Samples were predominantly (69%) stormflow (n=316); the remaining samples (n=141) were collected during baseflow. Of the baseflow samples, 58% (n=82) were perennial water samples, 67 of which were of effluent-dependent water. The remaining samples were most likely intermittent baseflow associated with spring snowmelt. Eight samples were perennial waters (Rito de Frijoles) within Bandelier National Monument (two stormflow, six baseflow).
  - DOC was estimated from total organic carbon (TOC) in 129 events: DOC = 0.861×TOC, $r^2$= 0.93 (see Figure 3). This relationship was very similar to that of the 0.83 multiplier used by the State of Oregon for BLM purposes (ODEQ 2016).

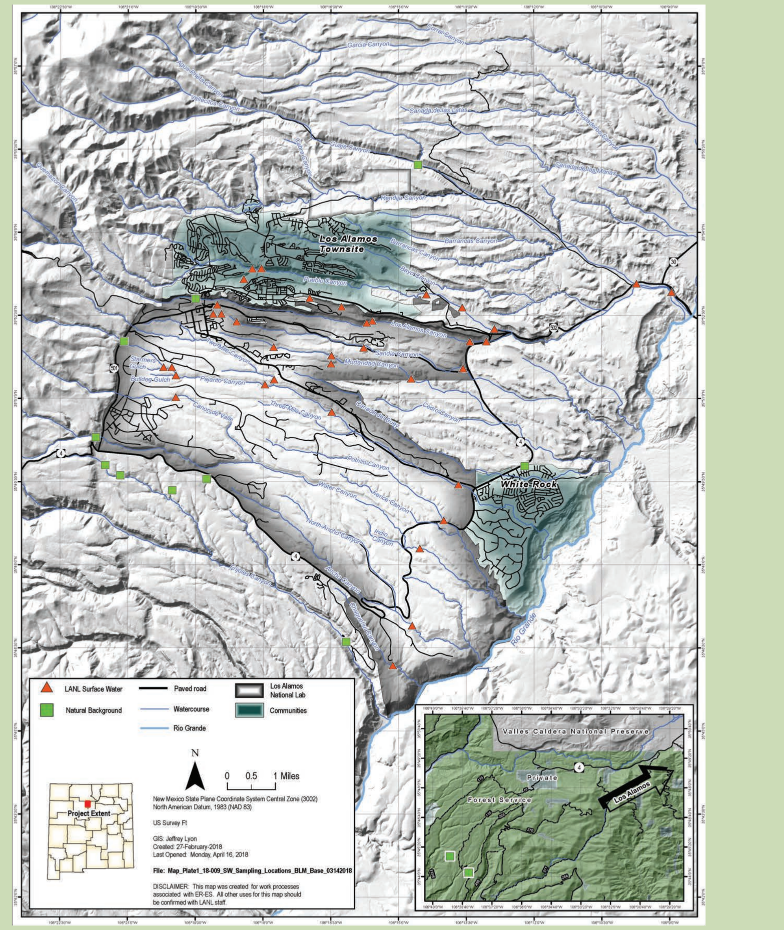

**Figure 2. Surface water sampling locations on the Pajarito Plateau in the vicinity of LANL**

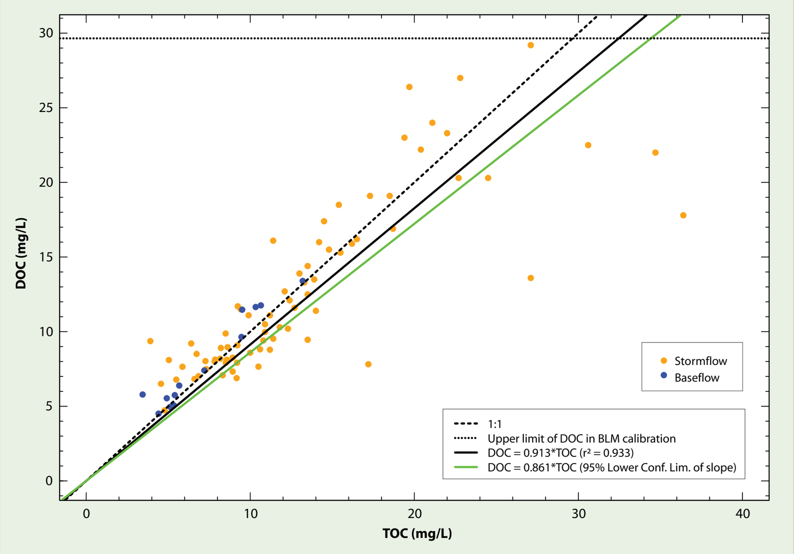


**Figure 3. Relationship used to estimate DOC from TOC data**

  - DOC was capped at the upper bound of the BLM calibration range (29.65 mg/L) for n=5 samples.
  - Sulfate (n=4) and chloride (n=5) were estimated from location-specific averages.
  - Temperature was assumed to be 10°C for all samples (temperature data not available).
- IWQC consistent with New Mexico and EPA AWQC, or potential AWQC consistent with EPA (1985) guidelines, were calculated (see Table 1).
- Samples were collected by staff from LANL, generally using Teledyne ISCO© automated samplers and following standard operating procedures.
- Samples were filtered and analyzed at accredited laboratories.
- All BLM inputs were for 0.45-µm filtered (F) sample results, except for approximately 70% of the alkalinity results, which were for unfiltered (UF) samples. Unfiltered alkalinity closely approximated filtered alkalinity: Alk (F) = 0.957[Alk (UF], $r^2$=0.992. Because the BLM is typically relatively insensitive to alkalinity, unfiltered results were used when filtered results for alkalinity were not available.

**Table 1. Approaches used to calculate IWQC**

| Metal | AWQC Approach | Description | Reference |
|---|---|---|---|
| Copper | BLM | EPA-recommended WQC | EPA (2007) |
| | New Mexico AWQC (= EPA 1996 AWQC) | hardness equation | NMAC.20.6.4.900(I) |
| Lead | BLM | mechanistic characterization of dissolved lead bioavailability | DeForest et al. (2017) |
| | New Mexico AWQC (= EPA 1996 AWQC) | hardness equation | NMAC.20.6.4.900(I) |
| Zinc | BLM | mechanistic characterization of dissolved zinc bioavailability | DeForest and Van Genderen (2012) |
| | New Mexico AWQC | hardness equation | NMAC.20.6.4.900(I) |
| Aluminum | BLM | mechanistic characterization of dissolved and precipitated aluminum bioavailability | Santore et al. (2018) |
| | New Mexico AWQC | hardness equation | NMAC.20.6.4.900(I) |
| | draft EPA WQC | MLR with pH, DOC, hardness | EPA (2017) |

## Results

Comparisons of acute IWQC outcomes for copper, lead, and zinc are shown in Figures 4 through 6 for all 457 samples. Figures 7 through 9 show chronic IWQC outcomes for the more limited dataset related to samples from the Pajarito Plateau's few perennial waters, for which chronic criteria are currently applicable (20.6.4.126 NMAC). These figures all plot toxicity units (TUs); a TU is the ratio of the observed dissolved metal concentration (0.45-µm filtrate) to the IWQC calculated for the water chemistry in that same sample. The TUs for BLM-based IWQC are plotted on the Y-axis, and those for hardness-based IWQC are plotted on the X-axis. Values plotted in the upper right and lower left quadrants signify consistent assessment outcomes between the different IWQC (i.e., unequivocal "fail" or "pass," where TUs are > 1 or < 1 for either IWQC basis, respectively). In contrast, values plotted in the lower right and upper left represent disagreement between BLM- and hardness-based IWQC (i.e., false positives and false negatives, respectively). The relative magnitude of disagreement increases as points fall farther from the 1:1 diagonal dashed line. Samples collected after major forest fires in the area (Las Conchas, 2011) are shown separately in Figures 4 through 9 and do not appear to skew results.

Results for aluminum BLM-based IWQC are too uncertain to be provided herein but are included in the associated DQO document (Windward 2018). The aluminum BLM is being updated to include new ecotoxicology data to expand its calibration range. Both of the typical measurement methods for aluminum—"dissolved" and total recoverable concentrations—have been shown to be inappropriate in some cases; more appropriate sample preparations must be used to limit potential bias from non-toxic aluminosilicate solids while simultaneously representing amorphous, freshly precipitated aluminum that may or may not be present. *Please see the associated platform presentation No. 421 at the SETAC North America 2018 conference.*

Table 2 presents the results of a re-assessment of area water AUs that are currently 303(d) listed for copper, including five new AUs listed in the 2018 draft New Mexico Integrated Report (NMED 2018). For two AUs, data were not available in the BLM dataset, apparently because prior assessments had been based on samples that may have contained only results for hardness, or incomplete BLM input datasets; this study was limited to complete datasets.

Figure 10 shows that median BLM-based IWQC for copper, lead, and zinc are substantially greater than 2015 LANL draft NPDES TALs, which employ geometric mean IWQC using observed hardness for some of the main canyon surface waters within and around LANL (LANL 2008). Only locations with 10 or more samples are included in the medians in this figure; additional BLM outcomes exist that can be used to enrich results aggregated to higher spatial groupings of the 7 main canyons of the Pajarito Plateau within and around LANL. Note that the 2015 draft NPDES permit TALs are based on geometric mean hardness in area waters and apply to dissolved metal measurements in stormwater samples.

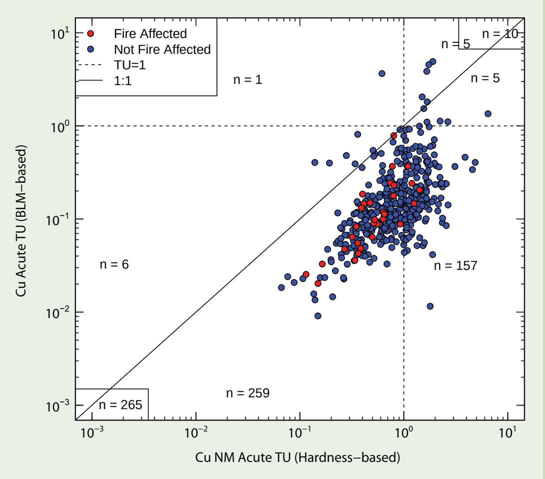

**Figure 4. Comparison of acute dissolved copper IWQC TUs between EPA 2007 BLM and New Mexico hardness-based AWQC**

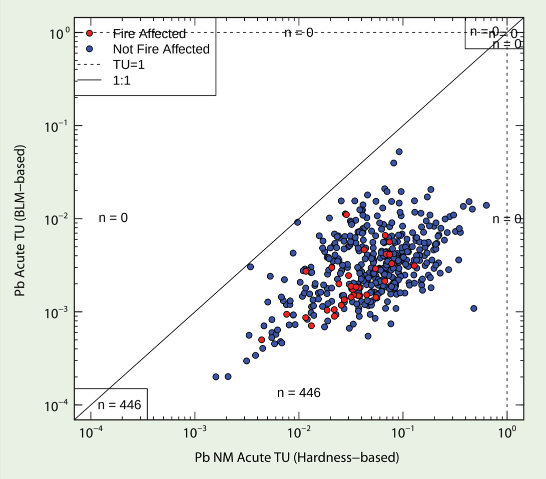

**Figure 5. Comparison of acute dissolved lead IWQC TUs between BLM and New Mexico hardness-based AWQC**

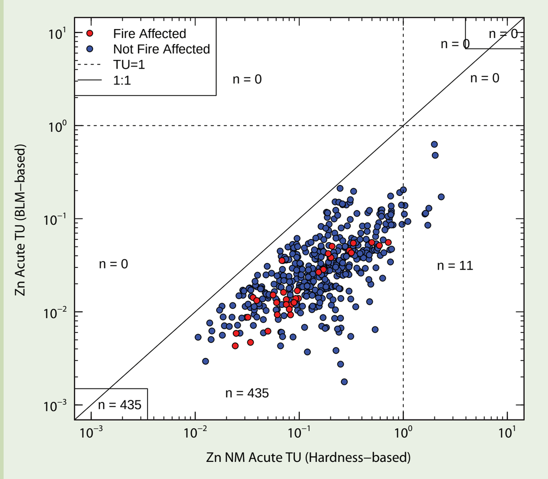

**Figure 6. Comparison of acute dissolved zinc IWQC TUs between BLM and New Mexico hardness-based AWQC**

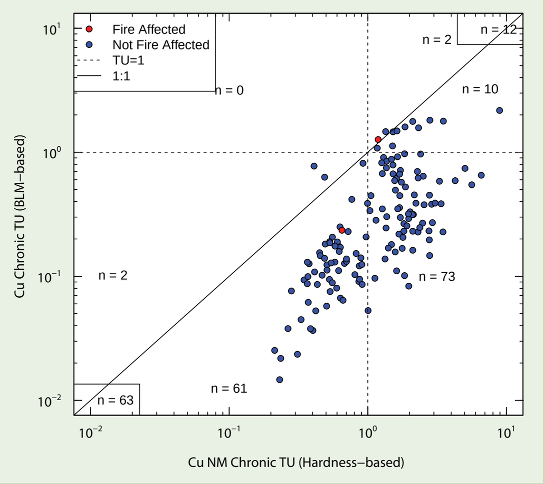

**Figure 7. Comparison of dissolved copper chronic IWQC TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters**

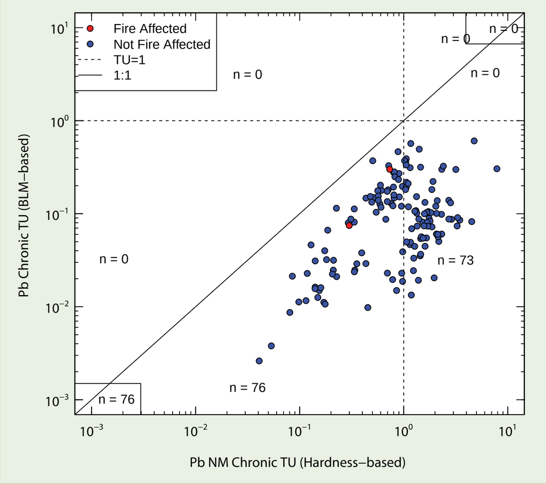

**Figure 8. Comparison of dissolved lead chronic IWQC TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters**

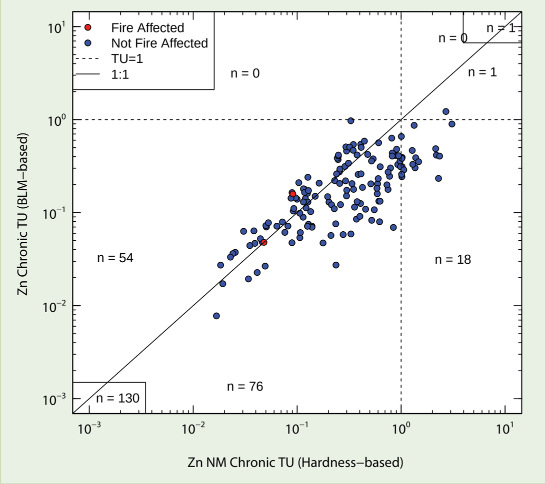

**Figure 9. Comparison of dissolved zinc chronic IWQC TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters**

**Table 2. Comparison of copper acute IWQC attainment based on BLM and New Mexico IWQC generated for 303(d) Impaired Waters Listings in LANL area waters**

| 2016 303(d) listings - NMED 2016, 2018 proposed (adapted from NMED 2018) | | | 2018 LANL BLM DQO/DQA Dataset Basis | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | New Mexico IWQC | | | BLM-based IWQC | | | |
| AU Name | Impairment | Cycle First Listed | n | TU>1 | exc freq (%) | n | TU>1 | exc freq (%) | Locations |
| Pajarito Canyon (Two Mile Canyon to Arroyo de La Delfe) | copper, acute | 2016 | 9 | 7* | 78% | 9 | 1* | 11% | E243 |
| Mortandad Canyon (within LANL) | copper, acute | 2010 | 17 | 7 | 41% | 17 | 0 | 0% | E200, E201, E204 |
| Sandia Canyon (Sigma Canyon to NPDES outfall 001) | copper, acute | 2010 | 128 | 61 | 48% | 127 | 4 | 3% | E121, E122 (2), E123 |
| Acid Canyon (Pueblo to headwaters) | copper, acute | 2010 | 27 | 1* | 4% | 27 | 1* | 4% | E055.5, E056 |
| Walnut Canyon (Pueblo Canyon to headwaters) | copper, acute | 2014 | no data | | | | | | |
| Graduation Canyon (Pueblo Canyon to headwaters) | copper, acute | 2010 | no data | | | | | | |
| South Fork Acid Canyon (Acid Canyon to headwaters) | copper, acute | 2014 | 7 | 0 | 0% | 7 | 0 | 0% | E055.5 |
| DP Canyon (Grade control to upper LANL bnd) | copper, dissolved | 2018 | 49 | 15 | 31% | 49 | 0 | 0% | E038, E039.1 |
| Pueblo Canyon (Acid Canyon to headwaters) | copper, dissolved | 2018 | 13 | 5 | 38% | 13 | 0 | 0% | E055 |
| Arroyo de la Delfe (Pajarito Canyon to headwaters) | copper, dissolved | 2018 | 4 | 3 | 75% | 4 | 0 | 0% | E242.5 |
| Pajarito Canyon (Lower LANL bnd to Two Mile Canyon) | copper, dissolved | 2018 | 18 | 5 | 28% | 18 | 0 | 0% | E245.5, E250 |
| Two Mile Canyon (Pajarito to headwaters) | copper, dissolved | 2018 | 10 | 5* | 50% | 10 | 0 | 0% | E244 |

*exceedance uncertain, TUs calculated for non-detects at reported detection limit (DL), a number of which were 10 µg/L.

**Figure 10. Comparison of LANL draft NPDES stormwater target action levels for dissolved copper, lead, and zinc with median BLM-based IWQC for main canyon waters at LANL**

## Discussion and Conclusions

- Sensitivity evaluations showed that copper and zinc BLM-based IWQC were insensitive to temperature, but BLM-based IWQC for aluminum increased with temperature (see Figure 11).
- Assumption of 10°C used for missing temperature data would not affect copper and zinc BLM-based IWQC, but the assumption would tend to bias the BLM-based aluminum IWQC outcomes lower where actual temperatures were higher than 10°C.
- Observed dissolved copper concentrations exceeded acute BLM-based IWQC for copper far less frequently (n=11) than they exceeded hardness-based copper IWQC (n=167): The hardness-based acute copper IWQC generated 36% false positive exceedances when compared to BLM-based IWQC (see Figure 4).
- The BLM-based acute IWQC for copper could render current 303(d) listings for copper in area waters (12 water body assessment units) unnecessary (except one potential case). While observed dissolved copper concentrations have exceeded hardness-based New Mexico IWQC, they have not exceeded respective BLM-based acute IWQC that are consistent with EPA (2007) nationally recommended AWQC (see Table 2).
- The authors have recommended that the New Mexico Environment Department consider proposing new water quality standards that adopt BLM-based AWQC for copper and zinc. Current New Mexico standards allow site-specific application of the copper BLM, which requires time-consuming rulemaking and EPA approval. Instead, New Mexico might want to consider following the examples of Idaho and Oregon in adopting the copper BLM as statewide AWQC, without the need for site-specific, case-by-case water quality criteria derivation, rulemaking, and EPA approval.
- For lead, hardness-based acute IWQC did not generate false positive or false negative exceedances when compared with BLM-based acute IWQC. However, hardness-based acute TUs tended to be about 10 times greater (or more) than BLM-based acute TUs, with a few outcomes approaching false positives (note the right-shifted pattern in Figure 5).
- For zinc, hardness-based acute IWQC generated 2.4% false positive exceedances (n=11) and no false negative exceedances when compared with BLM-based acute IWQC. Similarly to lead, the right-shifted pattern indicates a tendency for greater acute TUs for hardness-based acute IWQC (see Figure 6).
- For the chronic IWQC, the different outcomes between BLM- and hardness-based chronic IWQC are more pronounced (i.e., false positives were 49% for copper and lead and 12% for zinc) (see Figures 7 through 9). Where exceedances of chronic hardness-based criteria have been observed (e.g., certain perennial waters), further evaluation using the BLM may be warranted.
- Because the BLM is considered more accurate than hardness-based AWQC, and since the BLM is accepted as a scientific tool for more accurately evaluating metal bioavailability in general, BLM-based AWQC should also be considered for use in NPDES permits. Clean Water Act compliance needs could be vastly different under the BLM, yet still achieve EPA's intended level of aquatic life protection where AWQC are used as screening levels to determine the need for corrective actions (e.g., new or updated stormwater best management practices).

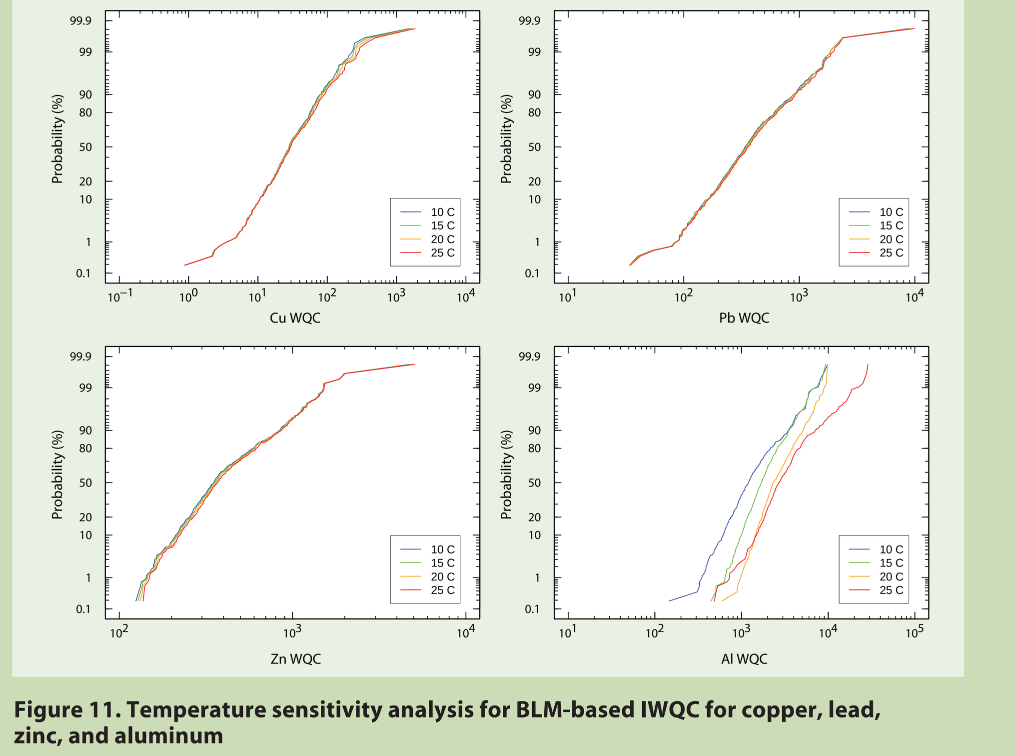

**Figure 11. Temperature sensitivity analysis for BLM-based IWQC for copper, lead, zinc, and aluminum**

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