2018-2020

State of New Mexico Clean Water Act Section 303(d)/ Section 305(b) Integrated Report

Appendix C

Response to Comments

Prepared by:
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Surface Water Quality Bureau
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https://www.env.nm.gov/surface-water-quality/

RESPONSE TO COMMENTS

ON THE
2016-2018 STATE OF NEW MEXICO
CLEAN WATER ACT
§303(d)/§305(b)
INTEGRATED LIST OF ASSESSED SURFACE WATERS

July 23, 2018

Table of Contents

PLEASE NOTE:

Original letters and emails were converted to Microsoft Word. All submitted comments were converted to Calibri font with standard page margins for ease of collation. Personal identification information such as phone numbers, street addresses, and e-mail addresses from private citizens were removed for privacy reasons. All original comment letters/emails are on file at the SWQB office in Santa Fe, NM.

MINOR CHANGES TO THE DRAFT 2018-2020 INTEGRATED REPORT, LIST (Appendix A of the Integrated Report), AND ASSOCIATED ASSESSMENT RATIONALE (formerly "ROD") BASED ON ADDITIONAL SWQB STAFF REVIEW DURING THE COMMENT PERIOD:

1. Figure 8 was revised to display only priority streams as stated in the legend.
2. New IR Categories 3C and 5-ALT, as described in New Mexico's listing methodology (CALM, available at https://www.env.nm.gov/surface-water-quality/calm/), were added to Table 1 on page 8 of the Integrated Report. The definitions for IR Categories 3A and 3B were also corrected to match the CALM.
3. Unassessed waterbody **Glenwood Pond (AU ID NM-2603.B_10)** was removed from the CWA 303(d)/305(b) Integrated List (Appendix A) because it is not a surface water of the state per 20.6.4 NMAC. Specifically, it is part of the treatment system for the NMDGF Glenwood Springs Hatchery, NPDES Permit NM0030163. Therefore, this surface water falls under the below bolded section of 20.6.4.7.S(5):

> ***(5) "Surface water(s) of the state"*** *means all surface waters situated wholly or partly within or bordering upon the state, including lakes, rivers, streams (including intermittent streams), mudflats, sandflats, wetlands, sloughs, prairie potholes, wet meadows, playa lakes, reservoirs or natural ponds. Surface waters of the state also means all tributaries of such waters, including adjacent wetlands, any manmade bodies of water that were originally created in surface waters of the state or resulted in the impoundment of surface waters of the state, and any "waters of the United States" as defined under the Clean Water Act that are not included in the preceding description. Surface waters of the state does not include private waters that do not combine with other surface or subsurface water or any water under tribal regulatory jurisdiction pursuant to Section 518 of the Clean Water Act.* ***Waste treatment systems, including treatment ponds or lagoons designed and actively used to meet requirements of the Clean Water Act (other than cooling ponds as defined in 40 CFR Part 423.11(m) that also meet the criteria of this definition), are not surface waters of the state****, unless they were originally created in surface waters of the state or resulted in the impoundment of surface waters of the state.*

4. The Assessment Rationale for **Raton Creek (Chicorica Creek to headwaters), AU_ID NM-2305.A_253**, was corrected to the following (change underlined) –

   2018 ACTION: Sampled during 2015-2016 Canadian/Dry Cimarron survey. <u>1/7</u> E. coli exceedences. 4/8 TN and 8/8 TP threshold exceedences, with delta DO of 11.24 mg/L. Therefore, E. coli was removed and nutrients remains a cause of impairment. MWWAL may be under protective-- WQS review needed.

5. The following items that are related to the associated draft IR review spreadsheets were added to the Useful Definitions section of the Preface to the Integrated List (Appendix A of the IR):

IR Category 2A	This indicates a IR Category 2 parameter (currently non-impaired) where an associated Action exists (e.g., Approved TMDL, Alternative Restoration Approach, etc.).
PARAMETER(S) OF CONCERN	This includes parameters that are currently not documented as

impaired but that have previous TMDLs or other action plans.

6. The total ammonia listing for **Rio Puerco (Arroyo Chijuilla to northern bnd Cuba), AU_ID NM--2107.A_40,** was erroneously attached to a 2007 TMDL document. This document does not contain a TMDL for ammonia. Therefore, the parameter IR Category has been changed from 4A (TMDL Complete) to 5/5C (more data needed before scheduling TMDL).
7. Temperature was added as a cause of impairment (IR Category 5/5B) for **Sandia Canyon (Sigma Canyon to NPDES outfall 001), AU_ID NM-9000.A_047**, based on thermograph data submitted by LANL during the 2017 call for data. The Assessment Rationale (formerly named the ROD) was updated accordingly.
8. Specific conductance was removed as a cause of impairment for **Tecolote Creek (I-25 to Blue Creek), AU ID NM-2212_10**, because there is no longer an applicable specific conductance WQC. The Assessment Rationale (formerly named the ROD) was updated accordingly.
9. **Coyote Creek (Mora River to Williams Canyon), AU_ID NM-2306.A_020**, was split into:

    Coyote Creek (Mora River to Amola Ridge), AU_ID NM-2306.A_020

    Coyote Creek (Amola Ridge to Williams Canyon), AU_ID NM-2306.A_023

COMMENT SET 1 – San Juan Watershed Group, Aztec, NM

From: SanJuan WatershedGroup [mailto:sanjuanwatershedgroup@gmail.com]
Sent: Monday, May 7, 2018 1:26 PM
Cc: Melissa May <melissa.may@sanjuanswcd.com>
Subject: Comments to NMED SWQB 303(D)/ 305(B) Integrated Report

Dear Ms. Guevara,
The San Juan Watershed Group would like to submit the following comments in response to NMED's SWQB 303(D)/ 305(B) Integrated Report. We will also send these as formal, written comments in the mail.

1) The Animas River (San Juan River to Estes Arroyo) has been de-listed for Nutrients. We believe this is an error. The "Integrated List" still lists Nutrients as an impairment for this section of the Animas, while the "2018 De-Listed Impairments" says it has been de-listed due to "Applicable WQS attained; based on new data." However, the "Assessment Rationale (ROD)" does not say this section of the Animas was de-listed and it does not mention any 'new data' that the decision may have been based on. If this de-listing is correct and new data has been used to determine that water quality standards are being met, the data should be described in the ROD and made public to allow for review by SJWG (and others) before concurring with the de-listing.

2) The Animas River (Estes Arroyo to So. Ute Indian Tribe bnd) has been de-listed for Temperature. However, there is some conflicting information regarding this de-listing. The

"Integrated List" still lists Temperature as an impairment for this section of the Animas but, the "2018 De-Listed Impairments" says it has been de-listed due to "Applicable WQS attained; based on new data." Additionally, the Assessment Rationale (ROD) does not mention the de-listing, but states that the ALU has been changed to "coolwater." If new data has been used to determine that this water quality standard is being met, then the data should be made public and described in the ROD to allow for review before concurring with the de-listing. If the ALU has in fact been changed to "coolwater," then the SJWG would like to see further justification of this decision in the ROD.

3) In the Assessment Rationale (ROD) for the San Juan River (Canon Largo to Navajo Reservoir), the "2018 Action" statement is probably misplaced, and should be moved to the section for the downstream reach of the San Juan River (Navajo bnd at Hogback to Animas River). Metals transported from the Gold King Mine Spill would only have affected the San Juan River downstream of the confluence with the Animas River.

We hope that these comments will be addressed in the final report.
Thank you for your time,

Jaclynn Fallon
Watershed Coordinator
sanjuanwatershedgroup@gmail.com

SWQB RESPONSE: *Thank you for your review and comment on the draft 2018-2020 Integrated List (Appendix A of the IR) and associated spreadsheets. The "2018 De-Listed Impairments" spreadsheet did erroneously note the impairments you mention in item 1) and 2) as de-listed. We have corrected the report error and regenerated and re-posted the "2018 De-Listed Impairments" spreadsheet. Regarding item 3), the 2018 Action Statement for the San Juan River (Canon Largo to Navajo Reservoir) AU was incorrect and has been moved to the San Juan River (Navajo bnd at Hogback to Animas River) AU. The corrected information has been re-posted to our website.*

COMMENT SET 2 – Thor Sigstedt, Santa Fe, NM

From: Thor Sigstedt
Sent: Friday, May 11, 2018 9:53 AM
Cc: adventuretrails
Subject: Input for the Galisteo Creek ; Deer Creek to 2.2 miles above Lamy

Hello Lynette,

This letter is to let you know that I read the various pieces regarding the upper reaches of the Galisteo Creek, with continued interest, of course. I find the various letters and information a little bit confusing, but I think I got the jist of it. What I got was that the stretch I am most interested in has been designated high quality cold water and that down the road continued temperature data will be looked at in order to continue the classification. So my request to you is to make that more clear to me so that I can understand the status of the designation and the future of it.

In addition, I want you to continue to refer to my comments over the years as well as thank you for reading them and caring about them. You can access them on my blog at this location: https://thor-sigstedt.blogspot.com and scroll down on the right to "Thor's Letter to the NMENV" and the full text will be there.

In addition, I have been taking temperature data for some years now and have this latest data (which is in addition to other data segments that I have sent to you over the years), so please let me know if this is in a format that is helpful. I set up a data recording system in a location suggested by you all back then, so this should be helpful. This is air temperature data.

Please let me know if there are any issues that I should know about concerning this subject, so that I can respond. I wish I could see it more clearly, so anything you can give me (especially if there is something I am not aware of that threatens the high quality cold water designation...)

Thank You Very Much!,

Thor Sigstedt

SWQB RESPONSE: *Thank you for your continued interest and sharing of knowledge of Galisteo Creek, and for the air temperature data. The Galisteo Creek assessment unit, 2.2 miles upstream of Lamy to its headwater, continues to have a High Quality Coldwater aquatic life use designation on the CWA 303(d)/305(b) Integrated List. Stream temperature information collected in the summer of 2014 indicated that Galisteo Creek (2.2 miles upstream of Lamy to headwaters) was not meeting the High Quality Coldwater aquatic life use temperature criteria. Consequently, a Total Maximum Daily Load (TMDL) document for temperature was completed and approved in 2017. Therefore, this stream is now eligible for development of a watershed-based planning document laying out opportunities to address problems impacting temperature within the watershed, as well as the subsequent availability of EPA non-point source restoration grants that could further our common goal in fostering a healthy watershed for Galisteo Creek. Funding opportunities and other restoration information are available at: https://www.env.nm.gov/surface-water-quality/watershed-protection-section/.*

COMMENT SET 3 – Lauren Chavez, Placitas, NM

From: Lauren Chavez
Sent: Thursday, May 31, 2018 4:56 PM
Subject: Fwd: Las Huertas Creek

RE: NM Clean Water Act 303(D)/ 305(B) Public Comment-

Dear Lynette,
I'm not sure if this particular case would fall under the impaired surface waters that the NM Clean Water Act 303(D)/ 305(B) is trying to list and assess, but if not, please refer me to the correct department. This case involves Las Huertas Creek, which is on the north side of the Sandias. NM Highway 165 runs up east through Placitas, and toward the canyon, and its approximately 1.5 miles from where the paved road turns to dirt road, where you'll find in the creek to the left, a concreted culvert acting as a dam, which diverts 100% of the water into Las Huertas Community Ditch's acequia. This work was done over the last few years, and the legality is in question. It is decimating Las Huertas Creek. Whether they have water rights is not the question, but whether they have viable agriculture to take 100% of this flow, and whether they attained an environmental impact permit from the Army Corp. of Engineers before building/altering land in National Forest Land. In a hydrological study done several years back, hydrologist Peggy Johnson found that this creek feeds much of the aquifer/water shed in the Placitas area. It is of major concern that the springs which our water system Las Acequias de Placitas and many other wells in the area are being impacted by this diversion, not to mention the riparian life down the creek. As you go further up the canyon, you'll see more culverts and diversions they've installed. If this falls under the category of this assessment, please add Las Huertas Creek to the list.

Please see the attached photos, and please call if you have any questions.

Thank you,

Lauren Chavez
Placitas, NM

SWQB RESPONSE: *Thank you for providing this information regarding flow alteration on Las Huertas Creek. Based on the information you provided, Las Huertas Creek has been changed to IR Category 4C – impaired due to Flow Regime Modification – on NM's Integrated List. In New Mexico, IR Category 4C waters are eligible for watershed-based planning and subsequent restoration funding through our CWA 319 program. Funding opportunities and other restoration information are available at: https://www.env.nm.gov/surface-water-quality/watershed-protection-section/. Regarding your other questions pertaining to land use, water rights, and whether or not this type of diversion is permitted, you will need to consult with the NM Office of the State Engineer (Middle Rio Grande area at the District 1 Albuquerque office) and the U.S. Army Corps of Engineers, respectively.*

COMMENT SET 4 – Los Alamos National Laboratory, Environmental Protection Division, Los Alamos, NM

Environmental Protection Division
Los Alamos National Laboratory PO
Box 1663, K490
Los Alamos, New Mexico 87545
(505) 667-0666

Date: **MAY 31 2018**
Symbol: EPC-DO: 18-210
LA-UR: 18-24658
Locates Action No.: *NIA*

Ms. Lynette Guevara
Environmental Scientist
New Mexico Environment Department
Surface Water Quality Bureau
P.O. Box 5469
Santa Fe, NM 87502

Subject: Los Alamos National Laboratory Comments to Draft 2018 - 2020 State of New Mexico Clean Water Act (CWA) Sections 303(d)/305(b) Integrated List of Assessed Surface Waters Integrated Report

Dear Ms. Guevara:

Enclosed for your consideration are Los Alamos National Laboratory's (LANL) comments to the New Mexico Environment Departments 2018-2020 CWA Sections 303(d)/305(b) Integrated List of Assessed Surface Waters Integrated Report (IR). LANL appreciates the opportunity to provide comments.

Please contact Robert Gallegos (505) 665-0450 of the Environmental Compliance Programs if you have questions.

Sincerely,

Taunia S. Van Valkenburg
Group Leader

TSVV:MTS:RMG:cmh

Enclosure:

1) LANL Comments to Draft 2018 - 2020 State of New Mexico Clean Water Act (CWA) Sections 303(d)/305(b) Integrated List of Assessed Surface Waters Integrated Report
    a) Attachment 1 - BLM Data-Quality Objectives and Data Quality
    b) Attachment 2 - Aluminum Manuscript

Copy: Shelly Lemon, NMED/SWQB, Santa Fe, NM, (E-File)
Kristopher Barrios, NMED/SWQB, Santa Fe, NM, (E-File)
Karen E. Armijo, NA-LA, (E-File)
William R. Mairson, ADESH, (E-File)
Enrique Torres, EPC-00, (E-File)
Taunia S. Van Valkenburg, EPC-CP, (E-File)
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ENCLOSURE 1

LANL Comments to Draft 2018 - 2020 State of New Mexico Clean Water Act (CWA) Sections 303(d)/305(b) Integrated List of Assessed Surface Waters Integrated Report

Attachment 1 - BLM Data-Quality Objectives and Data Quality
Attachment 2 - Aluminum Manuscript

EPC-DO: 18-210

LA-UR-18-24658

Date: MAY 3 1 2018

Comments on 2018 - 2020 NMED Integrated Report – 303(d) Listings

Comments to NMED

Los Alamos National Laboratory (LANL) provides the following comments to the New Mexico Environment Department (NMED) regarding its 2018 proposed 303(d) listings integrated report (IR) released on April 18, 2018 for public comment.

1) New and existing copper 303(d) listings

The five Assessment Units (AUs) proposed to be added to the 303(d) list with the existing seven AUs for 5C impairments due to copper should be reconsidered in light of the recent Biotic Ligand Model (BLM) Data Quality Objective (DQO)/data quality assessment (DQA) evaluations and findings (Windward 2018 - Attachment 1). Comparing Ambient Water Quality Criteria (AWQC) assessments for these five AUs in side-by-side samples, the hardness-based NM AWQC generate false positives[1] while BLM-based copper AWQC are not exceeded (acute AWQC). See Section 4.8 and Table 4-14 from the 2018 BLM DQO/DQA document (Windward 2018a). Given this information and that the NM AWQC have not yet been updated to adopt the current EPA 304(a) AWQC for copper[2] (i.e., the BLM), at a minimum, the 5C listing should be changed to Category 5B because the water quality standard is in question (i.e., the NM copper AWQC are based on 1996 EPA 304(a) criteria which were updated by EPA in 2007 to incorporate the BLM).

In the prior seven AU listings for copper, some of the samples had non-detect copper reported at a relatively high detection limit of 10 µg/L. Therefore, hardness-based and BLM-based AWQC exceedances based on the detection limit are uncertain (e.g., Pajarito Canyon, Two Mile Canyon to Arroyo de la Delfe, and Acid Canyon [Pueblo to headwaters]. Such exceedances could be re-evaluated using estimation techniques for the non-detected results (or the non-detected results could be excluded). In the case of BLM-based AWQC, these were the sole exceedances of the criterion.

Consider that BLM-based copper AWQC for Upper Sandia Canyon locations yielded a 3% exceedance frequency. Dissolved copper in 4 of 128 samples exceeded the acute BLM-based AWQC. Meanwhile hardness-based AWQC yielded a 48% exceedance frequency (i.e., 61 of 128 samples exceeded the acute hardness-based AWQC). This large difference in potential assessment conclusions illustrates the importance of considering the use of BLM-based AWQC for copper, rather than relying on the hardness-based AWQC. Similar findings existed for lead and zinc BLM-based AWQC, though no new listings are proposed and the one zinc listing for a LANL AU is proposed for de-listing because more recent data have attained hardness-based zinc AWQC (South Fork Acid Canyon).

SWQB RESPONSE: *Thank you for your review and comment. CWA 303(d)/305(b) assessments must be completed using the approved water quality standards identified in 20.6.4 NMAC (available at: https://www.env.nm.gov/surface-water-quality/wqs/) and the procedures specified in the current listing*

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[1] A false positive means a sample concentration would exceedance the status quo New Mexico hardness-based AWQC but would not exceed the prospective AWQC, in this case EPA 2007 freshwater copper AWQC (EPA 2007).

[2] The BLM is the basis of EPA 2007 nationally recommended AWQC for copper (EPA 2007). The copper BLM-based AWQC are acknowledged as one of the site-specific water quality criteria (SSWQC) options in New Mexico water quality standards [20.6.4.10(D)(4)(c)].

methodology (CALM, available at: https://www.env.nm.gov/surface-water-quality/calm/). At this time, SWQB cannot assess against BLM-based AWQC to determine CWA 303(d)/305(b) status. The above-mentioned copper impairments on the Pajarito Plateau have been changed from IR Category 5C to 5B in recognition of potential segment-specific criteria development. The 2018 Assessment Rational (formerly named the ROD) has also been updated with this information.

There were two dissolved copper results reported as non-detects with a detection limit of 10 ug/L in the assessment datasets provided by LANL in 2017 for Pajarito Canyon, Two Mile Canyon, Arroyo de la Delfe, and Acid Canyon [Pueblo to headwaters]. One of the Two Mile Canyon data points was assessed as Full Support for acute copper because the applicable WQC was 12.56 ug/L. Per the listing methodology (CALM, available at: https://www.env.nm.gov/surface-water-quality/calm/), the other data point was not assessed because the applicable WQC was less than 10 ug/L.

2) New and existing aluminum 303(d) listings

Given the concerns summarized below, aluminum listings should be changed to category 5B and notes added to the 2018 IR and ROD documents explaining that natural background sources overshadow and confound assessments of aluminum AWQC in most cases. NMED has used the 5B designation in the past for numerous other waters impacted by natural background sources of aluminum, but has not applied category 5B to LANL AUs listed for aluminum. TMDLs for aluminum are unrealistic if seeking only to control natural background sources. Revisions to the aluminum AWQC and its implementation guidance are needed. Perhaps the use of aluminum AWQC should focus only on known anthropogenic aluminum discharges or certain natural sources that may pose a realistic toxicity threat due to the presence of bioavailable aluminum (e.g., truly "dissolved" forms) and/or where precipitated aluminum hydroxide forms are present or likely to exist.

a. Use of "total recoverable" as a measurement basis for aluminum doesn't seem appropriate in this instance. While the criteria are currently based on "total recoverable" in NMAC, this is really a misnomer because attainment is based on results of samples analyzed after filtration, with filter size to be determined by NMED (NMED 2012, 2013, 2015). Perhaps a clearer basis could be provided for each affected listing in accordance with NMED guidance by stating the actual filter size used for the assessments and for determining the non-attainment, (i.e., whether an unfiltered sample or a 10-µm filtered sample).
b. In discussions with LANL and others, NMED has recognized that measurements of total recoverable aluminum are inappropriate and instead must rely on some pre-filtration to remove non-toxic mineral forms of aluminum present as a natural background source in suspended sediments in typical surface water samples (NMED 2012, 2013, 2015). Recent work at LANL has shown that using filter sizes including 10, 1, and 0.45-µm will result in non-attainment of the aluminum AWQC for undeveloped watersheds where anthropogenic sources are absent and the aluminum is attributable to natural background sources, e.g., Bandelier tuff geologic deposits (Windward 2018b; Windward and LANL [in press]).
c. The likelihood of potentially toxic precipitated aluminum hydroxide forms being present in typical natural surface waters is low to non-existent as suggested by the recent evaluations of historical data with respect to speciation and saturation(Windward and LANL (Attachment 2). While such forms of aluminum are known to be present in the toxicity test data used to generate AWQC, they appear to be transient and in the environment may not occur at all or may occur only under certain circumstances. LANL has been collaborating with NMED to develop further testing of environmental samples to determine if such potentially toxic forms of aluminum are present on the Pajarito Plateau (Windward 2018b).
d. In 2017, EPA issued new draft aluminum AWQC under §304(a) (EPA 2017). While these draft criteria have

not been finalized, public comments have echoed some of the above concerns as well as others, for which EPA has not yet responded. The recent work completed by LANL is important for EPA to consider before they finalize the aluminum AWQC (Windward and LANL [in press]; Windward 2018b, 2016a, b). Other work has shown that the EPA 2017 draft AWQC tend to be significantly higher than the current NM hardness-based AWQC and potentially significant differences in assessment outcomes are possible (Windward 2018a). Specifically, recent work showed that NM AWQC would result in false positive[3] AWQC exceedances for 11% of the unfiltered samples (n=457), 41% of the samples pre-filtered using a 10µm filter (n=149), 29% using a 1µm filter (n=34) and 44% using a 0.45µm filter (n=457). False negatives were zero for each sample preparation, except for the 0.45µm basis where false negatives using NM AWQC over EPA 2017 draft AWQC were negligible at 0.2%. Thus, many of the existing and new listings of AUs impaired by aluminum might be erroneous and TMDLs might be unnecessary if assessments were based on the current draft EPA 2017 AWQC for aluminum.

SWQB RESPONSE: *CWA 303(d)/305(b) assessments must be completed using the approved water quality standards identified in 20.6.4 NMAC (available at: https://www.env.nm.gov/surface-water-quality/wqs/) and the procedures specified in the current listing methodology (CALM, available at: https://www.env.nm.gov/surface-water-quality/calm/). At this time, SWQB cannot assess against draft EPA 2017 Aluminum AWQC to determine CWA 303(d)/305(b) status. The above-mentioned total recoverable aluminum impairments on the Pajarito Plateau have been changed from IR Category 5C to 5B in recognition of potential segment-specific criteria development and the draft EPA 2017 Aluminum AWQC guidance. The 2018 Assessment Rational (formerly named the ROD) has also been updated with this information.*

Regarding aluminum pre-filtration, section 3.1.2.1 of the Main CALM document describes the Department's approach to "…minimize mineral phases…" per 20.6.4.900J(2)(e) NMAC. Samples with concurrent turbidity greater than 30 NTU must be filtered with a 10-micron filter prior to analysis. Since concurrent turbidity data were not available for LANL stormwater data, all samples were presumed to have concurrent turbidity greater than 30 ug/L. Therefore, only the results from 10-micron filtered samples were assessed.

3) 303(d) Listings for PCBs

Two new AU 303(d) listings for PCBs are proposed in the 2018 IR to add to the existing list of 26 LANL AUs and 10 other AUs 303(d)-listed for PCBs across the state. In early 2018, LANL's contractor computed an updated 95-95 UTL[4] of 0.058 µg/L for PCBs attributable to anthropogenic baseline runoff, which is 90 times higher than the NM Human Health (HHWQC) for PCBs (0.00064 µg/L). This UTL represents 41 samples of runoff collected from 2009 to 2016 from undeveloped northern and western reference watersheds near LANL[5]. In NMED's 2018 IR assessment dataset in the Sandia Canyon AUs where PCBs exceeded the 0.00064 µg/L HHWQC (n=107). PCBs were less than the updated PCB baseline UTL in 44 % of the samples, and were less than the LANL 2012 baseline PCB UTL of 0.013 µg/L

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[3] A false positive means a sample concentration would exceedance the status quo New Mexico hardness-based AWQC but would not exceed the prospective AWQC, in this case EPA 2017 draft aluminum AWQC (EPA 2017).

[4] Upper tolerance limit. A 95-95 UTL is calculated at the 95 percent confidence limit on the 95th percentile, a common metric used by LANL and others in the past for characterizing background conditions in the environment (Dale et al. 2013; Ryti et al. 1998).

[5] The updated UTL was computed according to the background characterization framework described in the 2017 sampling and monitoring SEP DQO/DQA (Appendix B, Section B-6.1).

in 27% of the samples. Similarly, in the Pueblo Canyon AU dataset, 79% of the 58 PCB results were less than the updated PCB baseline UTL and 21% were less than the prior UTL. For the PCB dataset that exceeded the HHWQC in all other Pajarito Plateau AUs (n=190), 62% were less than the updated UTL and 29% were less than the prior UTL.

Thus, it is likely that exceedances of the PCB HHWQC are attributable to the baseline anthropogenic PCB concentrations. Therefore, we recommend NMED consider adding a note to this effect in its 2018 IR and ROD documents, as well as consider changing the PCB listing category from 5C to 5B. Finally, the current 5C status indicates additional data are needed, but it is not clear what these additional data needs are. Upon definition of the additional data needs, LANL will provide the requested information to NMED.

SWQB RESPONSE*: CWA 303(d)/305(b) assessments must be completed using the approved water quality standards identified in 20.6.4 NMAC (available at:* https://www.env.nm.gov/surface-water-quality/wqs/*) and the procedures specified in the current listing methodology (CALM, available at:* https://www.env.nm.gov/surface-water-quality/calm/*). SWQB is not in agreement with LANL regarding anthropogenic baseline runoff as a reason to change the CWA 303(d)/305(b) listing to 5B as PCBs are not naturally-occurring. In addition, while site-specific criteria can be based on natural background proven to protect the designated use (including a quantifiable human contribution), 20.6.4.10(E) NMAC prohibits modification of human-health criteria based on natural background. Therefore, these listings will remain IR Category 5C.*

4) 303(d) Listings for adjusted gross alpha

While NMED proposes no new listings of AUs impaired for adjusted gross alpha, across the state, a total of 30 AUs are currently 303(d)-listed for gross alpha, with 25 of these listings for LANL area waters. Similar to concerns expressed for baseline PCBs, natural background levels of gross alpha exist as has been demonstrated in several LANL reports over the years (LANL 2017b, 2014, 2013, 2007). In early 2018, LANL's contractor computed an updated 95-95 UTL for gross alpha normalized to suspended sediment concentration (SSC) of 190 pCi/g SSC attributable to natural background runoff. This UTL represents 43 samples of runoff collected from 2009 to 2017 from undeveloped northern and western reference watersheds near LANL, as well as the new SEP reference watersheds[6].

Using 25th and 75th percentile SSC values for this group of locations, the SSC-normalized UTL is back- transformed to 170 and 1900 pCi/L concentrations, respectively, which are one to two orders of magnitude higher than the 15 pCi/L WQC for livestock watering. In the 2018 IR dataset for LANL where gross alpha exceeded livestock watering WQC (n=132), all but one sample was less than the 75th percentile-based 1900 pCi/L UTL, and 74% were less than the 25th percentile-based UTL of 190 pCi/L. Comparing the 2018 IR dataset for LANL to the previous gross alpha UTL of 1490 pCi/L derived by LANL (LANL 2013) returns similar results indicating that gross alpha found in Pajarito Plateau waters is dominated by natural background sources. Thus, we recommend NMED consider adding a note to this effect in its 2018 IR and ROD documents, as well as consider changing the gross alpha listing category from5C to 5B until such a time as site specific WQC for gross alpha are adopted.

SWQB RESPONSE*: CWA 303(d)/305(b) assessments must be completed using the approved water quality standards identified in 20.6.4 NMAC (available at:* https://www.env.nm.gov/surface-water-quality/wqs/*) and the procedures specified in the current listing methodology (CALM, available at:* https://www.env.nm.gov/surface-water-quality/calm/*). Therefore, SWQB cannot assess using SSC-*

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[6] The updated UTL was computed according to the background characterization framework described in the 2017 sampling and monitoring SEP DQO/DQA (Appendix B, Section B-6.1).

normalized UTLs to determine CWA 303(d)/305(b) status. The above-mentioned adjusted gross alpha impairments on the Pajarito Plateau have been changed from IR Category 5C to 5B in recognition of progress towards potential segment-specific criteria development. The 2018 Assessment Rational (formerly named the ROD) has also been updated with this information.

5) Category 4B

Category 4B – In addition to the semi-annual report provided on June 29, 2017, please consider the following storm water management activities, currently being executed through the Supplemental Environmental Projects (SEPs), before reaching a final decision for withdrawal of Category 4B status in the Sandia Canyon AU:

a. A Low Impact Development (LID) Master Plan has been developed and finalized. The LID Master Plan will guide and prioritize future development of LID projects at LANL. The LID Master Plan applies to developed areas across the Laboratory and focuses on identifying opportunities for storm water quality and hydrological improvements in the heavily urbanized areas of Technical Areas 03, 35 and 53. TA-03 primarily drains to Sandia, Mortandad, Two Mile and Los Alamos Canyons. The LID Master Plan is organized to allow the addition of LID projects for other technical areas as time and funds allow in the future.
b. The LID Master Plan identifies a number of LID projects within the Sandia AU. Under the SEP, 5 projects will be designed and 2-3 will be constructed prior to the end of calendar year 2018. These projects are designed and constructed with the specific goal of improved storm water management.
c. Water Quality and Flow Monitoring – This work was carried out in 2017 and will continue through the rest of 2018. The monitoring will fill data gaps to characterize the sources of pollutants in storm water runoff and impacts on receiving waters in and around the Laboratory including the Sandia AU. Data gaps in discharge (volume and flow) will be addressed. A broad range of pollutants (including dissolved copper) are targeted from the following sources: Laboratory developed areas, Laboratory firing sites, natural landscapes, and atmospheric deposition.

***SWQB RESPONSE**: SWQB appreciates the planning and implementation efforts undertaken to reduce dissolved copper levels in the Sandia watershed. As stated in the Assessment Rationale (formerly named the ROD), the IR Category 4B demonstration for dissolved copper in this AU has been withdrawn following consultation with EPA Region 6. Storm water urban runoff is a significant contributor to dissolved copper water quality exceedances in the AU. In 2015, EPA issued a preliminary municipal separate storm water sewer system (MS4) determination for portions of Los Alamos County, including the Laboratory. As a result of EPA's preliminary determination, LANL suspended development and implementation of the Storm Water Management Plan. EPA has not yet issued a final MS4 determination, and LANL has not renewed efforts to develop and implement a storm water management plan. The IR Category 4B demonstration requires development and implementation of a comprehensive Storm Water Management Plan to address contamination in storm water runoff. When a comprehensive Storm Water Management Plan is developed and implemented, the IR Category 4B demonstration can be updated and reviewed for reinstatement. The IR Category 5C dissolved copper listing on the public comment draft has been changed to IR Category 5B (see SWQB response to LANL Comment #1, above).*

6) Sandia Canyon 2014-2016 Stream Temperature Data

In July 2014, LANS initiated a stream temperature study in the upper Sandia Canyon AU (NM-9000.A_047). The study will continue through 2018. The information derived from the study will be used to determine if a site specific standard or change in the designated use is warranted for Segment

20.6.4.126 NMAC in Sandia Canyon. Thermographs were placed at 5 locations within the AU. Interim findings, of data gathered in 2014 and 2016, indicate that the designated use of cold water aquatic life may not be attainable:

- Marginal cold water or cool water may best describe conditions in this reach because natural water temperatures resulting from natural ambient air temperatures prevent attainment of ColdWAL aquatic life use.
- The data show that the AUs measured surface water temperatures correlate to July average air temperatures in support of NMED's model.

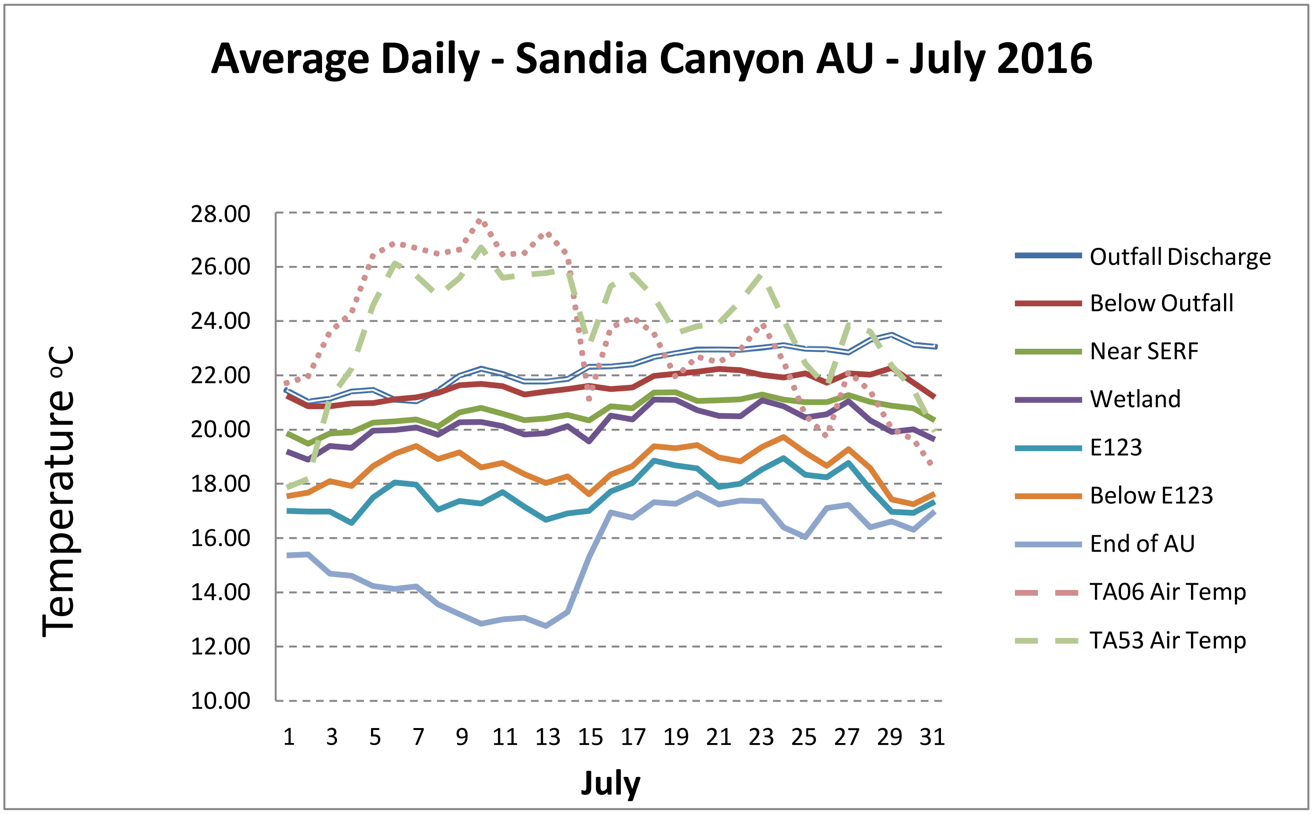
Thermograph Location	**Observed[a] Average Water Temperature °C**	**Observed[a] Maximum Water Temperature °C**	**PRISM[b]**			**ATEMP[c] °C Monthly Average**			**Average Air Temperature °C (1981 to 2010)[e]**	**Predicted 6T3 °C**	**Predicted Maximum (TMAX) °C**
			2014	2015	2016	2014	2015	2016	1991 - 2010		
Below Outfall	21.60	24.20	21.58	20.52	25.15	19.3	18.8	23.74[d]	20.1	25.75[c]/ (22.0)[e]	30.35[c]/ (26.4)[e]
Near SERF	20.65	24.58									
E123	17.67	23.16									
Below E123[f]	18.58	23.49									
At Sigma Canyon[f]	15.46	20.08									

Notes:

a. July 2016
b. PRISM – Lat: 35.8694 Lon: -106.3073 Elev: 7149
c. July Average Air Temperature – LANL TA-06 (and where noted TA-53) Monitoring Station ATEMP
d. LANL TA-53 Monitoring Station July 2016 (Insufficient Temp Data Available for the TA-06 Monitoring Station)
e. July Average Air Temperature 1981-2010 – LANL TA-06 Monitoring Station
f. Location added in 2016

Based on the information provided above, the IR Category designation of 5B should be retained because the temperature criteria is under review and cold water aquatic life (ColdWAL) use may not be existing or attainable. The figure below provides a July 2016 overview of stream temperatures at monitored sites.

SWQB RESPONSE: *Recognizing LANL has developed a draft UAA workplan for a proposed change from a Coldwater to Marginal Coldwater or Coolwater aquatic life use, SWQB agrees that the Sandia Canyon AU extending from Outfall 001 to Sigma Canyon (NM-9000.A_47) should be classified as IR Category 5B. The Integrated List and Assessment Rational (formerly named the ROD) have been updated with this information.*



7) Stipulated Agreement between NMED, Amigos Bravos and LANS

Pursuant to the Stipulated Agreement between NMED, Amigos Bravos and LANL, entered during the last Triennial Review, the United States Department of Energy and LANL agreed to meet and confer with Amigos Bravos regarding the appropriate level of water quality classifications for waters currently listed in Segment 128 (ephemeral and intermittent waters located within Los Alamos National Laboratory). In 2017, the Hydrology Protocol (HP) was applied to the AUs listed below. NMED, Amigos Bravos and LANS are working on a process to appropriately classify these waters to determine the most protective designated use:

- Ancho Canyon (below spring) - NM.9000.A_054
- Water Canyon (above State Road 501 to LANL Boundary) - NM.128.A_12
- DP Canyon (below grade control) - NM-128.A_10
- DP Canyon (above grade control) - NM-128.A_14

SWQB RESPONSE: *A note acknowledging these efforts was added to the Assessment Rational (formerly named the ROD). SWQB looks forward to working with LANS and Amigos Bravos on the other waters identified for water quality standards review under the Stipulated Agreement (e.g., Los Alamos, Mortandad, Pajarito, Ten Site, Two Mile, and Water canyons).*

8) Other Concerns for 2018 IR

a) Calculations and comparisons of observed concentrations to respective water quality criteria were not provided with NMED's public notice of the 2018 draft IR. LANL would appreciate the opportunity to receive and review NMED's related spreadsheets. We also would like to confirm that the sampling locations are appropriately representative of waters of the state.

SWQB RESPONSE*: SWQB is not required to provide all data and assessment spreadsheets as part of the public notice and has not done so in the past; there are a substantial number of individual files associated with each assessed watershed or region making this impractical. However, SWQB frequently fulfills requests to review and inspect public records and data. On May 23, 2018, SWQB fulfilled a public records request from LANL contractor Windward Environmental, LCC for the 2018 IR Pajarito Plateau datasets and draft 2018 IR conclusions. These final assessment datasets were based on files provided by LANL as stated in the QA review. The data files provided by LANL were re-formatted through a standard series of steps to create assessment input files for SWQB's automated assessment routines. These assessment input files were provided in response to the public records request by Windward Environmental, LLC. Regarding site selection and representation, watershed stations at the bottom of an assessment unit are presumed to be representative of the assessment unit unless other information indicates conditions in the assessment unit are not homogeneous.*

b) NMED's spreadsheet for new impairments appears to include 5 duplicated listings of AUs in the LANL vicinity, LANL respectfully requests that these duplicates be removed from the list.
    a. total recoverable cyanide – Upper and Lower Los Alamos Canyon
    b. total recoverable selenium – Upper Los Alamos Canyon and Lower Pueblo Canyon
    c. total PCBs – Arroyo de la Delfe

SWQB RESPONSE*: Thank you for your review and comment on the associated Integrated List spreadsheets. The "New Impairments" spreadsheet was automatically generated from our in-house assessment database and did indeed include duplicate new impairment rows because these new causes are impairing more than one Designated Use in their respective Assessment Units. The NMED IT Department has added a Designated Use field to this report so now each row is unique. The improved report has been regenerated and re-posted to* https://www.env.nm.gov/surface-water-quality/2018-2020-ir/*.*

c) Section II(A) (page 14) describes the state WQS review and update process. We appreciate the state's efforts to keep abreast of national science and policy regarding WQS (i.e., updates to §304(a) criteria). Because more than three years have passed since the most recent triennial review was completed (2014), NMED will likely begin preparations for the next triennial review process. In particular, LANL is interested in helping NMED adopt the EPA 2007 BLM-based copper AWQC statewide, as well as further refining the aluminum AWQC and its implementation guidance.

***SWQB RESPONSE**: Thank you for your continued interest in BLM-based copper AWQC and the aluminum AWQC. New Mexico's Water Quality Control Commission (WQCC) approved the most recent triennial review in January 2017 and EPA's final approval and technical support document were received in August 2017. Scoping for the next triennial review will begin in 2019. SWQB looks forward to any proposals that LANL would like to submit to the WQCC for consideration during the next triennial regarding BLM-based copper and aluminum AWQC.*

d) LANL is also interested in working with NMED to refine characterizations of natural background concentrations of constituents of concern (COCs) including but not limited to aluminum and gross alpha. LANL continues to believe consideration of natural background levels is vital in any clean water act compliance decision making, and that site specific water quality criteria based on natural background are needed. LANL has prepared a number of reports on natural background in the past that have led to productive discourse between NMED and LANL staff on the merits of the related data evaluation processes and findings. In 2017, LANL updated its background characterization framework (BCF) based on input from NMED. The updated BCF is described in the 2017 sampling and monitoring SEP DQO/DQA (Appendix B, Section B-6.1)(LANL 2017a). In 2018, LANL completed preliminary evaluations of historic data, as well as new datasets collected as part of the SEP intended for characterizing natural background concentrations of COCs. LANL would like to revisit the BCF with NMED and discuss the preliminary results mentioned in the specific comments above on aluminum, PCBs and gross alpha.

***SWQB RESPONSE**: SWQB appreciates these efforts. Please set up a meeting with our Standards, Planning and Reporting team to discuss further.*

e) Along the same lines as comment number 5 above, we are interested in working with NMED to refine characterizations of anthropogenic baseline COCs including, but not limited to, PCBs. LANL's preliminary evaluations of historic data in 2018 also included characterization of anthropogenic baseline and LANL would like to revisit the BCF with NMED and discuss these results.

***SWQB RESPONSE**: SWQB appreciates these efforts. However, PCBs are not eligible for consideration as natural background. Please see the response to LANL Comment #3. Please set up a meeting with our Standards, Planning and Reporting team to discuss other COCs further.*

f) In the Public Comment Draft of the IR, under Section V (C)(4) Storm water, text on Page 50-51 raises concerns and LANL respectfully recommends the text be revised to incorporate the following comments:
    a. The first sentence of the last paragraph states that storm water typically exceeds WQS. This seems to be an over generalization that might confuse the public about

regulatory programs such as NPDES vs §305(b) Integrated Assessments. While WQS can be used to screen discharges such as storm water, state WQS are typically not applied directly to discharges outside of NPDES permits, which often account for mixing and other instream water quality conditions. It would be more appropriate to say that in certain cases, storm water may contribute to exceedances of WQS in state waters, in which case NPDES permits would likely be required (via "reasonable potential analysis").

SWQB RESPONSE: *The first sentence has been changed from "Stormwater runoff also typically contains elevated concentrations of a variety of constituents that exceed WQS" to "Stormwater runoff often contains elevated concentrations of a variety of constituents that many contribute to WQS exceedences." The reference to NPDES permits in this sentence is unnecessary because there may not be a point source involved.*

b. The fourth sentence in the last paragraph provides a list of storm water quality concerns by including a statement that untreated storm water can kill aquatic life, i.e., via acute toxicity. The sentence makes it sound as though *any* untreated storm water would present such a concern. Typically, treatment is one line of defense in adaptive management after source control best management practices are found inadequate. Specific evidence of untreated storm water killing aquatic life is generally lacking. Therefore, LANL recommends that the sentence be revised to state the concern more generally, "storm water may carry certain toxicants that may be a concern depending on the nature of the receiving water and aquatic life".

SWQB RESPONSE: *The fourth sentence has been changed from "Untreated stormwater entering our waterways can kill aquatic life and result in the contamination of fish tissue and drinking water supplies; prohibit or limit swimming, fishing or boating; present dangers to public health and safety; and increase the frequency and magnitude of flooding" to "Depending on the nature of the receiving water, untreated stormwater entering our waterways may carry certain toxicants that may negatively impact aquatic life or drinking water supplies; prohibit or limit swimming, fishing or boating; present dangers to public health and safety; and increase the frequency and magnitude of flooding."*

g) The 2018-2020 IR lists the following AUs (within Sandia and Pueblo Canyon Watersheds) for total recoverable aluminum and dissolved copper as a cause of impairment for aquatic life use. Some water quality data were collected during storm water events and the resulting data represent periods of hydrologic instability that should not be used for assessment of chronic criteria, per NMED's CALM guidance. Thus, LANL requests that NMED add clarification as to whether the listings are based on exceedances of acute or chronic criteria.

- Acid Canyon (Pueblo to headwaters) - NM-97.A_002
- Pueblo Canyon (Acid Canyon to headwaters) - NM-9000.A_043
- Pueblo Canyon (Los Alamos Canyon to Los Alamos WWTP) - NM-99.A_001
- Graduation Canyon (Pueblo Canyon to headwaters) - NM-97.A_005
- South Fork Acid Canyon (Acid Canyon to headwaters) - NM-97.A_029
- Walnut Canyon (Pueblo Canyon to headwaters) - NM-97.A_004
- Sandia Canyon (Sigma Canyon to NPDES outfall 001) - NM-9000.A_047

a. Pueblo Canyon – In the fall of 2017 NMED's Hydrology Protocol (HP) was applied to waters within the Pueblo Canyon Watershed. The HPs were conducted as part of SEPs to determine stream flow hydrology. These waters are currently subject to the default water quality standards contained in NMAC 20.6.4.98 for intermittent waters. All of the Pueblo Canyon Watershed AUs were evaluated and received HP scores ranging from 2.5 to 24.5:

- Pueblo Canyon (Acid Canyon to Headwaters) - NM-9000.A_043
- Pueblo Canyon (Los Alamos WWTP to Acid Canyon – NM-97.A_006
- Pueblo Canyon (Los Alamos Canyon to Los Alamos WWTP) - NM-99.A_001
- Walnut Canyon (Pueblo Canyon to Headwaters) - NM-97.A_004
- Kwage Canyon (Pueblo Canyon to headwaters) - NM-97.A_003

Level 2 HP evaluations are warranted, and will be conducted in 2018, for Kwage, Graduation, Pueblo at E055 and Pueblo above E055. The current water standard is subject to confirmation via the HP and NMED/EPA approval, thus an IR Category designation of 5B may be warranted.

SWQB RESPONSE: *The above listings are based on exceedences of acute criteria in accordance with Section 3.1.2.2 of the listing methodology (CALM, https://www.env.nm.gov/wp-content/uploads/2017/03/FINAL-2018-Main-CALM.pdf). An AU Comment has been added to these listings. Aluminum and copper listings were changed to IR Category 5/5B in response to LANL Comments #1 and #2, above. Kwage Canyon is listed as IR Category 3C (Not Assessed) due to insufficient data.*

h) In Los Alamos Canyon and DP Canyon to Upper LANL Boundary (NM-9000.A_063), mercury (T) was first listed as a cause of impairment in the 2006-2008 IR. A review of data from May 2012 April 2018 do not show exceedances of the Livestock Watering use criteria of 10ug/l. Please consider removing Mercury (T) as a cause of impairment for Livestock Watering.

Location ID	Sample Date	Hg Report (ug/L)
Los Alamos abv DP	7/24/2012	0.2
Los Alamos abv DP	8/3/2012	3.29
Los Alamos abv DP	10/12/2012	0.629
Los Alamos abv DP	7/12/2013	1.59
Los Alamos abv DP	9/12/2013	1.81
Los Alamos abv DP	7/29/2014	1.28
Los Alamos abv DP	7/31/2014	2.42
Los Alamos abv DP	9/29/2017	0.255
Los Alamos abv DP	10/4/2017	0.524
Los Alamos blw Ice Rink	9/12/2013	0.798
Los Alamos blw Ice Rink	7/31/2014	0.243
Los Alamos blw Ice Rink	8/2/2015	0.272

SWQB RESPONSE: *Thank you for catching this error. Total mercury data collected on 7/11/2012 and 7/24/2012 at the station above DP Canyon (both 20 ug/L) indicated two exceedences of the 10 ug/L Livestock Watering criterion. However, these results were qualified as below the sample detection limit. Since the sample detection limit of 20 ug/L for these data points is greater than the 10 ug/l criterion, the results cannot be used for assessment. Therefore, total mercury has been removed as a cause of impairment for Livestock Watering. The 2018 Assessment Rational (formerly named the ROD) has also been updated with this information.*

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DATA-QUALITY OBJECTIVES AND DATA QUALITY ASSESSMENT: APPLICATION OF THE BIOTIC LIGAND MODEL TO GENERATE WATER QUALITY CRITERIA FOR FOUR METALS IN SURFACE WATERS OF THE PAJARITO PLATEAU NEW MEXICO

Prepared for:
Los Alamos National Security

April 27, 2018

Prepared by: Windward environmental LLC

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Table of Contents

Tables

Figures

Acronyms

%HA	percent humic acid
ACR	acute-to-chronic ratio
AOC	area of concern
AU	assessment unit
AWQC	ambient water quality criteria
BDL	below detection limit
BLM	biotic ligand model
DOC	dissolved organic carbon
DL	detection limit
DQA	data quality assessment
DQO	data quality objective
E	ephemeral
EIM	Environmental Information Management
EF	exceedance factor
EPA	US Environmental Protection Agency
ESA	Endangered Species Act
FAV	final acute value
FMB	fixed monitoring benchmark
gw	grams wet weight
I	intermittent
IP	individual permit
IWQC	instantaneous water quality criteria
LANL	Los Alamos National Laboratory
MLR	multiple linear regression
MTAL	maximum target action level
NMAC	New Mexico Administrative Code
NMED	New Mexico Environment Department
NMFS	National Marine Fisheries

NPDES	National Pollutant Discharge Elimination System
NTU	nephelometric turbidity unit
NWQMC	National Water Quality Monitoring Council
P	perennial
QC	quality control
SEP	supplemental environmental project
SMWU	storm water management unit
SR	state route
SSWQC	site-specific water quality criteria
SWQB	Surface Water Quality Bureau (of NMED)
TAL	target action level
TOC	total organic carbon
TU	toxic unit
USDA	US Department of Agriculture
USGS	US Geological Survey
WER	water effect ratio
Windward	Windward Environmental LLC
WM	snowmelt
WP	Persistent water
WQBEL	water quality-based effluent limit
WQS	water quality standard
WS	surface water
WT	storm water
WWTF	wastewater treatment plant

1 Introduction

The purpose of this document is to use the data quality objective (DQO) and data quality assessment (DQA) process to define an appropriate water quality dataset and then use it, in conjunction with the biotic ligand model (BLM), to generate preliminary ambient water quality criteria (AWQC) for aluminum, copper, lead, and zinc applicable to surface waters of the Pajarito Plateau in the vicinity of the Los Alamos National Laboratory (LANL). The BLM-based AWQC will be compared with current state of New Mexico AWQC for these four metals; the current New Mexico AWQC are based on hardness.

The BLM mechanistically accounts for the effects of multiple water chemistry variables on the bioavailability and toxicity of metals. This method is widely recognized nationally and internationally as the most scientifically advanced means of generating bioavailability-based AWQC. Typical BLMs employ measurements of up to 10 water quality variables, as described in Section 2. All BLMs characterize metal speciation and have the capacity to estimate metal toxicity to certain organisms, but only certain BLMs have been adapted to generate AWQC according to US Environmental Protection Agency (EPA) guidelines(EPA 1985), or other relevant international guidance. When in accordance with EPA guidelines, the AWQC generated by the BLM are regarded as instantaneous water quality criteria (IWQC), much like AWQC that are based on measurements of hardness at the time of sampling (i.e., state and EPA hardness-based AWQC).

EPA released nationally recommended AWQC for copper based on the BLM in 2007, after its initial draft in 2003 (EPA 2007, 2003a, b). In 2017, EPA considered a BLM for aluminum in its draft AWQC for that metal (EPA 2017). The state of New Mexico, like many other states, permits the use of the BLM as an option for generating SSWQC for copper, per EPA's 2007 copper AWQC (EPA 2007). However, SSWQC in general are subject to EPA review and approval until AWQC such as BLM-based copper criteria are adopted on a statewide basis; this recently occurred in the states of Idaho and Oregon (IDAPA 58.01.02, and OAR 340-041-8033 in (ODEQ 2016b, a) as a result of EPA Region 10 mandates related to Endangered Species Act (ESA) consultations on state WQS.

Ideally, the use of EPA's nationally recommended AWQC such as the 2007 BLM-based copper AWQC, would not lead to the need for SSWQC development for a particular location. In other words, EPA 2007 BLM-based copper AWQC should in one sense be as readily applicable as IWQC as are hardness-based copper AWQC stemming from EPA 1996 nationally recommended AWQC.

Key Definitions

- AWQC –ambient water quality criteria are state regulations or national policy documents and statements that define Section 304(a) criteria intended to broadly protect designated or beneficial uses regulated under the Clean Water Act; these regulations are applicable to wide geographic areas. AWQC are expressed as either fixed values or equations (models). The latter depend on one or more ambient water quality variables (e.g., hardness [metals], pH, or temperature [ammonia]) or more complex models such as multiple linear regression (MLR) models and the BLM.
- IWQC – Instantaneous water quality criteria are based on the application of AWQC to a particular set of values of dependent variables measured, calculated, or estimated for a particular set of conditions for a certain time at a location of interest. IWQC, by definition, will be time variable where dependent water quality parameters vary over time. Section 305(b) water quality assessments typically compare observed pollutant concentrations to concurrent IWQC.
- SSWQC – Site-specific water quality criteria (SSWQC) are AWQC that have been adjusted to local water quality conditions, typically to account for different bioavailability between the site of interest and laboratory toxicity testing waters used by EPA to generate nationally recommended AWQC. Typical SSWQC approaches include, but are not limited to, the water effect ratio (WER), recalculation, and resident species procedures (EPA 1994). SSWQC are typically used in long-term projections to determine the need for and set water quality-based effluent limits (WQBELs) in National Pollutant Discharge Elimination System (NPDES) permits. SSWQC are subject to EPA review and approval after adoption by state authorities in state water quality standards (WQS).

The DQO process, as described in Section 3, will be used to develop performance and acceptance criteria and to define study objectives with regard to using water quality data that have already been collected by LANL. Consequently, the focus of the DQO process will be to define the appropriate use of the existing data for the purpose of generating BLM-based IWQC. As an objectives-oriented and planning approach, the DQO process will establish data sufficiency and data handling rules that will help identify and minimize decision errors associated with analysis/project outcomes.

Each step of the DQO process is described in Section 3; given that data have already been obtained, Step 7 will be replaced with a description of a DQA. The DQA process (described in detail in Section 4) will evaluate the appropriateness and completeness of the data obtained from prior monitoring efforts conducted by LANL for surface waters of the Pajarito Plateau in the vicinity of LANL.

The focus of this evaluation process will be to maximize the number of appropriately usable water chemistry datasets for discrete surface water stormflow or baseflow sampling events. To characterize metal (i.e., copper, lead, zinc, and aluminum) bioavailability and calculate IWQC (using each applicable approach), a sufficient suite of BLM chemistry inputs is needed for each discrete water sampling event. The DQA process will identify the number of discrete sampling events for which complete or sufficiently complete BLM chemistry inputs are available and usable.

Sufficiently complete BLM chemistry inputs are somewhat dependent upon the metal being considered: For all of the metals in this evaluation, pH and dissolved organic carbon (DOC) are necessary key BLM inputs. Other chemistry inputs, such as alkalinity and hardness cations (e.g., calcium and magnesium), are also important, but values for these parameters can be estimated if information for other parameters is available. For example, alkalinity can be estimated from pH and the ambient concentration of carbon dioxide in the atmosphere, and major ions can be estimated from hardness and known or assumed ion ratios (Windward 2017). In addition, EPA (2016) provides nationwide eco-regional estimates (10th percentiles) of most BLM inputs and describes analyses that, based on correlations between BLM inputs and conductivity and stream order, can be used to estimate missing values for BLM inputs. Both approaches are similar in that missing BLM inputs can be estimated for a water body of interest if certain water quality data are available, while other parameters are estimable as indicated in EPA (2016).

In addition to identifying sufficiently complete datasets, the DQA process will identify data gaps and will describe the outcomes of analyses intended to support applicable data substitutions or estimates. Generally, if the dataset is rich enough, substitution or estimation of missing data can be supported by evaluating potential relationships among water chemistry variables (e.g., relationships between DOC and total organic carbon [TOC], or relationships between major ions and hardness or specific conductance). After completion of the DQA process, the goal will be to use the aggregated dataset to perform analyses that will address the objectives of this study.

The overall objective of this work is to evaluate the use of the BLM as a potential approach for developing SSWQC for copper, lead, zinc, and aluminum applicable to surface waters of the Pajarito Plateau in the vicinity of LANL. The State of NM has only adopted EPA 2007 copper AWQC as an SSWQC option in state water quality standards (20.6.4.10.D((4)(c) NMAC).

Prior to evaluating the applicability of the BLM, the availability of a sufficiently robust dataset of BLM inputs must be established. To aid evaluations, IWQC will be calculated using multiple approaches, including current New Mexico and EPA hardness-based AWQC, and BLM-based IWQC. For aluminum, an additional approach will be to calculate IWQC based on the current MLR approach proposed by EPA in its 2017 draft aluminum AWQC (EPA 2017). Each approach will be used in the context of AWQC, so that the intended level of protection is consistent with EPA guidelines for AWQC (EPA 1985).

Comparisons of IWQC and potential water quality assessment outcomes generated using each of the approaches will provide information regarding potential decision errors between the more accurate BLM-based approach and nationwide or statewide AWQC approaches. Additionally, this evaluation will consider resolving time-variable IWQCs to potential SSWQC using applicable approaches driven by the richness of the dataset. For example, use of fixed percentiles of the IWQC distribution or the fixed monitoring benchmark (FMB) approach may be applicable at specific locations or spatial aggregations of interest.

Specific objectives of this work include:

- Communication of the purpose and appropriate use of the BLM for generating IWQC and approaches for developing SSWQC based on the BLM
- Generation of hardness- and BLM-based IWQC for copper, lead, zinc, and aluminum, and MLR-based IWQC for aluminum based on available datasets at a wide array of sampling locations and events
- Evaluation of the different assessment outcomes for each metal by comparing observed dissolved metals concentrations with each of the IWQC outcomes for each sampling event
- Calculation of FMBs where sufficient data are available (concurrent IWQC and metals concentrations)
- Consideration of various spatial aggregations with regard to using locations individually or combining locations according to spatial features or assessment units (AUs) recognized by the Surface Water Quality Bureau (SWQB) of the New Mexico Environment Department (NMED).
- Recommendation of potential SSWQC approaches, limitations, and outcomes (e.g., FMB, MLR equation, or percentiles of IWQC)

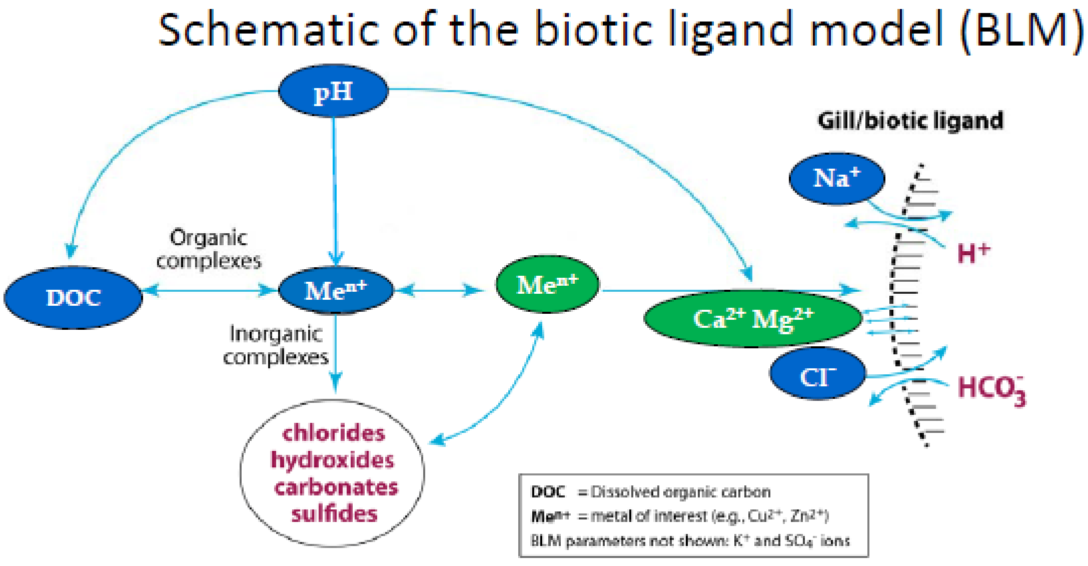
2 Background

This section provides background information about the development and use of the BLM, the LANL area waters and State of NM Water Quality Standards.

2.1 BLM BACKGROUND

The BLM is depicted schematically in Figure 2-1. The BLM is a tool that can mechanistically predict the bioavailability of a variety of metals under the wide range of water chemistry conditions that are observed in surface waters. The BLM is scientifically robust and defensible, user friendly, and freely available. BLMs have been developed for metals in both freshwater and saltwater environments. Windward

Environmental LLC (Windward) staff developed the BLM software that the EPA adopted as the basis of its 2007 nationally recommended freshwater AWQC for copper. The states of Oregon and Idaho have adopted the EPA 2007 copper AWQC statewide[1] and use the Windward BLM software. Other states have adopted the copper BLM on a more limited basis.



Green indicates only parameters used in hardness-based AWQC
Blue indicates additional parameters used in BLM-based AWQC

Adapted from Figure 1 in Paquin et al., 2002, Comp Biochem Physiol Part C, 133

Figure 2-1.Schematic of the BLM

Several BLMs, including those for aluminum, lead, and zinc have been evaluated for potential use as water quality standards (e.g., Santore et al. 2018; DeForest et al. 2017; DeForest and Van Genderen 2012). In addition to generating AWQC consistent with EPA 1985 guidelines, the BLM software can also generate metal speciation data as well as predictions for a variety of toxicity endpoints for various organisms and metals.

The BLM executable program that drives the user-friendly Windows Interface version of the BLM software (available at: http://www.windwardenv.com/biotic-ligand-model/) can be used in batch mode (i.e., with a command prompt) to perform BLM calculations efficiently for large datasets. Coupled with a data analysis platform such

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[1] Pursuant to ESA-related consultations on state WQS, EPA Region 10 required Oregon and Idaho to do away with hardness-based copper AWQC (EPA 1996 basis) and replace them, statewide, with EPA 2007 BLM-based AWQC for copper. As related to the 2012 National Marine Fisheries (NMFS) biological opinion (NMFS 2012), EPA did not approve the Oregon hardness-based copper AWQC (as well as other AWQC) in 2013 (EPA 2013). Similar ESA-related consultations in Idaho resulted in similar NMFS and EPA actions, leading to the 2015-2016 copper AWQC rulemaking and 2017 statewide adoption of copper BLM-based AWQC by Idaho.

as R (R Development Core Team 2010), the BLM executable provides a means to rapidly generate BLM outcomes (e.g., IWQC calculations, toxicity predictions for specific organisms/endpoints, or speciation calculations) for surface waters of interest. Such an approach, using the BLM in batch mode and R for analyses and graphics, was employed herein.

2.2 DESCRIPTION OF BLM INPUTS AND FUNCTIONS

Most metal BLMs, like the EPA 2007 copper BLM (EPA 2007), rely on 11 user inputs: pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, alkalinity, temperature, and percent humic acid (%HA). While %HA is an input parameter, measurements are not frequently available, so the BLM user's guide has recommended a default of 10% since EPA released the BLM-based copper AWQC in 2007 (HydroQual 2007; Windward 2015, 2017) Observed metals concentrations are not needed to generate BLM-based (or hardness-based) IWQC, because the IWQC depends only on the chemistry of the water of interest. Observed metals concentrations are needed for the purpose of generating toxic units[2] (TUs), which are the ratio of the observed metal concentration to the IWQC associated with a particular sample. The BLM user interface software generates TUs if user input is provided.

Observed metals concentrations are also needed to generate FMBs, which rely on distributions of observed metals and TUs. The FMB approach was first described in a 2008 report related to the approach's development and use in Colorado to address time-variable BLM-based IWQC (HydroQual 2008). EPA has been working on related FMB guidance (EPA 2012a), and more recent works further describe the FMB approach (Ryan et al. [in press]). The FMB approach is also mentioned as an implementation option in the Idaho and Oregon BLM-related copper AWQC documentation (McConaghie and Matzke 2016; IDEQ 2017).

Generally, measured concentrations in water samples that have been filtered through a 0.45-µm filter (i.e., operationally defined as dissolved concentrations) are used as BLM inputs. However, if it can be demonstrated that dissolved and total concentrations of BLM inputs are similar, then total (i.e., unfiltered) concentrations can be substituted if dissolved concentrations are not available for particular samples.

In addition to substitution approaches, it may be necessary to estimate concentrations for some BLM input parameters based on other measured parameters. However, this

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[2] TUs are meant to describe the quotient of the measured metal concentration and the IWQC (e.g., [metal]/[IWQC]). This quantity can also be described as an exceedance factor (EF). Regardless of the term used to describe the quotient, it is intended to provide information about the relative magnitude of the measured metal concentration with respect to the IWQC. A value > 1 indicates that the metal concentration exceeds the IWQC magnitude, and a value < 1 indicates that the metal concentration is less than the IWQC magnitude. A TU > 1 does not by itself indicate a water quality standard violation, nor does it mean that toxicity has occurred or is likely to occur; the TU is intended as a frame of reference for initial decision making.

estimation approach is contingent upon a demonstration that such estimates are appropriate and defensible (e.g., calcium and magnesium may be estimated from hardness; DOC may be estimated from TOC; other cations or anions may be estimated from relationships with conductivity or specific conductance).

Another approach to substituting missing BLM inputs makes use of the ecoregion-specific "default" estimates proposed by EPA (2016). Such an approach is being used by the state of Oregon to generate "default" criteria for purposes of initial screening assessments (ODEQ 2016a, b; McConaghie and Matzke 2016), although based on state-specific datasets rather than the EPA 2016 values. In either case, this type of approach will only be considered during this evaluation if available data limitations are extensive. It is not anticipated that this type of approach will be necessary with the LANL dataset.

2.3 APPLICATION OF BLM-BASED AWQC

BLM-based AWQC are intended to be applied to ambient receiving waters subject to numeric criteria applicable to existing, designated, or attainable uses, such as those defined in 20.6.4.97 through 20.6.4.899 of the New Mexico Administrative Code (NMAC). While BLMs can be used to evaluate the potential toxicity of a particular discharge, BLM-based AWQC are not intended to be applied directly to discharges. The State of NM has only adopted EPA 2007 copper BLM-based AWQC as a SSWQC option in state water quality standards (20.6.4.10.D((4)(c) NMAC).

2.4 SURFACE WATERS OF THE PAJARITO PLATEAU IN THE LANL VICINITY

For the Pajarito Plateau waters in the vicinity of LANL, the NMED SWQB has assigned various AUs to particular groups of water bodies with designated aquatic life uses specified in 20.6.4.121, 126-128 NMAC. NMED's § 305(b) assessments have resulted in § 303(d) listings for a number of Pajarito Plateau AUs, especially those within or adjacent to LANL, determined to be impaired by metals such as aluminum, copper, and zinc (NMED 2012b, 2018).

The vast majority of water bodies in the LANL vicinity are classified as ephemeral or intermittent streams, which are designated for a limited aquatic life use (20.6.4.128 NMAC), so these water bodies are subject only to acute numeric criteria. Just a few water bodies in the area are classified as perennial waters with higher-level designated aquatic life uses that apply both acute and chronic criteria (e.g., Upper Sandia Canyon, and isolated segments of Canon de Valle and Pajarito canyons linked with springs; and Rio Frijoles in Bandelier National Monument [20.6.4.126 and 20.6.4.121 NMAC, respectively]).

A number of other water bodies outside of LANL but within greater Los Alamos County are not specifically classified in state standards, but are protected as default intermittent waters under 20.6.4.98 NMAC. These waters are designated with a marginal warm water aquatic life use, which in turn also applies both acute and chronic criteria. These waters are largely found in Pueblo, Bayo and Guaje Canyons and associated tributaries, as well as segments of Canon de Valle, Pajarito and Water canyons upstream of the LANL western boundary.

3 Data Quality Objectives

EPA's *Guidance on Systematic Planning Using the Data Quality Objectives Process* (EPA 2006) will be used to establish DQOs. Per EPA, "The DQO Process is used to develop performance and acceptance criteria (or data quality objectives) that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions." Through DQO planning team involvement, the DQO process will systematically evaluate the problem, goals, and approach, as well as the intended use of the environmental data collected. EPA indicates that there are two primary types of intended use: decision making and estimation. The DQO process will identify the intended use and performance or acceptance criteria for the existing datasets provided by LANL necessary to meet the intended use.

The EPA DQO process is divided into the seven steps listed below:

1) State the problem.
2) Define study objectives.
3) Identify information inputs.
4) Define study boundaries.
5) Develop an analytical approach.
6) Specify performance and acceptance criteria.
7) Develop plan for obtaining data.

3.1 DQO STEP 1: STATE THE PROBLEM

Current federal and certain state WQS lag behind scientific advances in understanding metal bioavailability. Therefore, decision making using existing WQS may lead to significant errors that either under- or over-protect aquatic environments.

Examples of scientific advancements that have yet to be implemented as regulatory policy include development of BLMs for several metals in addition to copper; EPA does not yet recommend these BLMs for use as AWQC. Mature BLMs that have been evaluated for potential use as AWQC, using guidelines for the derivation of AWQC (EPA 1985), include lead (DeForest et al. 2017) and zinc (DeForest and Van Genderen 2012). The aluminum BLM (Santore et al. 2018) and a MLR for aluminum (DeForest et al. 2018) have both been evaluated by EPA (2017) as potential tools to use for the derivation of aluminum AWQC.

These approaches characterize the influence of water chemistry on metal bioavailability, through either mechanistic (i.e., understanding chemical speciation and accounting for the effect of bioavailable species) or empirical (i.e., utilizing the direct relationships between water chemistry and observed effects) means, to predict the potential for adverse effects under various water chemistry conditions. Many current AWQC for metals consider water hardness as the only toxicity-modifying factor in surface waters; the failure to account for the effects of other toxicity-modifying factors (e.g., pH, DOC, alkalinity, etc.) may lead to AWQC that are not appropriately protective in the waters to which they are applied. In other words, outdated approaches could lead to false negative and false positive compliance decision-making errors, which might otherwise be alleviated or minimized by using the most current science: the BLM.

3.2 DQO STEP 2: IDENTIFY STUDY GOALS

3.2.1 Primary study goals

The study goals are:

- Identify and use appropriate data to generate BLM-based IWQC for locations on or around the Pajarito Plateau in the vicinity of LANL.
- Characterize the potential decision-making errors in using current state or EPA AWQC that might be eliminated or minimized by using BLM-based AWQC.
- Provide recommendations regarding potential use of the BLM for the derivation of SSWQC outcomes.

In addition to BLM-based AWQC, other approaches—such as the MLR for aluminum described by DeForest et al. (2018) for characterizing the effects of toxicity-modifying factors (other than hardness)—will be considered.

3.2.2 Possible outcomes from the study

If application of the BLM to waters of the state on the Pajarito Plateau in the vicinity of LANL indicates that current AWQC are under- or over-conservative, then stakeholders could consider the following:

1) Alternative 305(b) assessments using the BLM, which could lead to an alternative determination, wherein the BLM shows that application of NMAC AWQC leads to false positives, or conversely, supporting a 303(d) Category 5 listing wherein the BLM shows that application of NMAC AWQC leads to false negatives
2) Implementing BLM-based AWQC, such as via SSWQC for the Pajarito Plateau waters appropriately characterized

3) More broadly adopting BLM-based AWQC as statewide options subject to the "performance-based" approach recommended by EPA (Wilcut and Beaman 2015).

If BLM-based SSWQC are demonstrated to be feasible for surface waters on the Pajarito Plateau in the vicinity of LANL, communication regarding the appropriate use of the BLM and/or other bioavailability-based WQC approaches should be provided as next steps.

3.3 DQO STEP 3: IDENTIFY INFORMATION INPUTS

3.3.1 Types of information needed

The following types of data and information are needed:

- Sufficiently complete sets of BLM input parameters for discrete water sampling events for surface waters in the LANL vicinity. Table 3-1 provides information regarding the importance and use of each BLM input parameter.
- Data for related parameters such as TOC, hardness, conductivity, and specific conductance should also be compiled for the purpose of evaluating potential strategies for filling data gaps for BLM inputs.
- Water chemistry data used for BLM calculations should have an appropriate "pedigree:" a defined sampling plan, sampling and analytical methods, sample handling, and quality control (QC) review.
- Generally, BLM inputs refer to dissolved concentrations (i.e., in sample filtered through a 0.45-µm filter prior to analysis), because the chemical interactions characterized by the BLM do not consider solubility or the presence of solid phases (with the exception of amorphous aluminum hydroxide(s) when predicting effect concentrations for aluminum). However, total (i.e., unfiltered) concentrations for BLM inputs will be considered as substitutions for dissolved concentrations if these types of substitutions are supported by the data.
- Measured dissolved metals concentrations are necessary for copper, lead, and zinc so that TUs can be computed (a TU being the ratio of an observed dissolved metal concentration to IWQC generated for the water chemistry in that same sample).
- For aluminum, unfiltered ("UF," i.e., total) and filtered concentrations (using filter pore sizes of 10-, 1-, and 0.45-µm; denoted as F10, F1, and F or F0.45, respectively) will be used for comparisons with IWQC and for calculation of TU values corresponding to each sample preparation type. Preparing computations based on all four bases for aluminum (UF, F0.45, F1 and F10) will help illustrate the potential differences in outcomes for the various sample preparations currently under consideration (UF by EPA 2017, F10 by NMED, F1 by LANL as a potential improvement over F10, and F0.45 status quo "dissolved").

The data and information inputs described above will determine the number of BLM-based IWQC that can be generated for the particular waters that have sufficient data. The EPA's recommended default estimated BLM input values for local ecoregions will not be employed, but they may be used for relativistic comparisons that might be instructive when considering further extrapolation. Aggregation of the BLM input data will identify where data gaps exist. Simultaneous aggregation of data for other water chemistry characteristics (e.g., TOC, hardness, specific conductance, etc.) will allow for evaluation of potential strategies to fill data gaps while systematically documenting which events are affected by data substitutions. Documenting substitutions will facilitate the identification of uncertainties associated with BLM-based IWQC calculations.

Table 3-1. BLM input parameters

Parameter	Comments
Metal of interest (e.g., aluminum, copper, lead, zinc)	not necessary for calculation of IWQC, but necessary to calculate TUs (or exceedance factors)
Temperature	required for all BLMs
pH	necessary for speciation and competing ion; required for all BLMs
DOC	necessary for speciation; required for all BLMs[a]
%HA	typically assumed to be 10% per BLM User Guides (i.e., 10% of organic matter assumed to be humic acid); required for all BLMs
Calcium (Ca)	necessary as a competing ion; required for all BLMs[b]
Magnesium (Mg)	necessary as a competing ion; required for all BLMs[b]
Sodium (Na)	necessary as a competing ion; required for all BLMs[b]
Potassium (K)	necessary for charge balance; required for all BLMs[b]
Sulfate (SO_4)	necessary for charge balance; required for all BLMs[b]
Chloride (Cl)	necessary for charge balance; required for all BLMs[b]
Alkalinity	necessary for inorganic speciation calculations; required for all BLMs[c]

[a] Input for DOC is needed; if missing, fraction of TOC could be substituted, if relationship is demonstrated.

[b] Input for major ions is needed; if missing, could be estimated from hardness, conductivity, specific conductance, or location average, if relationships are identified or if substitution is deemed defensible (HydroQual 2007; EPA 2016).

[c] If missing, alkalinity can be estimated using pH and atmospheric carbon dioxide (HydroQual 2007).

%HA – percent humic acid
BLM – biotic ligand model
DOC – dissolved organic carbon
IWQC – instantaneous water quality criteria
TOC – total organic carbon
TU – toxic unit

3.3.2 Sources of information needed

The primary source of information for this evaluation will be surface water monitoring data collected by LANL. The data will be queried and extracted from LANL's Environmental Information Management (EIM) database. Data collected by NMED will not be used because they lack measured DOC data. In addition to data from

LANL, surface water data from the National Water Quality Monitoring Council (NWQMC) will be used to identify other relevant data for surface waters in the LANL vicinity and greater New Mexico area (e.g., the Rio Grande at Otowi Bridge, Rio Grande below Cochiti Dam, and Rio Grande at San Felipe). The NWQMC's data portal consolidates water quality data from EPA's STORET database, the US Geological Survey's (USGS's) National Water Information System database, and the US Department of Agriculture's (USDA's) STEWARDS database (https://www.waterqualitydata.us/wqp_description/).

3.4 DQO STEP 4: DEFINE STUDY BOUNDARIES

3.4.1 Temporal boundaries

The temporal boundaries associated with this effort will be determined by the time periods over which sufficiently complete BLM input data exist for surface waters in the LANL vicinity. If supplemental data are obtained for additional waters within the LANL vicinity (e.g., the Rio Grande), the temporal boundaries associated with those data will be dictated by national water monitoring programs at various historical and current monitoring locations. Surface water sampling events can be either some form of dry weather baseflow (springs, snowmelt) or wet weather stormflow generated by rainfall; both baseflow and stormflow can be sampled by one or more of LANL's storm water monitoring programs.

Regarding appropriate application of IWQC calculations for AWQC durations, the temporal nature of the receiving water will be considered. Acute IWQC will be relevant for all locations that are considered ephemeral, intermittent, or perennial waters. Chronic IWQC will be relevant only for defined perennial waters in the area: Frijoles in Bandelier [20.6.4.121 NMAC] and perennial waters within LANL [20.6.4.126 NMAC]. If usable data are available, chronic IWQC may also be evaluated for the effluent-dependent waters in upper Sandia Canyon and lower Pueblo Canyon as they relate to the discharges from the LANL wastewater outfall 001, and Los Alamos County wastewater treatment plant, respectively.

3.4.2 Spatial boundaries

BLM-based IWQC will be generated for each of the surface water locations in the LANL vicinity that have usable datasets. These locations are generally similar to those identified in the 2017 sampling and monitoring supplemental environmental project (SEP) DQOs (LANL 2017a). The locations are expected to represent a broad array of surface waters that include the major and minor watersheds on the Pajarito Plateau in the LANL vicinity. LANL has already characterized the watersheds associated with many sampling locations as predominated by either developed or undeveloped characteristics. Sampling locations within some of the developed watersheds have been designated as "Site," because they are downstream from actual or potential storm water runoff from solid waste management units and areas of concern regulated under LANL's NPDES individual permit.[3]

Numerous locations within undeveloped watersheds have been sampled extensively as part of past efforts to characterize natural background concentrations of various constituents stemming from upstream locations, i.e., the LANL western boundary, and Northern Reference Watersheds(LANL 2014, 2013, 2012). In addition, more recent sampling programs were develop to characterize additional natural background reference locations further removed and upwind from LANL activity, i.e., the new SEP Reference Watershed monitoring commenced in 2017(LANL 2017a). Where usable data exist, BLM-based IWQC will be generated for nearby perennial waters where the USGS operates monitoring stations (e.g., Rio Grande River).

3.5 DQO STEP 5: DEVELOP ANALYTICAL APPROACH

The source dataset will be provided by LANL, based on a query of the LANL EIM database constructed to provide all available records for the following:

1) BLM analytes, starting with pH & DOC pairs
2) Secondary analytes that can aid in filling data gaps and further interpretation of the BLM dataset and outcomes
3) Water sample types including surface water (WS), snowmelt (WM), persistent flow (WP), and storm water (WT)
4) Sampling location names, aliases, and coordinates for known surface waters
5) QC and other information available from EIM

LANL staff will provide additional information about sample locations (e.g., developed/undeveloped landscape designations, major/minor watershed names). LANL staff will also identify data potentially affected by wild fires; fire-affected data will not be removed but will be plotted separately in various evaluations to help visualize potential anomalies.

The LANL dataset will be aggregated and evaluated to determine the extent to which BLM-based IWQC can be generated for each discrete event for the locations provided. Initial dataset aggregation will be intended to identify the number of complete BLM scenarios that can be considered, as well as the number of data gaps present. Subsequent to initial dataset aggregation, strategies to fill data gaps will be evaluated.

For the purpose of calculating BLM-based IWQC, a measurement of pH and organic carbon for each sampling event will be required (either measured DOC or an

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[3] Collectively, LANL refers to storm water management units (SWMUs) and areas of concern (AOCs) as "Sites" (with a capital "S").

appropriate estimate of DOC calculated from measured TOC). Steps for establishing BLM inputs for any sampling event include:

1) With the exception of alkalinity, DOC, and pH, determine measured concentrations of each input from filtered samples for each event.
2) If measured concentrations are not available from filtered samples, determine if measured concentrations are available from an unfiltered sample from the same event, and evaluate if those data can be used to determine estimates.
3) If measured concentrations are not available from filtered or unfiltered samples, determine if BLM input can be estimated from another water chemistry characteristic (e.g., hardness or specific conductance).
4) If measured concentrations are not available from filtered or unfiltered samples, determine if a location-specific estimate (e.g., location average) can be used as an estimate.
5) If no data are available for a BLM input, determine if regional information can be used.
6) If no data are available for a BLM input, and regional information are not available or suitable, perform a sensitivity analyses to identify an appropriately conservative input value (this may be most appropriate for temperature).

During data aggregation and summary, supporting information will be provided to demonstrate the adequacy and defensibility of strategies used to fill data gaps. It is known that temperature data are missing for the entire dataset, so a uniform temperature will need to be assumed, and a sensitivity analysis will need to be performed across the range of BLM calibration temperatures, e.g., 10 to 25 °C specified in the BLM user's guides (HydroQual 2007; Windward 2015).

Detection statuses of analyte concentrations will be considered during data aggregation, and BLM inputs will be treated differently than the metals of interest (i.e., aluminum, copper, lead, and zinc). For BLM input parameters, concentrations that are flagged as below detection limit (BDL) or not detected will be replaced by ½ of the reported detection limit (DL). Because a zero concentration is not allowed as an input to the BLM, a substitution approach using ½ of the reported DL is reasonable, as other approaches (e.g., maximum likelihood estimation and regression on order statistics) are not appropriate for discrete samples. When the concentration of a metal of interest is reported as BDL, the DL will be used and the sample will be flagged as BDL. This convention is used so that comparisons between metal concentrations and associated IWQCs will be conservative. Generally, concentrations of BLM inputs are not often affected by detection limits, whereas metals concentrations are affected more frequently.

Using the aggregated data, IWQC will be generated for each metal considered using the approaches described in Table 3-2, summarized as follows:

- Aluminum:
    - BLM-based chronic (and potentially acute) WQC using Santore et al. (2018)
    - MLR-based acute AWQC using EPA (2017) [4]
    - Hardness-based acute WQC using NMAC.20.6.4.900(I)
- Copper:
    - BLM-based acute AWQC using (EPA 2007)
    - Hardness-based acute WQC using NMAC. 20.6.4.900(I)
- Lead:
    - BLM-based acute AWQC using DeForest et al. 2017
    - Hardness-based acute WQC using NMAC. 20.6.4.900(I)
- Zinc
    - BLM-based acute AWQC using DeForest and Van Genderen (2012)
    - Hardness-based acute WQC using NMAC.20.6.4.900(I)

The relevant BLMs will be applied to the aggregated BLM input dataset using the BLM binding constants provided in Table 3-3, which represent the strength of binding of bioavailable metal species and competing cations to the biotic ligand. Reactions at the biotic ligand are characterized as equilibrium complexation reactions at a toxicologically relevant surface (e.g., gill surface), facilitating the competitive interactions among metal species and competing cations. The BLM parameter descriptions for copper, lead, and zinc are taken directly from EPA (2007), DeForest et al. (2017), and DeForest and Van Genderen (2012), respectively. For aluminum, the BLM description in Table 3-3 represents calibration to chronic toxicity data and is taken directly from Santore et al. (2018). A conservative translation of chronic aluminum IWQC to acute aluminum IWQC will be performed using an acute-to-chronic ratio (ACR) derived from EPA (2017). If resources are sufficient to apply the chronic aluminum BLM to the acute AWQC dataset described by EPA (2017), a direct calculation of acute aluminum IWQC may be performed using the aluminum BLM described by Santore et al. (2018).

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[4] The EPA (2017) MLR approach uses the following equations from DeForest et al. (2018) to normalize the acute and chronic species sensitivity distributions for aluminum to facilitate calculation of WQC:

Normalized Invertebrate ECX =

$$exp^{\left(\ln(ECX_{meas})-0.525*(\ln(DOC_{meas})-\ln(DOC_{site}))-11.282*(pH_{meas}-pH_{site})-2.201*(\ln(hardness_{meas})-\ln(hardness_{site}))+0.663*(pH^2_{meas}-pH^2_{site})+0.264*(pH_{meas}*\ln(hardness_{meas})-pH_{site}*\ln(hardness_{site}))\right)}$$

Normalized Vertebrate ECX =

$$exp^{\left(\ln(ECX_{meas})-0.503*(\ln(DOC_{meas})-\ln(DOC_{site}))-3.131*(pH_{meas}-pH_{site})-3.443*(\ln(hardness_{meas})-\ln(hardness_{site}))+0.494*(pH_{meas}*\ln(hardness_{meas})-pH_{site}*\ln(hardness_{site}))\right)}$$

Table 3-2. AWQC calculation approaches

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

BLM – biotic ligand model
DOC – dissolved organic carbon
EPA – US Environmental Protection Agency
MLR – multiple linear regression
NMAC – New Mexico Administrative Code
WQC – water quality criteria

The hardness- and MLR-based equations for aluminum AWQC described above, will also be applied to the BLM input dataset. For all approaches utilizing hardness to generate IWQC, hardness will be either the value reported for filtered samples, or the value calculated based on calcium and magnesium concentrations reported for filtered samples.

Where suitable observed metal concentrations are available (i.e., dissolved concentrations for copper, lead, and zinc; total and dissolved concentrations for aluminum), they will be compared to calculated IWQC. These comparisons will be made by calculating a TU (or quotient of the reported metal concentration and the IWQC) for each approach that is used to calculate IWQC (e.g., hardness-, MLR-, or BLM-based). When a metal concentration is flagged as BDL and is then compared to a calculated IWQC by determination, the TU will be described as less than the calculated value.

Table 3-3. BLM-binding constants for copper, lead, zinc, and aluminum

Biotic Ligand Model Parameter	Copper (EPA 2007)	Lead (DeForest et al. 2017)	Zinc (DeForest and Van Genderen 2012)	Aluminum (Santore et al. 2018)
Biotic ligand (BL) reactions with specified chemical constituent; logarithm of equilibrium constant is shown (i.e., Log K)[a]				
BL-H	5.4	4	6.39	5.4
BL-Ca	3.6	5.1	3.82	4.8
BL-Mg	3.6	4	3.31	
BL-Na	3	4.2	2.59	3.3
BL-Cu	7.4	X	X	X
BL-CuOH	-1.3	X	X	X
BL-Pb	X	6.65	X	X
BL-PbOH	X	-0.4	X	X
BL-Zn	X	X	5.41	X
BL-ZnOH	X	X	-2.4	X
BL-Al	X	X	X	4.4
BL-AlOH	X	X	X	-1.9
BL-$Al(OH)_2$	X	X	X	-7.75
BL-$Al(OH)_4$	X	X	X	-21
BL-AlF	X	X	X	8.5
Sensitivity parameters for calculating 5th percentiles of genus sensitivity distributions[b]				
Acute critical accumulation (nmol/gw)	0.03395	0.0628	5.388	na
Chronic critical accumulation (nmol/gw)	X	0.000341	0.345	na
ACR ratio (if used)	3.22	X	X	5

[a] Log K represents the overall formation of the biotic ligand (BL) complex indicated. For example: $BL^- + Cu^{2+} + OH^- = BL\text{-}CuOH$; Log K = -1.3.

[b] Acute and chronic critical accumulation values represent the amount of metal required at the biotic ligand to elicit an effect commensurate with the 5th percentile of the acute or chronic genus sensitivity distribution.

ACR – acute-to-chronic ratio na – not applicable gw – grams wet weight

The calculated TUs will be used as a basis for evaluating the frequency of decision errors that may be encountered when using a hardness-based IWQC approach vs. a BLM-based IWQC approach. To evaluate potential decision error frequencies among the various AWQC bases, a quadrant diagram will be used (Figure 3-1). Such diagrams provide a simple summary of the relative differences among potential outcomes, and the magnitude of those differences when using different approaches to generate IWQC.

- TUs plotted in the lower right quadrant indicate a “false positive” where TUs are > 1 based on hardness but < 1 based on the BLM[5].
- TUs plotted in the upper left quadrant indicate a “false negative” where TUs are < 1 based on hardness, but > 1 based on the BLM.
- TUs plotted in the upper right and lower left quadrants indicate equivocal results (exceedances and non-exceedances, respectively).
- Perfect agreement between the two outcomes would be indicated by data points falling on the 45 degree line intersecting the origin (where the TU axes cross at values of 1).
- Relative discord between outcomes increases logarithmically as data points fall further from the 45 degree line. In other words, besides decision errors, tendencies towards incipient errors can also be visualized rapidly using quadrant plots like Figure 3-1.

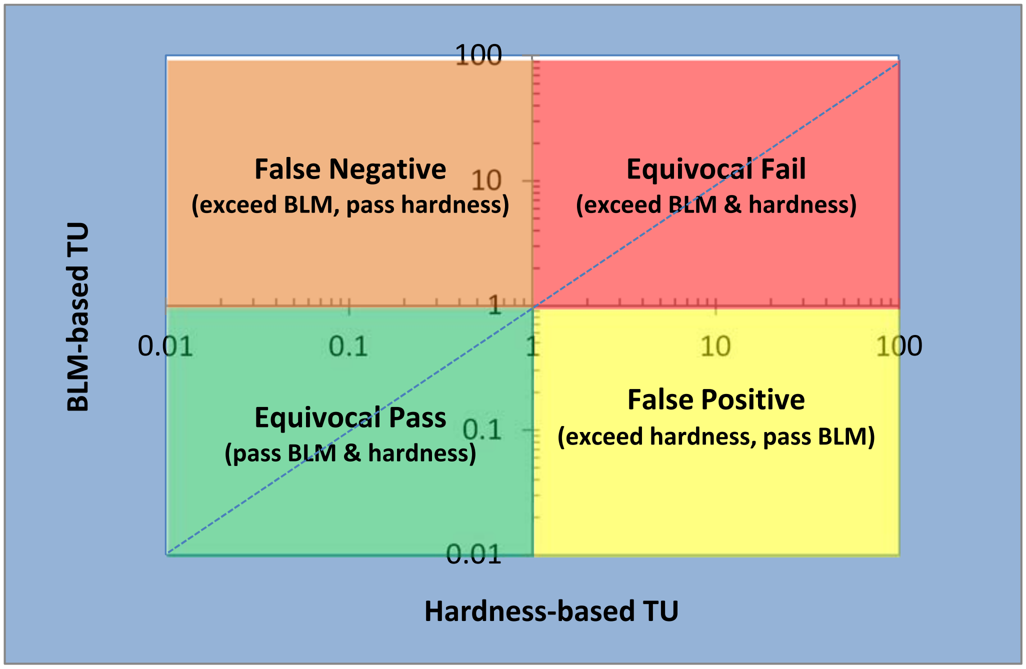

Figure 3-1.TU quadrant diagram for evaluating decision error frequency and magnitudes

In addition to the simple comparisons of various IWQC approaches, TUs can be used with reported concentrations and IWQCs to calculate FMBs for a given location (Ryan et al. [accepted]). An FMB for a given location is intended to provide a benchmark

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[5] For aluminum, TU quadrant diagrams will also be used to compare the EPA 2017 MLR-based IWQC with hardness-based IWQC.

that, if not exceeded, is an indicator of WQC attainment. An FMB has potential utility as a SSWQC when IWQC time variability needs to be taken into account but is contingent upon the availability of a sufficient number of BLM datasets with BLM inputs and concurrent observed metals data.

With respect to the number of samples needed for calculation of FMBs, a definitive number of samples necessary is not known *a priori*. FMB calculations are affected by the variability of measured metal concentrations and calculated IWQCs, and their correlation. For the purpose of generating initial FMBs, calculations will only be performed when ten or more paired metal and IWQC observations are available for a particular location (or other relevant level of spatial scale). The FMB approach was originally developed for discrete locations (e.g. those downstream from a wastewater outfall), but aggregation of locations among AUs will be considered for this project, as well as potential larger spatial scales (watersheds) and different temporal scales (base flow vs. storm flow).

3.6 DQO STEP 6: SPECIFY PERFORMANCE AND ACCEPTANCE CRITERIA

The performance and acceptability of the BLM-based IWQC results will be primarily based on whether sufficient water chemistry data are available to generate BLM-based IWQC for the locations of interest. If data substitutions or estimates are necessary for the most important/sensitive BLM inputs (pH & DOC), the results of the BLM will be qualified as uncertain.

Performance criteria include:

- BLM- and other bioavailability-based WQC calculations should be performed only when pH and organic carbon (preferably DOC, but substitution based upon TOC may be appropriate) are measured for the same water sampling event.
- Substitution or estimation of other missing BLM input parameters should be supported by available data (e.g., relationship between dissolved and total concentration of input parameter).
- To evaluate potential decision errors based on various approaches for calculating WQC, measured metal concentrations must be available so that TUs can be calculated.
- To use the FMB approach to derive potential site-specific benchmarks, a sufficient number of TUs should be available (sufficient number depends on behavior of the data [i.e., distributions, correlations, variability]).

Acceptance criteria include:

- Sampling locations should be verified as surface waters (i.e., lying on NMED SWQB AUs) and not direct storm water discharges from developed areas.
- Data used for calculations should be validated.

- Models used for calculations should be applicable and defensible for the purpose of calculating WQC.
- Uncertainty should be characterized qualitatively and quantitatively (where possible) for decision making.

3.7 DQO STEP 7: DEVELOP PLAN FOR OBTAINING DATA

Surface water data, including BLM inputs, have been collected by LANL at a variety of locations since 2005. Routine monitoring for BLM inputs appears to have begun in 2013 at many additional locations. To perform the analyses described above, water quality data associated with receiving water samples collected by LANL were requested in January 2018. Data were queried by LANL staff from LANL's EIM database and provided in Excel format. Supplemental water quality data for the Rio Grande and other locations of potential interest will be obtained from the water quality portal: https://www.waterqualitydata.us/wqp_description/

4 Data Quality Assessment

This section describes the results of the DQA for the BLM dataset provided by LANL. A dataset, consisting of 95,743 records for various analytes (including BLM inputs) from 66 different locations was provided by LANL. This dataset was generated by a number of LANL monitoring programs that are understood to have had specific sampling plans and data quality comparable to those evaluated in LANL's recent sampling and monitoring SEP DQO/DQA (LANL 2018a, 2017a).

The LANL BLM dataset comprised 48 locations[6], which were surface water sampling locations known or believed to represent many surface water AUs recognized by the NMED SWQB. LANL provided the list of sampling locations with additional information that was used for these determinations[7] (Table 4-1). The 48 surface water sampling locations in the LANL BLM dataset represent two distinct groups: 1) 12 surface waters with watersheds outside of, or upstream from the LANL facility and Los Alamos town site ("undeveloped" landscape type in Table 4-1), and 2) 36 surface waters within or downstream from the LANL facility and Los Alamos town site and other unincorporated areas of Los Alamos County ("Site" landscape type in Table 4-1).

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[6] Data provided by LANL for 18 locations were excluded from the BLM dataset because they represented storm water discharge locations deemed inappropriate for the application of AWQC, i.e., they are not sampling locations in surface water AUs

[7] Sample location names were simplified by Windward to aid evaluations and plotting (the more information-rich mnemonics were selected between choices of Location ID and Location Alias).Windward also used GIS tools to measure distances to the nearest AU (based on NMED shapefiles for AUs.) In many cases in Table 4-1, the distances are considerable because sampling locations on small tributaries are well-removed from the mapped AU main stems.

Of the 12 upstream/offsite locations, 7 locations have been characterized as "natural background" locations[8] in various LANL reports that have characterized background water quality conditions(LANL 2007, 2010b, 2013, 2014, 2015, 2017b, 2018a), four locations are being characterized as part of the SEP[9], and 1 location is in Bandelier National Monument (E350). The 36 downstream locations ("Site" landscape type in Table 4-1) are some of the numerous gaging stations operated by LANL with relatively long periods of water quality and discharge monitoring data. All surface water sampling locations with sufficient BLM datasets, as described below, are shown in Plate 1.

In addition to results for the LANL dataset, supplemental BLM datasets from the NWQMC database for locations in New Mexico were acquired and evaluated. This dataset included data for a total of 18 locations in New Mexico, but most locations, with the exception of those from the Rio Grande, contained ≤ 5 complete BLM sampling events. Thus, the BLM evaluations will focus on the five Rio Grande locations.

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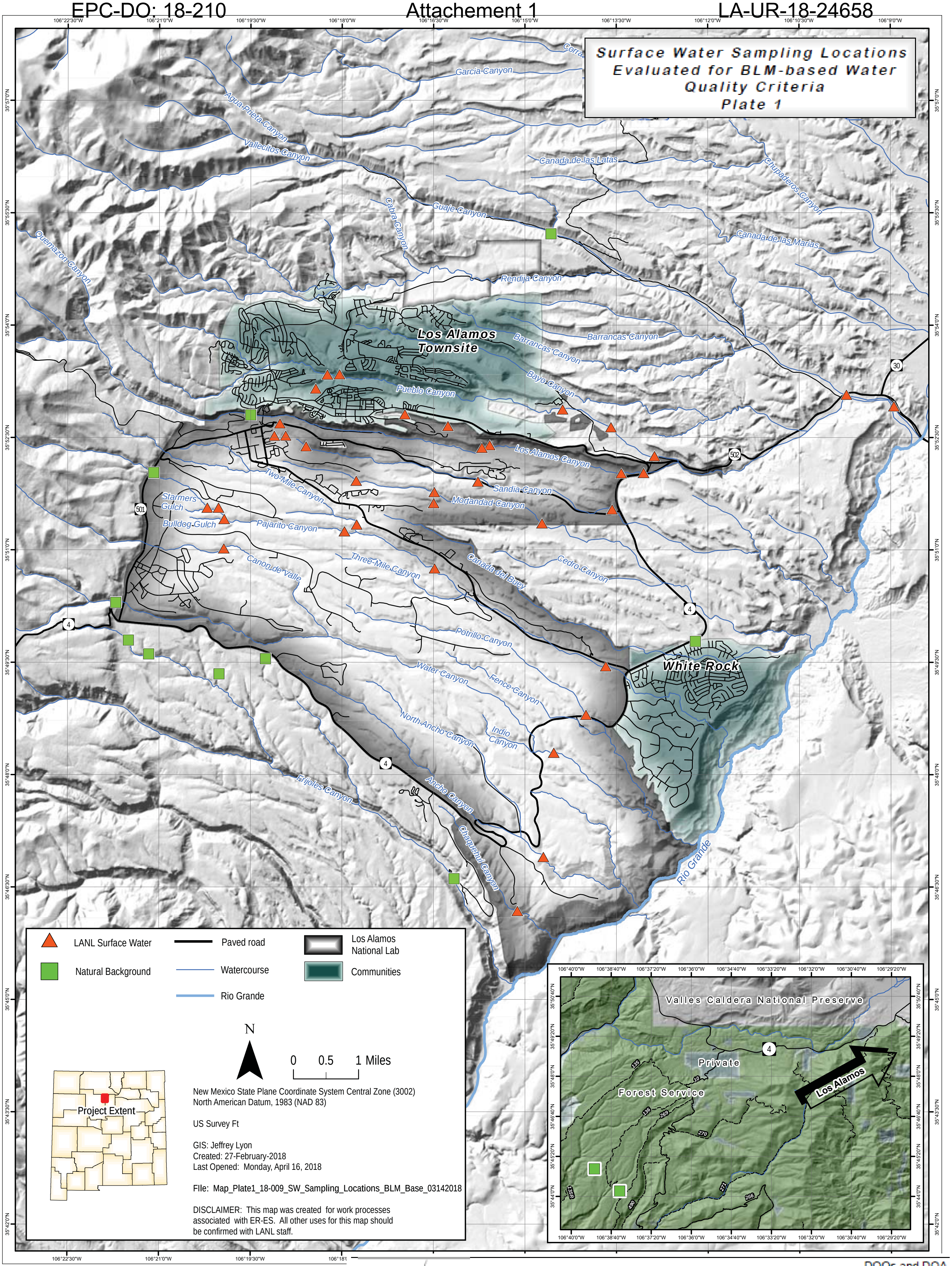
[8] E026, E240, E252, Guaje-REF-2, BAND-REF-3, BAND-REF-4, WR-REF-3

[9] The four SEP reference watershed locations are designated in Table 4-1 with location IDs beginning with "SEP".

Enclosure 1

EPC-DO: 18-210 Attachement 1 LA-UR-18-24658



Surface Water Sampling Locations Evaluated for BLM-based Water Quality Criteria
Plate 1

New Mexico State Plane Coordinate System Central Zone (3002)
North American Datum, 1983 (NAD 83)

US Survey Ft

GIS: Jeffrey Lyon
Created: 27-February-2018
Last Opened: Monday, April 16, 2018

FIle: Map_Plate1_18-009_SW_Sampling_Locations_BLM_Base_03142018

DISCLAIMER: This map was created for work processes associated with ER-ES. All other uses for this map should be confirmed with LANL staff.

Table 4-1. BLM evaluation locations

Location ID	Location ID Alias	Windward ID	Major Watershed	Minor Watershed	Landscape	Fire-affected Watershed	Y Axis	X Axis	Water Type	NMAC Class	Hydrology (E/I/P)	Nearest AU	Nearest AU Distance (ft)	Notes
Acid above Pueblo	E056	E056	Pueblo	Acid	site	no	1778790.921	1624431.601	surface water	98	intermittent	NM-97.A_002	54	
South Fork of Acid Canyon	E055.5	E055.5	Pueblo	Acid	site	no	1777746.088	1623467.575	surface water	98	intermittent	NM-97.A_029	11	
Ancho below SR-4	E275	E275	Ancho	Ancho	site	not determined	1739818.299	1641902.732	surface water	128	E/I	NM-9000.A_054	52	
La Delfe above Pajarito	E242.5	E242.5	Pajarito	Arroyo de la Delfe	site	yes	1767185.074	1616053.533	surface water	128	E/I	NM-128.A_16	17	
Canon de Valle below MDA P	E256 Canon de Valle below MDA P	E256	Water	Cañon de Valle	site	yes	1764811.076	1616017.769	surface water	126	perennial	NM-126.A_00	50	
Chaquehui at TA-33	E338	E338	Chaquehui	Chaquehui	site	not determined	1735450.235	1639792.836	surface water	128	E/I	NM-128.A_03	2.5	
DP above Los Alamos Canyon	E040	E040	Los Alamos	DP	site	yes	1773169.199	1637555.718	surface water	128	E/I	NM-128.A_10	32	
DP above TA-21	E038	E038	Los Alamos	DP	site	yes	1775660.775	1630683.66	surface water	128	E/I	NM-128.A_14	19	
DP below grade ctrl structure	E039.1	E039.1	Los Alamos	DP	site	yes	1774716.075	1634183.14	surface water	128	E/I	NM-128.A_10	9	
Guaje at SR-502	E099	E099	Los Alamos	Guaje	site	yes	1777248.77	1666451.92	surface water	98	intermittent			no AU in lower Guaje in Pueblo land
Los Alamos above DP Canyon	E030	E030	Los Alamos	Los Alamos	site	yes	1772912.232	1637449.1	surface water	128	E/I	NM-9000.A_063	41	
Los Alamos above low-head weir	E042.1	E042.1	Los Alamos	Los Alamos	site	yes	1770891.744	1648209.644	surface water	128	E/I	NM-9000.A_006	26	
Los Alamos above Rio Grande	E1099	E1099	Los Alamos	Los Alamos	site	yes	1776310.43	1670298.54	surface water	98	intermittent			no AU in lower Los Alamos Cyn in Pueblo land
Los Alamos below low-head weir	E050.1	E050.1	Los Alamos	Los Alamos	site	yes	1770920.631	1650021.007	surface water	128	E/I	NM-9000.A_006	17	
Mortandad above Ten site	E201	E201	Mortandad	Mortandad	site	no	1769370.925	1633074.678	surface water	128	E/I	NM-9000.A_042	38	
Mortandad at LANL Boundary	E204	E204	Mortandad	Mortandad	site	no	1766832.164	1641803.501	surface water	128	E/I	NM-9000.A_042	17	
Mortandad below Effluent Canon	E200	E200	Mortandad	Mortandad	site	no	1770288.738	1626750.385	surface water	128	E/I	NM-9000.A_042	44	
Pajarito above SR-4	E250	E250	Pajarito	Pajarito	site	yes	1755252.105	1646963.683	surface water	128	E/I	NM-128.A_08	63	
Pajarito above Starmers	E241	E241	Pajarito	Pajarito	site	yes	1768103.439	1614687.844	surface water	128	E/I	NM-128.A_07	38	
Pajarito above Threemile	E245.5	E245.5	Pajarito	Pajarito	site	yes	1763183.035	1633089.654	surface water	128	E/I	NM-128.A_08	38	
Pajarito above Twomile	E243	E243	Pajarito	Pajarito	site	yes	1766185.42	1625793.513	surface water	128	E/I	NM-128.A_06	148	
Potrillo above SR-4	E267	E267	Water	Potrillo	site	yes	1751323.246	1645352.039	surface water	128	E/I	NM-128.A_09	197	
Pueblo below GCS	E060.1	E060.1	Pueblo	Pueblo	site	no	1772289.42	1650902.66	surface water	128	E/I	NM-99.A_001	612	
E059.5 Pueblo below LAC WWTF	E059.5	E059.5	Pueblo	Pueblo	site	no	1776062.519	1643469.866	surface water	98	intermittent	NM-99.A_001	13	EDW
E059.8 Pueblo Below Wetlands	E059.8	E059.8	Pueblo	Pueblo	site	no	1774623.8	1647376.832	surface water	98	intermittent	NM-99.A_001	85	EDW
Pueblo above Acid	E055	E055	Pueblo	Pueblo	site	no	1778877.63	1624411.282	surface water	98	intermittent	NM-97.A_002	3	
Sandia above Firing Range	E124	E124	Sandia	Sandia	site	no	1770215.618	1636600.69	surface water	128	E/I	NM-128.A_11	194	
Sandia above SR-4	E125	E125	Sandia	Sandia	site	no	1767966.131	1647472.056	surface water	128	E/I	NM-128.A_11	15	

Location ID	Location ID Alias	Windward ID	Major Watershed	Minor Watershed	Landscape	Fire-affected Watershed	Y Axis	X Axis	Water Type	NMAC Class	Hydrology (E/I/P)	Nearest AU	Nearest AU Distance (ft)	Notes
Sandia below Wetlands	E123	E123	Sandia	Sandia	site	no	1773067.617	1622687.147	surface water	126	perennial	NM-9000.A_047	83	EDW, AU delineation begins downstream
Sandia left fork at Asph Plant	E122	E122.LFat AP	Sandia	Sandia	site	no	1773922.43	1620119.01	surface water	126	perennial	NM-9000.A_063	1,577	EDW, AU delineation begins downstream
Sandia right fork at Pwr Plant	E121	E121	Sandia	Sandia	site	no	1773840.385	1620124.03	surface water	126	perennial	NM-9000.A_063	1,659	EDW, AU delineation begins downstream
South Fork of Sandia at E122		E122.SF	Sandia	Sandia	site	no	1773924.5	1620114.1	surface water	126	perennial	NM-9000.A_063	1,575	EDW, AU delineation begins downstream
Starmers above Pajarito	E242	E242	Pajarito	Starmers	site	yes	1767983.726	1614644.252	surface water	128	E/I	NM-126.A_01	7	
Ten site above Mortandad	E201.5	E201.5	Mortandad	Tensite	site	no	1768470.302	1633024.952	surface water	128	E/I	NM-128.A_17	5	
Twomile above Pajarito	E244	E244	Pajarito	Twomile	site	yes	1766733.695	1626782.28	surface water	128	E/I	NM-128.A_15	68	
Water below SR-4	E265	E265	Water	Water	site	yes	1748258.527	1642753.28	surface water	128	E/I	NM-128.A_13	12	
Rio de los Frijoles at Band	E350	E350	Frijoles	Frijoles	undeveloped	yes	1738080.2	1634678.6	surface water	121	perennial	NM-2118.A_70	21	
Los Alamos below Ice Rink	E026	E026	Los Alamos	Los Alamos	undeveloped	yes	1775624.331	1618215.135	surface water	128	E/I	NM-9000.A_063	33	
Pajarito below SR-501	E240	E240	Pajarito	Pajarito	undeveloped	yes	1770945.505	1610350.084	surface water	128	E/I	NM-128.A_07	87	
BAND-REF-3	BAND-REF-3 at RF15BAND03	BAND-REF-3	Frijoles	Frijoles	undeveloped	yes	1757405.797	1608295.878	surface water	98	intermittent	NM-126.A_03	2,362	small trib to Frijoles mainstem AU
BAND-REF-4	BAND-REF-4 at RF15BAND04	BAND-REF-4	Frijoles	Frijoles	undeveloped	yes	1755871.917	1619402.965	surface water	98	intermittent	NM-128.A_13	1,177	small trib to Frijoles mainstem AU
SEP-REF-BM1 at RF17BM01		SEP-REF-BM1	Frijoles	Frijoles	undeveloped	yes	1754660.819	1615636.458	surface water	98	intermittent	NM-128.A_13	3,736	small trib to Frijoles mainstem AU
SEP-REF-P1 at RF17P01		SEP-REF-P1	Frijoles	Frijoles	undeveloped	yes	1756279.877	1609944.04	surface water	98	intermittent	NM-126.A_03	3,018	small trib to Frijoles mainstem AU
RF09GU02	GUAJE-REF-2	GUAJE-REF-2	Los Alamos	Guaje	undeveloped	yes	1790296.6	1642533.5	surface water	98	intermittent	NM-9000.A_005	10	
SEP-REF-SJM1 at RF17SJM01		SEP-REF-SJM1	Jemez River	Jemez River	undeveloped	no	1728030.12	1520615.217	surface water	98	intermittent	NM-2105.5_10	13,879	small trib to distant Jemez River AU
SEP-REF-SJM4 at RF17SJM04		SEP-REF-SJM4	Jemez River	Jemez River	undeveloped	no	1723545.512	1524751.695	surface water	98	intermittent	NM-2105.5_21	8,722	small trib to distant Jemez River AU
WR-REF-3 at RF13WR03	172 Meadow Lane	WR-REF-3	Mortandad	Mortandad	undeveloped	no	1757295.268	1654224.752	surface water	98	intermittent	NM-9000.A_053	1,429	small trib to Canada del Buey AU
Water above SR-501	E252	E252 up	Water	Water	undeveloped	yes	1760451.049	1607279.987	surface water	98	intermittent	NM-9000.A_052	76	

AU – assessment unit
BLM – biotic ligand model
DOE – Department of Energy
E – ephemeral
EDW – effluent-dominated water
I – intermittent
ID – identification
LANL – Los Alamos National Laboratory
NMAC – New Mexico Administrative Code
NMED – New Mexico Environment Department
P – perennial
Windward – Windward Environmental LLC
WWTF – wastewater treatment facility

4.1 DATA AGGREGATION AND EVALUATION

Initial data processing for the aggregation of BLM input data focused on summarizing analyte concentrations on the basis of a single location and date combination. As specified in Section 3.5, a requirement for BLM calculations was that a pH and DOC measurement had to be associated with a sample collected at the same location on the same day (or within a 24-hour period, or otherwise associated with a given sampling event). Among the 1,142 initial location-date pairings (i.e., events) in the BLM dataset, there were only 4 instances of pH (from a filtered sample) combined with DOC (from a filtered sample). After working through the steps specified in Section 3.5 for establishing BLM inputs, the following number of events were sequentially aggregated:

- 331 potential events total after including 227 events with pH from unfiltered samples and DOC from filtered samples
- 464 potential events after including 133 other events with representations or estimates of DOC
    - 1 event for which DOC was reported for an unfiltered sample
    - 3 events for which TOC was reported for a filtered sample
    - 129 events for which DOC was estimated from TOC
- 463 potential events after including representations of alkalinity
    - 132 events for which alkalinity was reported for a filtered sample
    - 331 events for which alkalinity was reported for an unfiltered sample
    - 1 event for which alkalinity was not reported
- 457 potential events after considering major cations
    - 6 events did not have concentration data for calcium, magnesium, sodium, and potassium
- 457 potential events after considering major anions
    - 4 events lacked sulfate concentrations, but those were estimated using location-specific averages
    - 5 events lacked chloride concentrations, but those were estimated using location-specific averages

Because estimation of DOC from TOC was necessary for 129 events, a comparison of DOC and TOC in samples for which both analytes were measured was performed (Figure 4-1). The conversion factor of 0.86 used to estimate DOC from TOC was taken as the lower 95% confidence limit for the slope of the relationship between DOC and TOC (e.g., green line in Figure 4-1). This approach and TOC to DOC conversion factor were very similar to that (0.83) used by Oregon Department of Environmental Quality in its copper BLM-based IWQC implementation guidance (ODEQ 2016a). In addition, a ceiling of 29.65 mg/L was used for DOC inputs to the BLM where reported or estimated DOC were greater than this upper bound of the calibration range specified in BLM user's guides (HydroQual 2007; Windward 2017).

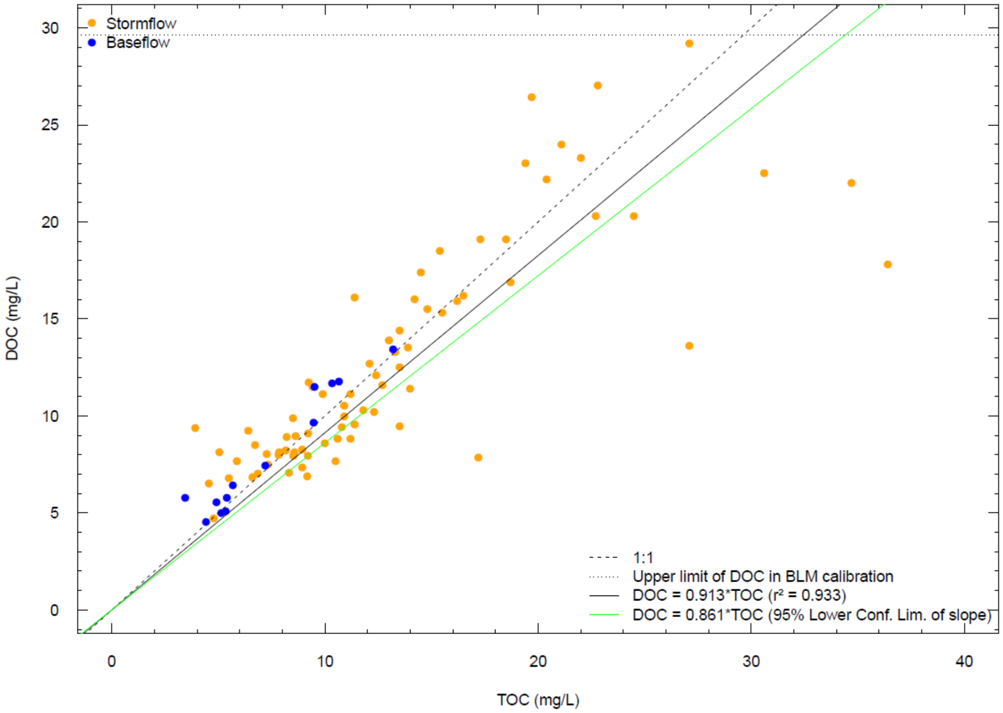


Figure 4-1.Relationship between DOC and TOC

Similarly, alkalinity from unfiltered samples was used as a substitute for missing dissolved alkalinity inputs. The relationship between filtered and unfiltered alkalinity from events for which both were measured, indicated that substitution of alkalinity from unfiltered samples provided a reasonable estimate of alkalinity in filtered samples (Figure 4-2).

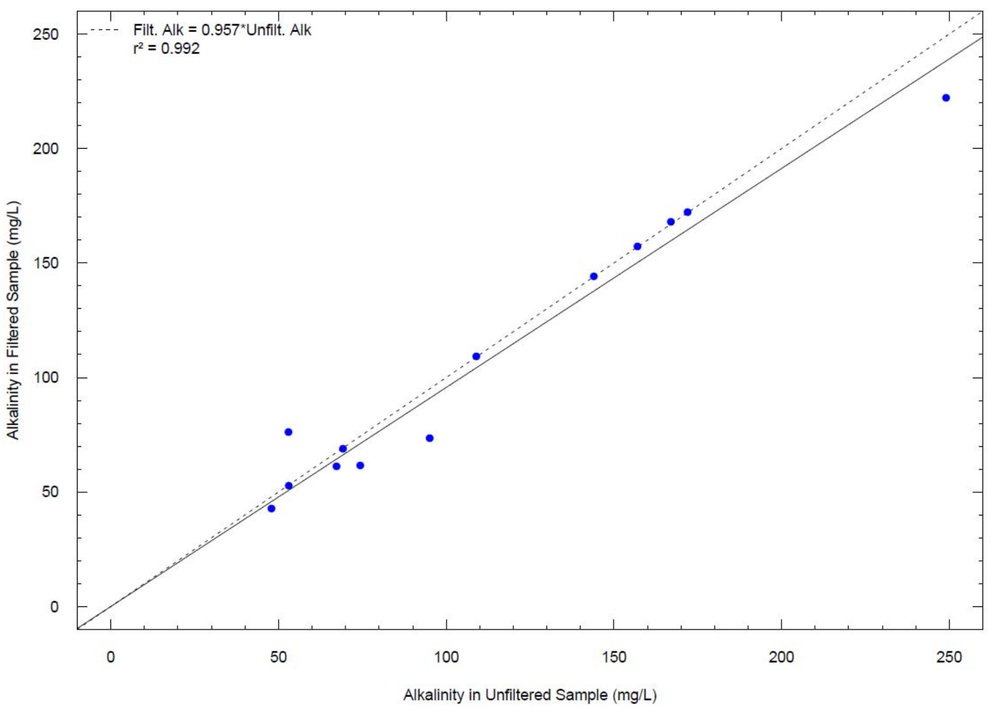


Figure 4-2. Relationship between alkalinity in filtered samples and alkalinity in unfiltered samples

Six potential BLM sample datasets lacked data for major cations, and were not considered further. Of the 457 remaining potential BLM events, 4 lacked sulfate concentrations and 5 lacked chloride concentrations. Because the purpose of these BLM inputs is to help satisfy charge balance, and because aluminum, copper, lead, and zinc BLM calculations are not sensitive to these inputs, location average concentrations were used to fill these data gaps.

No surface water data existed for temperature in the dataset considered herein, so a temperature sensitivity analysis was conducted across the BLM calibration range of 10 to 25°C. See Figure 4-3. The differences in BLM-based acute aluminum IWQC computed across the 10-25°C range varied little for copper, lead and zinc. For aluminum, the figure shows that BLM-based WQC differences were inversely proportional to temperature, with marked differences across the range, which was not unexpected given the known sensitivity of the aluminum BLM to temperature. Based on these results, a conservative assumption of 10°C was deemed appropriate (it is the lower bound of the BLM calibration range for temperature). The water temperature variable is not included in the MLR proposed by EPA in its 2017 draft aluminum AWQC, so if such AWQC are eventually adopted, the temperature sensitivity issue for aluminum appears to be moot for the MLR-based AWQC.

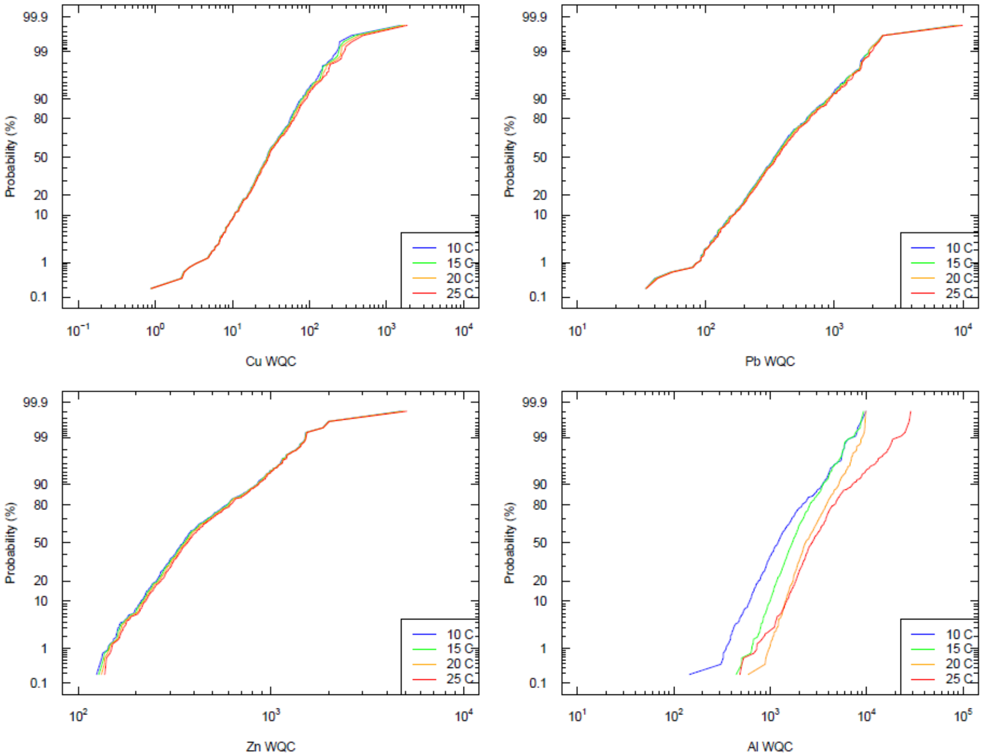


Figure 4-3. Temperature sensitivity analysis for copper, lead, zinc and aluminum BLMs

After the above considerations, the resulting dataset contained sufficient information to perform BLM calculations for 457 events. Table 4-2[10] provides a complete summary of all water sampling events considered when evaluating potential complete BLM datasets (i.e., 464 events). The detection status (i.e., "<," a value reported below the concentration indicated) and sources of any data substitutions are also indicated in Table 4-2. None of the BLM inputs were affected by detection limitations. A summary of the number of BLM events associated with each location is provided in Table 4-3, and a general spatial distribution of data richness is shown in Figure 4-4 (see Plate 1 for the geographic map of locations).

Table 4-2. LANL Surface Water Dataset for BLM Evaluations

(provided electronically in a separate Microsoft® Excel document)

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[10] Table 4-2 is provided electronically in a separate Microsoft® Excel document.

Table 4-3. Summary of complete BLM events by location

Location ID	Windward ID	Major Watershed	Minor Watershed	Landscape	Sample Type[a]	Events with Both pH and DOC			Events with Complete BLM Information		
						N	Min. Date	Max. Date	N	Min. Date	Max. Date
Ancho below SR-4	E275	Ancho	Ancho	site	WT	3	7/25/2013	6/25/2017	3	7/25/2013	6/25/2017
Chaquehui at TA-33	E338	Chaquehui	Chaquehui	site	WT	2	9/13/2013	7/23/2014	2	9/13/2013	7/23/2014
DP above Los Alamos Canyon	E040	Los Alamos	DP	site	WT	20	8/5/2013	9/28/2017	20	8/5/2013	9/28/2017
DP above TA-21	E038	Los Alamos	DP	site	WS, WT	25	9/2/2008	8/7/2017	25	9/2/2008	8/7/2017
DP below grade ctrl structure	E039.1	Los Alamos	DP	site	WT, WT+WS	26	6/14/2013	8/7/2017	26	6/14/2013	8/7/2017
Guaje at SR-502	E099	Los Alamos	Guaje	site	WT	1	8/5/2013	8/5/2013	1	8/5/2013	8/5/2013
Los Alamos above DP Canyon	E030	Los Alamos	Los Alamos	site	WM, WS, WT	4	4/28/2005	10/4/2017	4	4/28/2005	10/4/2017
Los Alamos above low-head weir	E042.1	Los Alamos	Los Alamos	site	WT	16	7/12/2013	10/4/2017	16	7/12/2013	10/4/2017
Los Alamos above Rio Grande	E1099	Los Alamos	Los Alamos	site	WT	4	7/25/2013	9/12/2013	4	7/25/2013	9/12/2013
Los Alamos below low-head weir	E050.1	Los Alamos	Los Alamos	site	WT	18	7/12/2013	10/5/2017	18	7/12/2013	10/5/2017
Mortandad above Ten Site	E201	Mortandad	Mortandad	site	WT	4	7/12/2013	7/31/2014	4	7/12/2013	7/31/2014
Mortandad at LANL Boundary	E204	Mortandad	Mortandad	site	WT	2	7/31/2014	10/4/2017	1	7/31/2014	7/31/2014
Mortandad below Effluent Canon	E200	Mortandad	Mortandad	site	WS, WP, WT	13	4/29/2005	10/4/2017	13	4/29/2005	10/4/2017
Ten Site above Mortandad	E201.5	Mortandad	Tensite	site	WT	1	9/13/2013	9/13/2013	1	9/13/2013	9/13/2013
La Delfe above Pajarito	E242.5	Pajarito	Arroyo de la Delfe	site	WT	4	7/20/2015	10/5/2017	4	7/20/2015	10/5/2017
Pajarito above SR-4	E250	Pajarito	Pajarito	site	WT	3	9/13/2013	7/21/2015	3	9/13/2013	7/21/2015
Pajarito above Starmers	E241	Pajarito	Pajarito	site	WT	2	7/15/2015	7/20/2015	2	7/15/2015	7/20/2015
Pajarito above Threemile	E245.5	Pajarito	Pajarito	site	WT	15	7/12/2013	10/5/2017	15	7/12/2013	10/5/2017

						Events with Both pH and DOC			Events with Complete BLM Information		
Location ID	**Windward ID**	**Major Watershed**	**Minor Watershed**	**Landscape**	**Sample Type[a]**	**N**	**Min. Date**	**Max. Date**	**N**	**Min. Date**	**Max. Date**
Pajarito above Twomile	E243	Pajarito	Pajarito	site	WP, WS, WT	12	8/29/2006	7/20/2015	12	8/29/2006	7/20/2015
Starmers above Pajarito	E242	Pajarito	Starmers	site	WT	3	7/6/2015	9/28/2017	3	7/6/2015	9/28/2017
Twomile above Pajarito	E244	Pajarito	Twomile	site	WP, WS, WT	14	8/29/2006	10/4/2017	14	8/29/2006	10/4/2017
Acid above Pueblo	E056	Pueblo	Acid	site	WT, WS, WP, WS+WT	21	5/3/2005	8/23/2017	21	5/3/2005	8/23/2017
South Fork of Acid Canyon	E055.5	Pueblo	Acid	site	WT	7	9/13/2013	7/29/2017	7	9/13/2013	7/29/2017
E059.5 Pueblo below LAC WWTF	E059.5	Pueblo	Pueblo	site	WT	5	7/29/2014	9/29/2017	5	7/29/2014	9/29/2017
E059.8 Pueblo Below Wetlands	E059.8	Pueblo	Pueblo	site	WT	3	10/21/2015	10/5/2017	3	10/21/2015	10/5/2017
Pueblo above Acid	E055	Pueblo	Pueblo	site	WT, WP, WS	14	5/3/2005	9/29/2017	14	5/3/2005	9/29/2017
Pueblo below GCS	E060.1	Pueblo	Pueblo	site	WT	2	7/2/2015	7/20/2015	2	7/2/2015	7/20/2015
Sandia above Firing Range	E124	Sandia	Sandia	site	WT	5	7/29/2014	9/29/2017	5	7/29/2014	9/29/2017
Sandia above SR-4	E125	Sandia	Sandia	site	WT	2	9/13/2013	7/31/2014	2	9/13/2013	7/31/2014
Sandia below Wetlands	E123	Sandia	Sandia	site	WP, WS, WT, WT+WS	49	7/12/2006	8/10/2017	48	7/12/2006	8/10/2017
Sandia left fork at Asph Plant	E122.LFatAP	Sandia	Sandia	site	WT	11	9/12/2013	8/21/2017	11	9/12/2013	8/21/2017
Sandia right fork at Pwr Plant	E121	Sandia	Sandia	site	WS, WT	47	11/3/2008	8/10/2017	46	11/3/2008	8/10/2017
South Fork of Sandia at E122	E122.SF	Sandia	Sandia	site	WS+WP, WP, WS	24	6/29/2006	8/10/2017	22	6/29/2006	8/10/2017
Canon de Valle below MDA P	E256	Water	Cañon de Valle	site	WP, WS, WT	19	1/29/2007	6/2/2017	19	1/29/2007	6/2/2017
Potrillo above SR-4	E267	Water	Potrillo	site	WT	1	7/2/2014	7/2/2014	1	7/2/2014	7/2/2014

						Events with Both pH and DOC			Events with Complete BLM Information		
Location ID	**Windward ID**	**Major Watershed**	**Minor Watershed**	**Landscape**	**Sample Type[a]**	**N**	**Min. Date**	**Max. Date**	**N**	**Min. Date**	**Max. Date**
Water below SR-4	E265	Water	Water	site	WT	3	9/13/2013	8/1/2015	3	9/13/2013	8/1/2015
BAND-REF-3	BAND-REF-3	Frijoles	Frijoles	undeveloped	WT	2	9/9/2015	10/20/2015	2	9/9/2015	10/20/2015
BAND-REF-4	BAND-REF-4	Frijoles	Frijoles	undeveloped	WT	1	10/20/2015	10/20/2015	1	10/20/2015	10/20/2015
Rio de los Frijoles at Band	E350	Frijoles	Frijoles	undeveloped	WP, WS, WT	8	9/20/2006	10/22/2015	8	9/20/2006	10/22/2015
SEP-REF-BM1 at RF17BM01	SEP-REF-BM1	Frijoles	Frijoles	undeveloped	WT	4	9/27/2017	10/5/2017	2	9/27/2017	9/28/2017
SEP-REF-P1 at RF17P01	SEP-REF-P1	Frijoles	Frijoles	undeveloped	WT	4	9/27/2017	10/5/2017	4	9/27/2017	10/5/2017
SEP-REF-SJM1 at RF17SJM01	SEP-REF-SJM1	Jemez River	Jemez River	undeveloped	WT	4	9/26/2017	10/4/2017	4	9/26/2017	10/4/2017
SEP-REF-SJM4 at RF17SJM04	SEP-REF-SJM4	Jemez River	Jemez River	undeveloped	WT	2	8/24/2017	9/27/2017	2	8/24/2017	9/27/2017
RF09GU02	GUAJE-REF-2	Los Alamos	Guaje	undeveloped	WT	3	7/29/2015	8/17/2015	3	7/29/2015	8/17/2015
Los Alamos below Ice Rink	E026	Los Alamos	Los Alamos	undeveloped	WM, WS, WT	4	4/29/2005	8/3/2016	4	4/29/2005	8/3/2016
WR-REF-3 at RF13WR03	WR-REF-3	Mortandad	Mortandad	undeveloped	WT	6	9/11/2013	8/27/2015	6	9/11/2013	8/27/2015
Pajarito below SR-501	E240	Pajarito	Pajarito	undeveloped	WT	9	8/20/2013	7/15/2015	9	8/20/2013	7/15/2015
Water above SR-501	E252 up	Water	Water	undeveloped	WP, WS, WT	12	1/24/2007	9/19/2013	12	1/24/2007	9/19/2013

[a] Sample types separated by a plus sign (i.e., "+") indicate that the specified sample types were associated with a single event at the specified location.

BLM – biotic ligand model
DOC – dissolved organic carbon
ID – identification
LANL – Los Alamos National Laboratory
WM – snowmelt
WP – persistent water
WS – surface water
WT – storm water
Windward – Windward Environmental LLC
WWTF – wastewater treatment facility

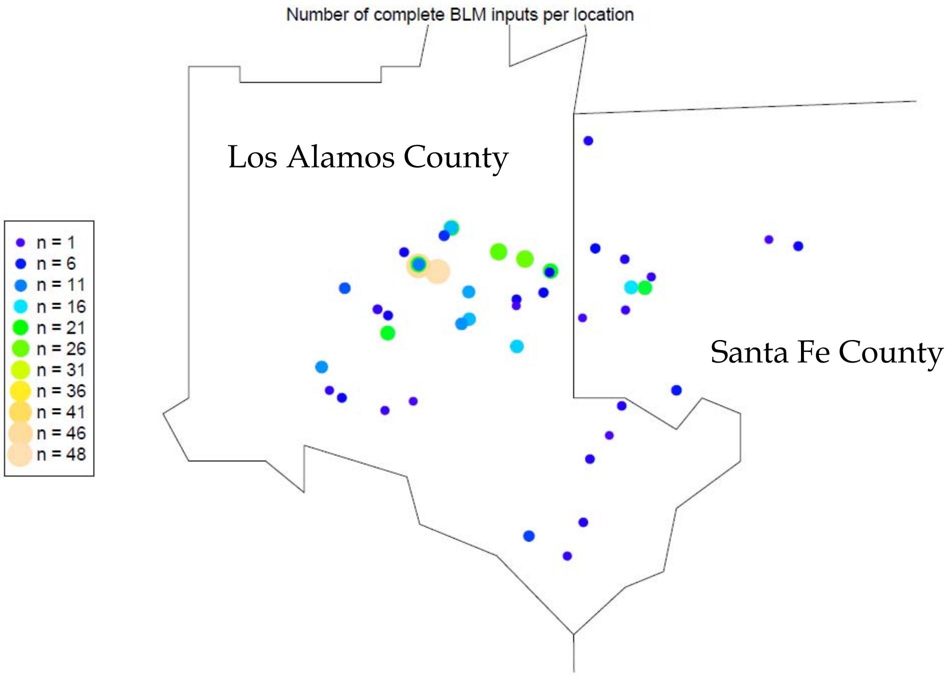

Figure 4-4. General spatial distribution of locations and data richness for BLM inputs (LANL dataset)

For the 457 events for which BLM calculations could be performed (i.e., the BLM dataset):

- 433 events had measured dissolved copper
- 446 events had measured dissolved lead and zinc
- 370 events had measured total (unfiltered) aluminum
- 150 events had measured 10-µm filtered aluminum
- 34 events had measured 1-µm filtered aluminum
- 457 events had measured dissolved (0.45-µm filtered) aluminum.

These large datasets of concurrent metal and IWQC indicate that a rich set of TUs can be calculated for the evaluation of decision errors using each WQC approach. The opportunities for calculating FMBs depends on the richness and variability of TUs and IWQCs at locations of interest (discrete and aggregated spatially). However, in these cases, the TUs will be uncertain when affected by metals results that were reported as below detection limits. For purposes of calculating TUs in these cases, the reported detection limit was used, rather than a typical basis of using ½ the detection limit[11].

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[11] Using the full detection limit was done to be conservative when comparing metal concentrations directly to IWQC and to flag any TUs affected by non-detects. The maximum likelihood estimation

Potentially fire-affected datasets were identified by LANL staff as occurring during the period Jul 4, 2011 through December 31, 2013 for particular watersheds affected by wildfires. The fire-affected watersheds are identified in Table 4-1. The IWQC based on sample data for locations and periods that may be potentially affected by wildfires are plotted as a separate data series in scatter plots presented in subsequent sections and appendices.

Lastly, the supplemental NWQMC dataset for the Rio Grande (Figure 4-5) included 78 BLM events for 5 different locations (e.g., near Taos, at Otowi Bridge, below Cochiti Dam, at San Felipe, and below Alameda Bridge). All BLM inputs for the NWQMC dataset, including temperature, were measured values (i.e., estimates or substitutions were not considered), with the exception of %HA, which was assumed to be 10%, consistent with all other BLM calculations herein.

4.2 APPLICATION OF BLMS FOR GENERATING IWQC

Acute BLMs were applied to the BLM dataset to derive acute IWQCs for copper, lead, and zinc using the BLMs described by EPA (2007), DeForest et al. (2017), and DeForest and Van Genderen (2012), respectively. In addition to BLM-based IWQC for these events, hardness-based IWQC were calculated using the measured hardness result and the relevant hardness-based equation for each metal's AWQC described in NMAC.20.6.4.900(I). All IWQC outcomes for the LANL dataset are provided in Table 4-2 (see columns to the right of the water quality dataset).

For aluminum, as noted in Section 3.5, the currently available BLM is limited to generating chronic IWQC. Consequently, the following process was used to generate preliminary acute aluminum BLM-based IWQC. First, the aluminum BLM (Santore et al. 2018) was applied to the BLM dataset to generate chronic aluminum IWQCs. Then, the chronic IWQCs were converted to acute IWQCs by multiplying each chronic BLM result by an ACR of 5.0. This ACR approach is often used by EPA, although most often in the converse situation (i.e., when deriving chronic criteria from acute toxicity datasets) (EPA 1985). In the recent draft WQC document for aluminum, EPA (2017) calculated a final ACR of 8.068, but the ACR is generally intended to convert a final acute value (FAV) to a final chronic value (or chronic criterion). Using the lowest genus mean chronic value for *Salmo* (508.5 µg/L) and the FAV of 2741 µg/L described in a scenario by EPA (2017), a conservative ACR would be 2741/508.5 = 5.39. For added conservatism here, calculation of preliminary aluminum acute BLM-based IWQCs used an ACR of 5.0. Further evaluations of the overall situation for aluminum are underway as part of other LANL efforts in collaboration with the NMED SWQB.

(MLE) technique used in FMB calculations accounts for censored (i.e., non-detect) data, and properly handles them when fitting distributions. When fitting distributions, this approach is generally favored over substitution (i.e., fabrication) approaches.

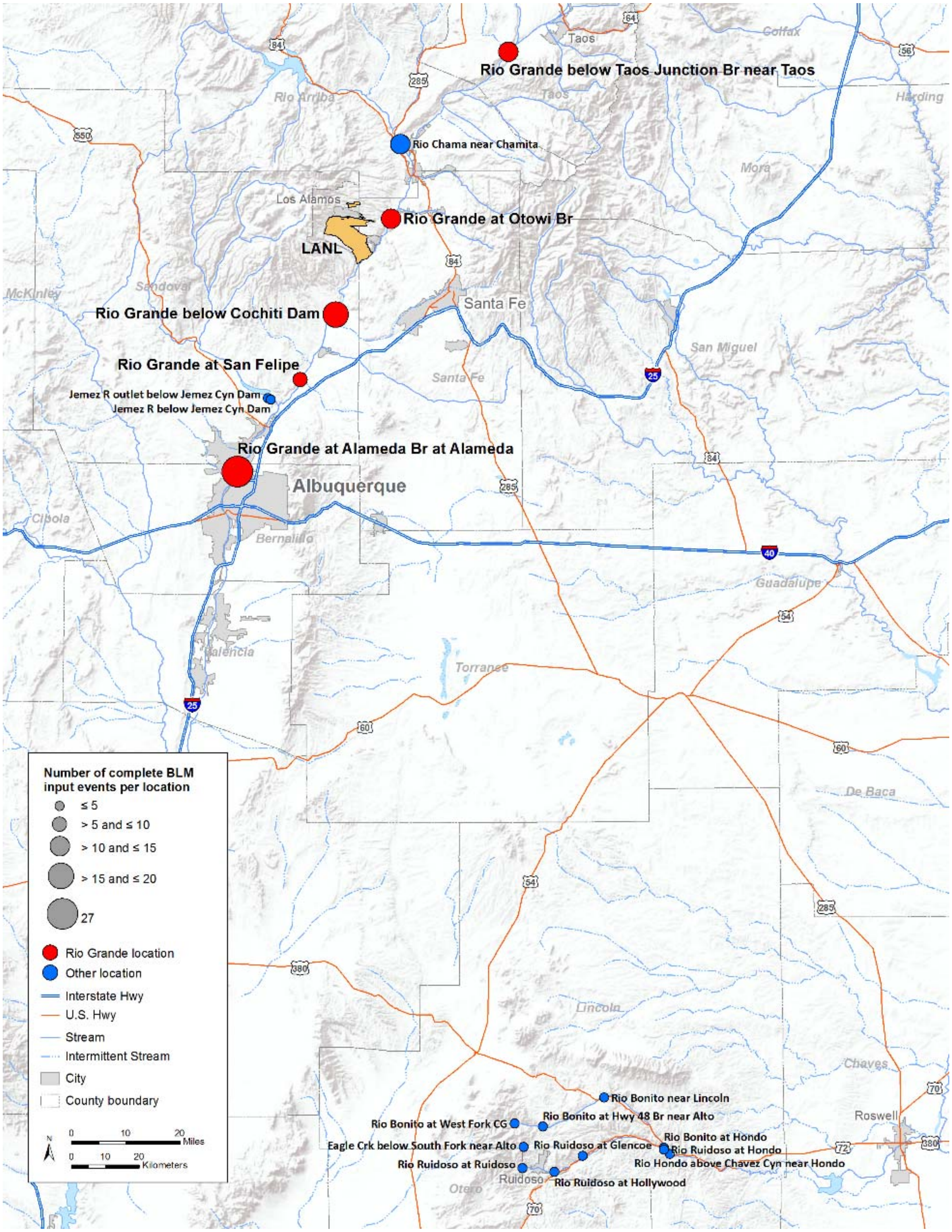

Figure 4-5. Spatial distribution of locations and data richness for BLM inputs from New Mexico locations in NWQMC dataset

4.3 OVERALL COMPARISONS OF BLM-BASED AND HARDNESS-BASED ACUTE IWQC

Comparisons of acute BLM- and hardness-based TUs for dissolved copper, lead, and zinc are shown in Figures 4-6 to 4-8 based on BLM input data for all locations and BLM events. Referring to Figure 3-1 aids interpretation of the magnitude and frequency of potential false positives and false negatives where the hardness-based IWQC were over- and under-conservative, respectively, with respect to BLM-based IWQC.

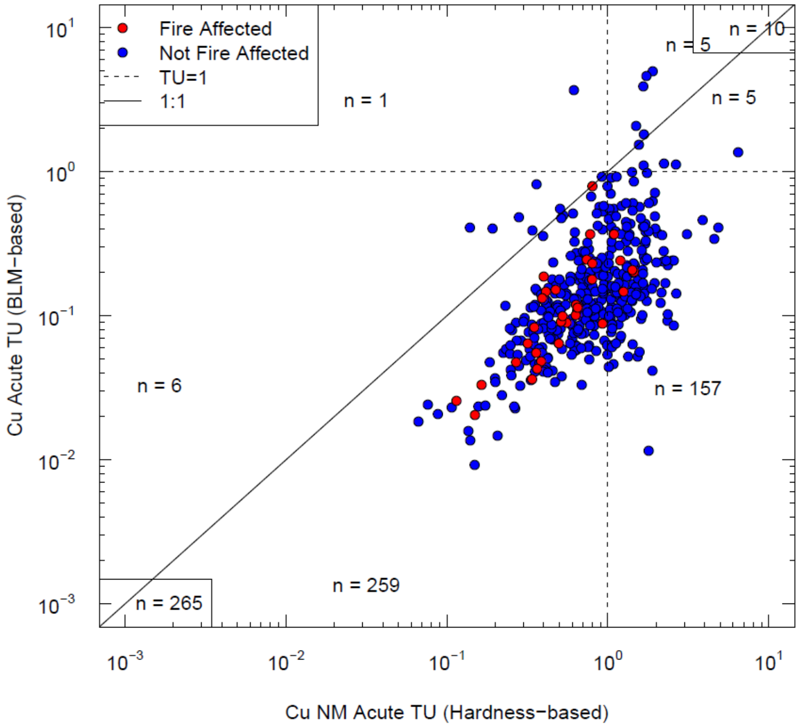

Figure 4-6. Comparison of acute <u>dissolved copper</u> IWQC TUs between EPA 2007 BLM and New Mexico hardness-based AWQC

For copper, Figure 4-6 shows that the hardness-based AWQC for copper frequently generated false positives, i.e., the 157 TU values plotted in the lower right quadrant indicate that the observed dissolved copper concentrations would exceed the New Mexico IWQC in 36% of the events, but would not exceed BLM-based IWQC. Meanwhile, application of the BLM identified one false negative, where the observed copper would exceed acute BLM-based IWQC but not the hardness-based IWQC. In the upper right, Figure 4-6 shows that the BLM and the New Mexico copper IWQC yield a consistent determination of a true exceedance in 2% (10) of the events and a true non-exceedance in 61% (265) of the events in the lower left.

For lead, Figure 4-7 shows that the BLM and New Mexico IWQC returned equivocal results (all observed concentrations did not exceed either basis) without decision errors, yet the New Mexico IWQC tended to return higher TUs than did the BLM-based IWQC (data points clustering further to the right and lower than the 1:1 line of perfect equivalency). For zinc (Figure 4-8), a similar pattern occurred, except only 2% (11) of the hardness-based IWQC TUs were false positives relative to BLM-based IWQC.

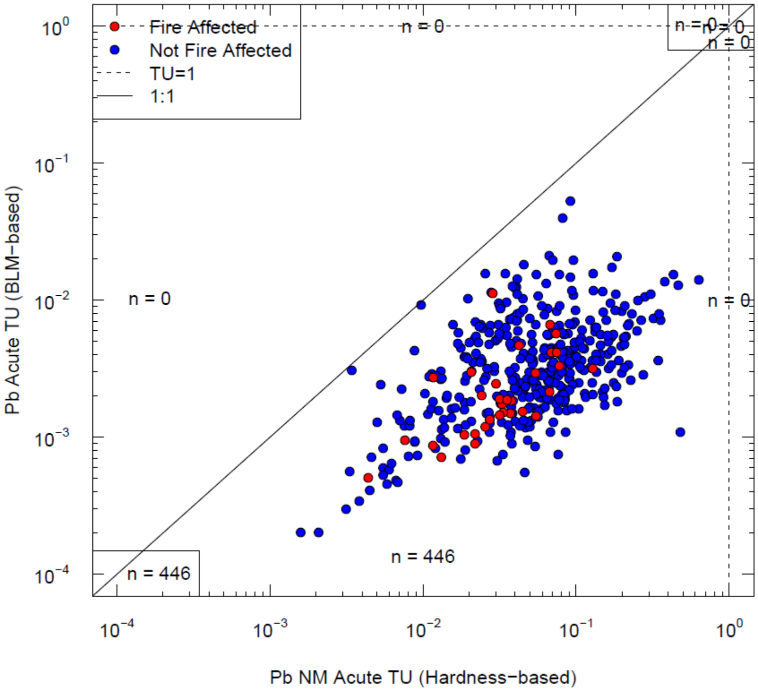

Figure 4-7.Comparison of acute <u>dissolved lead</u> IWQC TUs between BLM and New Mexico hardness-based AWQC

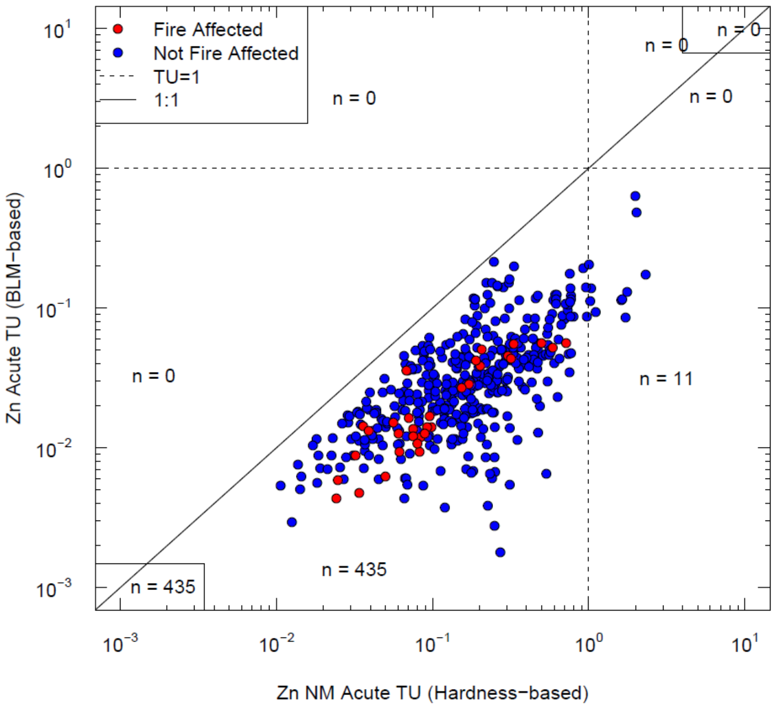

Figure 4-8. Comparison of acute dissolved zinc IWQC TUs between BLM and New Mexico hardness-based AWQC

For aluminum, the acute BLM- and hardness-based IWQC TU comparisons are shown in Figures 4-9 to 4-12 for unfiltered-, 10-µm-, 1-µm, and 0.45-µm-filtered aluminum concentrations. Similarly, comparisons of EPA draft MLR- and hardness-based acute TUs are shown for unfiltered-, 10-µm-, 1-µm, and 0.45-µm-filtered aluminum concentrations in Figures 4-13 to 4-16. Overall for aluminum, interpreting the patterns is complicated and subjective given the current uncertainty of 1) the sample filter preparation issue,[12] 2) the BLM and MLR basis of acute IWQC, and 3) implications of natural background[13] concentrations that are likely false positives (i.e., fine mineral forms of aluminum that are not bioavailable but that are included in the filtrates from all three sample filter sizes, which LANL has shown to be the case for 1-µm filtrates (LANL 2018b)). Thus, characterizing potential decision error rates at this time may be premature.

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[12] Current NMED guidance calls for analyzing “total” aluminum in filtrate from a 10-µm filter if turbidity is above 30 nephelometric turbidity units (NTU) (NMED 2012a, 2013, 2015). LANL staff and NMED have been discussing the problems that are apparent when using filters larger than 0.45-µm for aluminum analysis (i.e. the risk of significant false positive bias via inclusion of fine mineral forms of aluminum that are non-toxic) (LANL 2018b, 2016). Further evaluations are being planned by Windward and LANL staff in collaboration with NMED (95% draft toxicity testing plan).

[13] LANL has completed extensive data collection and characterization demonstrating significantly elevated natural background concentrations of aluminum and other constituents in storm water samples collected from various surface waters within and around LANL in the vicinity of the Pajarito Plateau (LANL 2007, 2010b, 2013, 2014, 2015).

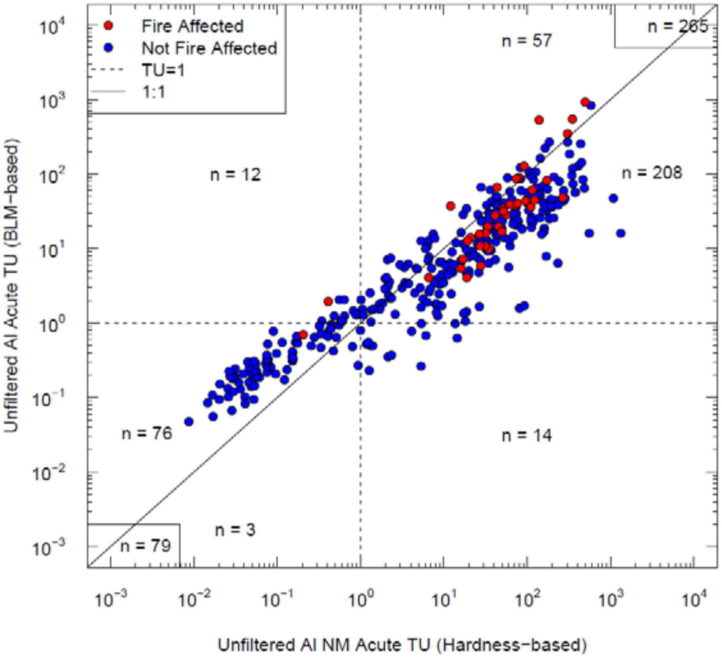


Figure 4-9. Comparison of acute aluminum IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of unfiltered aluminum)

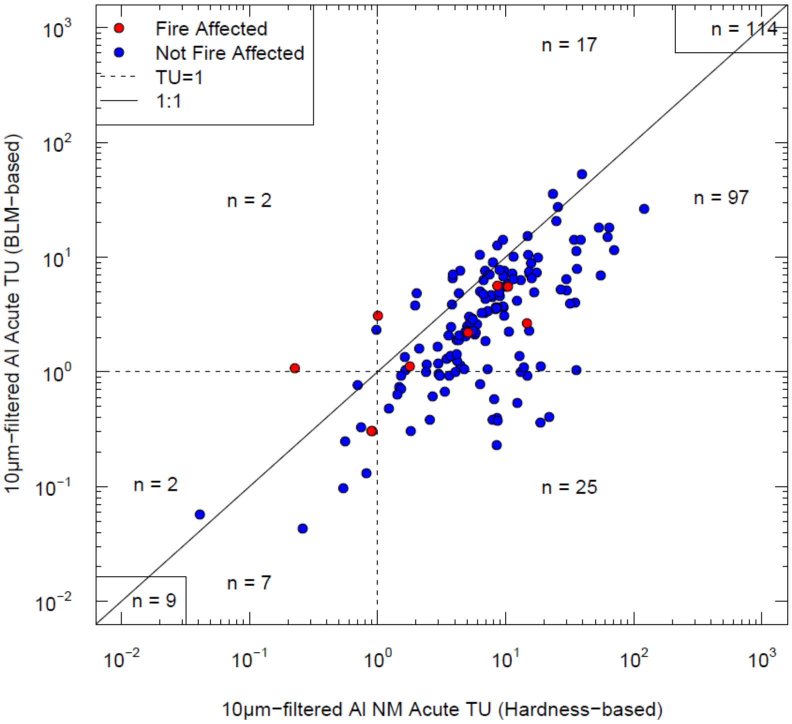


Figure 4-10. Comparison of acute aluminum IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of 10-µm filtered aluminum)

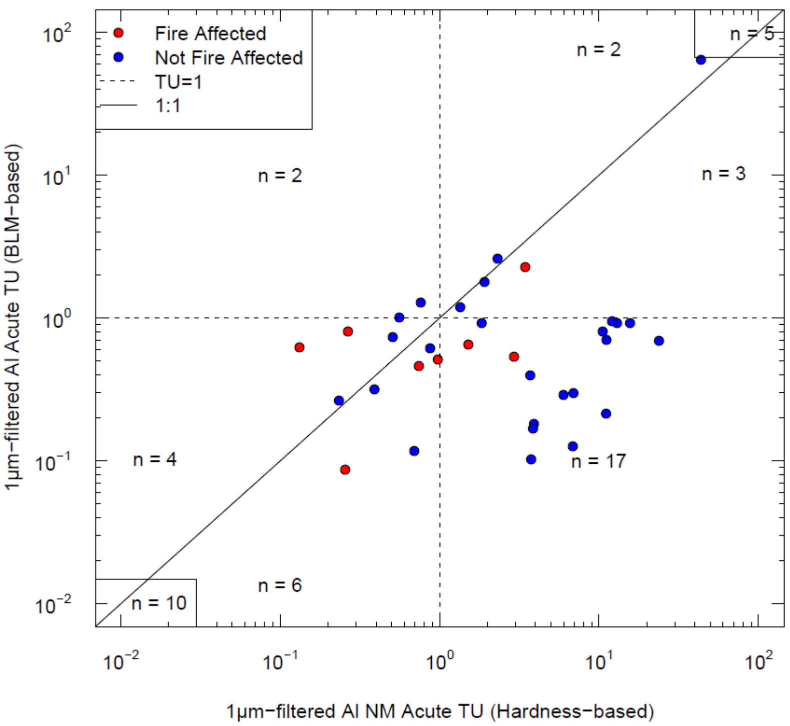


Figure 4-11. Comparison of acute <u>aluminum</u> IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of <u>1-µm filtered</u> aluminum)

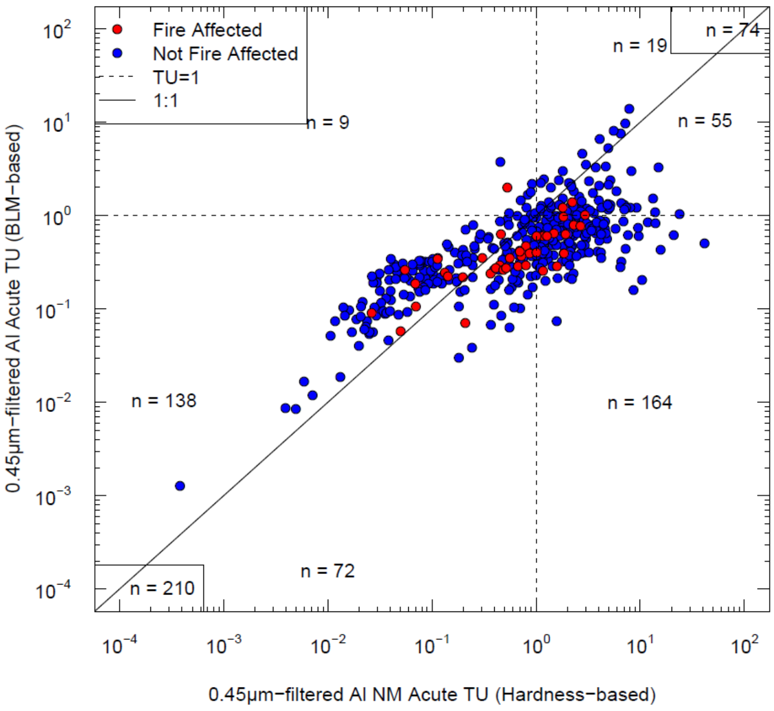


Figure 4-12. **Comparison of acute <u>aluminum</u> IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of <u>0.45 µm filtered</u> aluminum)**

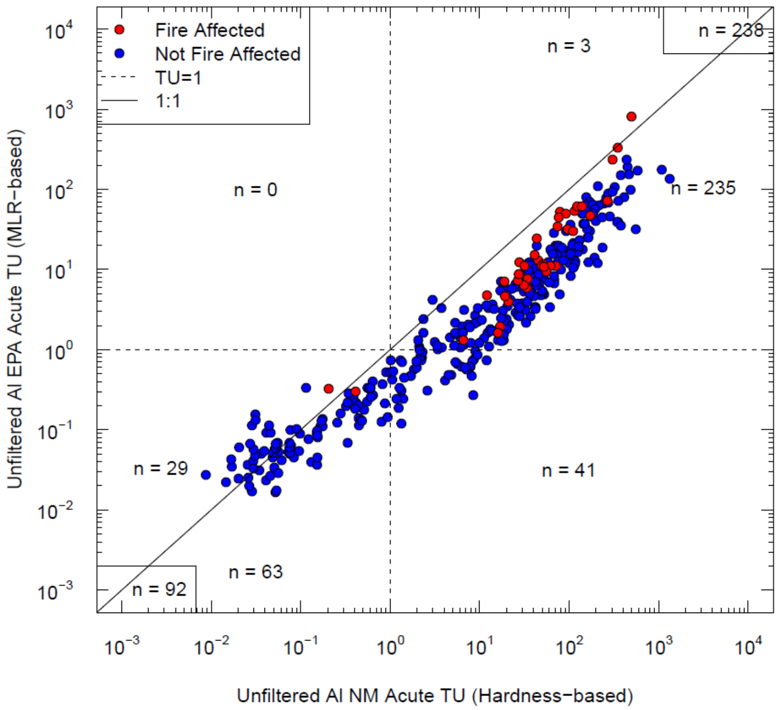


Figure 4-13. **Comparison of EPA draft <u>MLR-based</u> acute TUs and New Mexico hardness-based TUs for aluminum (for <u>unfiltered</u> aluminum)**

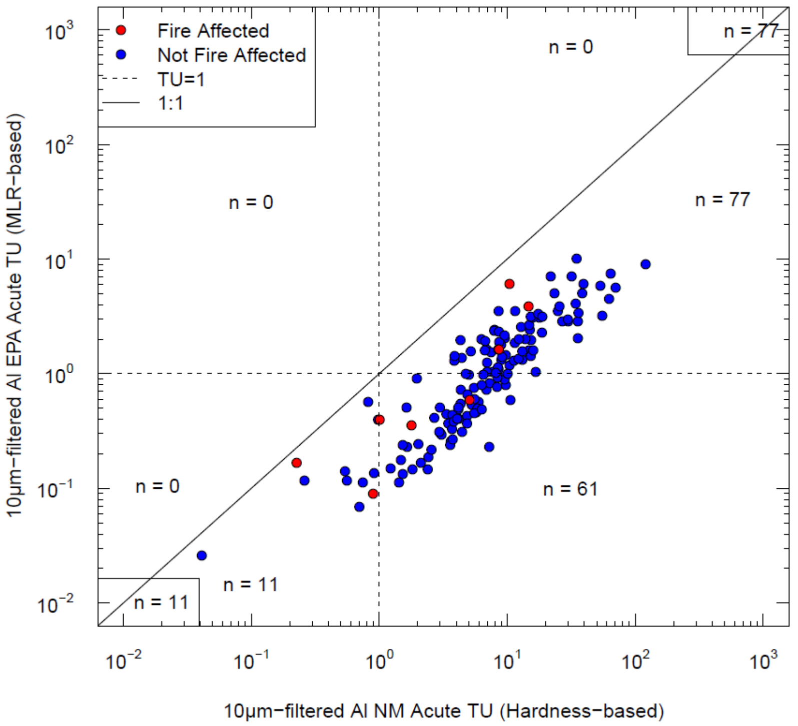


Figure 4-14. Comparison of EPA draft MLR-based acute TUs and New Mexico hardness-based TUs for aluminum (for 10-μm filtered aluminum)

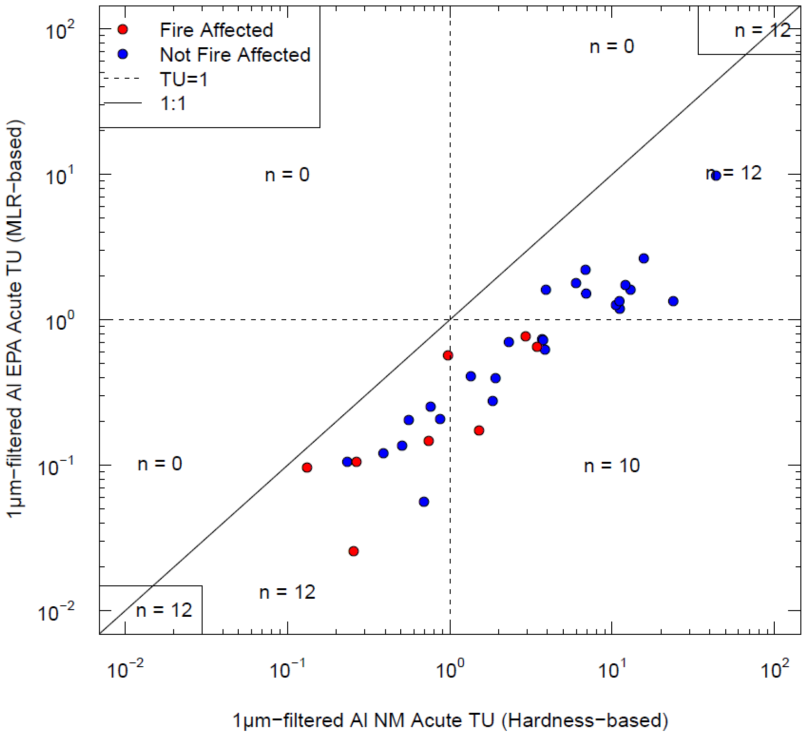


Figure 4-15. Comparison of EPA draft MLR-based acute TUs and New Mexico hardness-based TUs for aluminum (for 1-μm filtered aluminum)

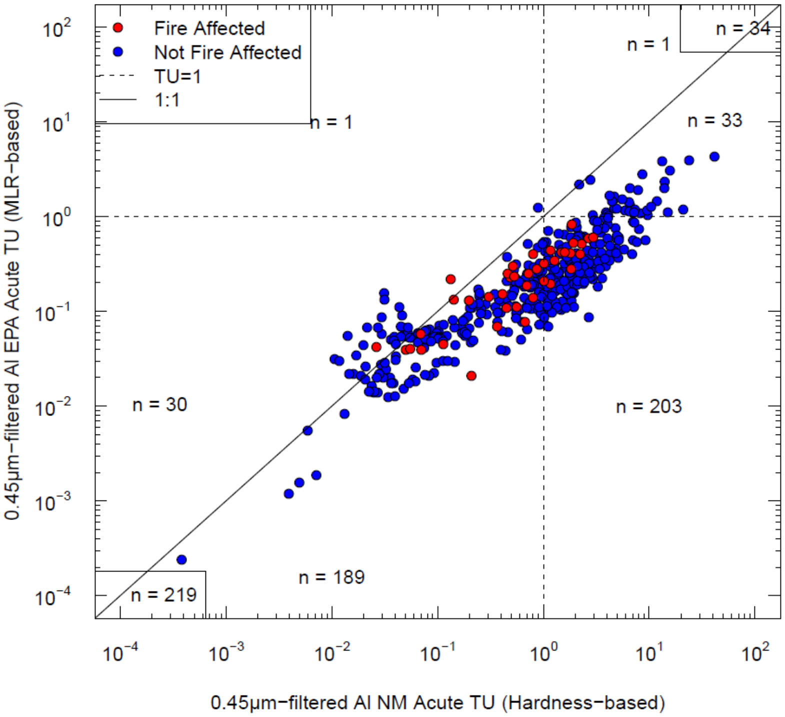


Figure 4-16. Comparison of EPA draft MLR-based acute TUs and New Mexico (2010; AWQC) hardness-based TUs for aluminum (for 0.45-µm filtered aluminum)

Table 4-4 provides a summary of acute BLM-based TUs for each location (i.e., description of percentage of TUs>1, number of TUs calculated, number of TUs affected by BDL metal concentrations, and number BDL-affected TUs>1). On the basis of acute BLM-based IWQC, there were no TUs > 1 for lead and zinc.

Table 4-4. Summary of acute BLM-based TUs by location

Location ID	Windward ID	Unfiltered Aluminum				10-µm Filtered Aluminum				1-µm Filtered Aluminum				0.45-µm Filtered Aluminum				0.45-µm Filtered Copper				0.45-µm Filtered Lead				0.45-µm Filtered Zinc			
			No.				No.				No.				No.				No.				No.				No.		
		% TU>1	TU	BDL	BDL TU>1	% TU>1	TU	BDL	BDL TU>1	% TU>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1
Acid above Pueblo	E056	88	17	1	0	100	4	0	0					24	21	2	0	**5**	20	4	**1**	0	21	5	0	0	21	1	0
Ancho below SR-4	E275	100	3	0	0									0	3	0	0	0	3	0	0	0	3	0	0	0	3	2	0
BAND-REF-3	BAND-REF-3	100	2	0	0	50	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2	2	0	0	2	2	0
BAND-REF-4	BAND-REF-4	100	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	1	0	0	1	0	0
Canon de Valle below MDA P	E256	27	15	1	0	100	1	0	0					0	19	12	0	0	18	17	0	0	19	19	0	0	19	16	0
Chaquehui at TA-33	E338	100	2	0	0									0	2	0	0	0	2	0	0	0	2	0	0	0	2	1	0
DP above Los Alamos Canyon	E040	100	10	0	0	100	13	0	0					35	20	0	0	0	20	0	0	0	20	0	0	0	20	1	0
DP above TA-21	E038	94	18	0	0	91	11	0	0	50	2	0	0	20	25	1	0	0	23	1	0	0	23	9	0	0	23	4	0
DP below grade ctrl structure	E039.1	100	18	0	0	92	12	0	0					31	26	0	0	0	26	0	0	0	26	5	0	0	26	2	0
E059.5 Pueblo below LAC WWTF	E059.5	100	3	0	0	100	2	0	0					0	5	0	0	0	5	0	0	0	5	0	0	0	5	0	0
E059.8 Pueblo Below Wetlands	E059.8	0	1	0	0	0	1	0	0					0	3	0	0	0	3	0	0	0	3	1	0	0	3	0	0
Guaje at SR-502	E099	100	1	0	0									0	1	0	0	0	1	0	0	0	1	1	0	0	1	1	0
La Delfe above Pajarito	E242.5	100	2	0	0	100	2	0	0					25	4	0	0	0	4	0	0	0	4	1	0	0	4	1	0
Los Alamos above DP Canyon	E030	50	2	0	0									0	4	0	0	0	4	2	0	0	4	2	0	0	4	0	0
Los Alamos above low-head weir	E042.1	100	10	0	0	100	7	0	0					25	16	0	0	0	16	0	0	0	16	0	0	0	16	2	0
Los Alamos above Rio Grande	E1099	100	4	0	0									0	4	0	0	0	4	0	0	0	4	0	0	0	4	1	0
Los Alamos below Ice Rink	E026	67	3	0	0	100	1	0	0					0	4	0	0	0	4	2	0	0	4	3	0	0	4	2	0
Los Alamos below low-head weir	E050.1	100	17	0	0	100	8	0	0					11	18	0	0	0	18	0	0	0	18	3	0	0	18	2	0
Mortandad above Ten Site	E201	100	4	0	0									0	4	0	0	0	4	0	0	0	4	0	0	0	4	0	0
Mortandad at LANL Boundary	E204	100	1	0	0									100	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0
Mortandad below Effluent Canon	E200	70	10	0	0									46	13	0	0	0	12	0	0	0	13	8	0	0	13	1	0
Pajarito above SR-4	E250	100	3	0	0	100	1	0	0					0	3	0	0	0	3	0	0	0	3	0	0	0	3	0	0
Pajarito above Starmers	E241	100	2	0	0	100	2	0	0					0	2	0	0	0	2	1	0	0	2	1	0	0	2	1	0
Pajarito above Threemile	E245.5	100	11	0	0	100	5	0	0					33	15	0	0	0	15	0	0	0	15	4	0	0	15	3	0
Pajarito above Twomile	E243	92	12	0	0	100	2	0	0					83	12	0	0	**11**	9	6	**1**	0	12	5	0	0	12	2	0
Pajarito below SR-501	E240	100	9	0	0	50	4	0	0	0	3	0	0	11	9	0	0	0	6	1	0	0	6	0	0	0	6	1	0
Potrillo above SR-4	E267	100	1	0	0									0	1	0	0	0	1	0	0	0	1	0	0	0	1	1	0
Pueblo above Acid	E055	60	10	1	0	67	3	0	0					21	14	2	0	0	13	4	0	0	14	6	0	0	14	1	0
Pueblo below GCS	E060.1	100	2	0	0	100	2	0	0					50	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0
RF09GU02	GUAJE-REF-2	100	3	0	0	100	3	0	0	100	3	0	0	0	3	0	0	0	3	0	0	0	3	1	0	0	3	1	0
Rio de los Frijoles at Band	E350	50	8	0	0	100	2	0	0	50	2	0	0	13	8	1	0	0	7	5	0	0	8	6	0	0	8	7	0
Sandia above Firing Range	E124	100	5	0	0	100	2	0	0					20	5	0	0	0	5	0	0	0	5	0	0	0	5	0	0
Sandia above SR-4	E125	100	2	0	0									0	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0

Location ID	Windward ID	Unfiltered Aluminum				10-µm Filtered Aluminum				1-µm Filtered Aluminum				0.45-µm Filtered Aluminum				0.45-µm Filtered Copper				0.45-µm Filtered Lead				0.45-µm Filtered Zinc			
			No.				No.				No.				No.				No.				No.				No.		
		% TU>1	TU	BDL	BDL TU>1	% TU>1	TU	BDL	BDL TU>1	% TU>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1	% TUs>1	TU	BDL	BDL TU>1
Sandia below Wetlands	E123	48	42	2	0	55	11	0	0					6	48	18	0	0	48	10	0	0	48	30	0	0	48	2	0
Sandia left fork at Asph Plant	E122.LFatAP	64	11	0	0	25	4	0	0					0	11	0	0	18	11	0	0	0	11	2	0	0	11	0	0
Sandia right fork at Pwr Plant	E121	63	38	9	0	53	15	0	0					4	46	12	0	4	46	5	0	0	46	35	0	0	46	2	0
SEP-REF-BM1 at RF17BM01	SEP-REF-BM1	0	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2	1	0	0	2	0	0
SEP-REF-P1 at RF17P01	SEP-REF-P1	75	4	0	0	50	4	0	0	0	4	0	0	25	4	0	0	0	4	0	0	0	4	0	0	0	4	1	0
SEP-REF-SJM1 at RF17SJM01	SEP-REF-SJM1	100	4	0	0	33	3	0	0	0	3	0	0	25	4	0	0	0	4	0	0	0	4	0	0	0	4	3	0
SEP-REF-SJM4 at RF17SJM04	SEP-REF-SJM4	100	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2	2	0	0	2	1	0
South Fork of Acid Canyon	E055.5	100	1	0	0	0	3	0	0					0	7	0	0	0	7	0	0	0	7	0	0	0	7	0	0
South Fork of Sandia at E122	E122.SF	5	19	6	0									5	22	14	0	0	22	13	0	0	22	16	0	0	22	3	0
Starmers above Pajarito	E242	100	2	0	0	100	2	0	0					33	3	0	0	0	3	0	0	0	3	1	0	0	3	1	0
Ten Site above Mortandad	E201.5	100	1	0	0									100	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0
Twomile above Pajarito	E244	91	11	0	0	100	2	0	0					21	14	0	0	0	10	4	0	0	14	7	0	0	14	5	0
Water above SR-501	E252 up	83	12	0	0	100	4	0	0	0	4	0	0	42	12	0	0	**71**	7	7	**5**	0	8	8	0	0	8	5	0
Water below SR-4	E265	100	3	0	0	100	1	0	0					100	3	0	0	0	3	0	0	0	3	0	0	0	3	1	0
WR-REF-3 at RF13WR03	WR-REF-3	100	6	0	0	100	6	0	0	33	6	0	0	17	6	0	0	0	4	0	0	0	4	3	0	0	4	3	0

Bold underlined values indicate % TUs >1 is uncertain due to all TU>1 based on non-detected copper result with TU calculated using the 10-µg/L detection limit.

BDL – below detection limit
BLM – biotic ligand model
ID – identification
LANL – Los Alamos National Laboratory
TU – toxic unit
Windward – Windward Environmental LLC
WWTF – wastewater treatment plant

For the supplemental NWQMC Rio Grande dataset, Figures 4-17 and 4-18 show comparison of acute BLM- and hardness-based TUs for dissolved copper and zinc based on BLM input data for the five Rio Grande locations. Lead concentrations were not obtained, so TUs were not calculated for lead. There were no TUs > 1 for copper or zinc using BLM- or hardness-based IWQC. Figures 4-17 and 4-18 indicate that the BLM- and New Mexico hardness-based approaches consistently denote non-exceedances for both copper and zinc at the Rio Grande locations considered. Table 4-5 provides a summary of acute BLM-based TUs for each Rio Grande location identified in the NWQMC dataset.

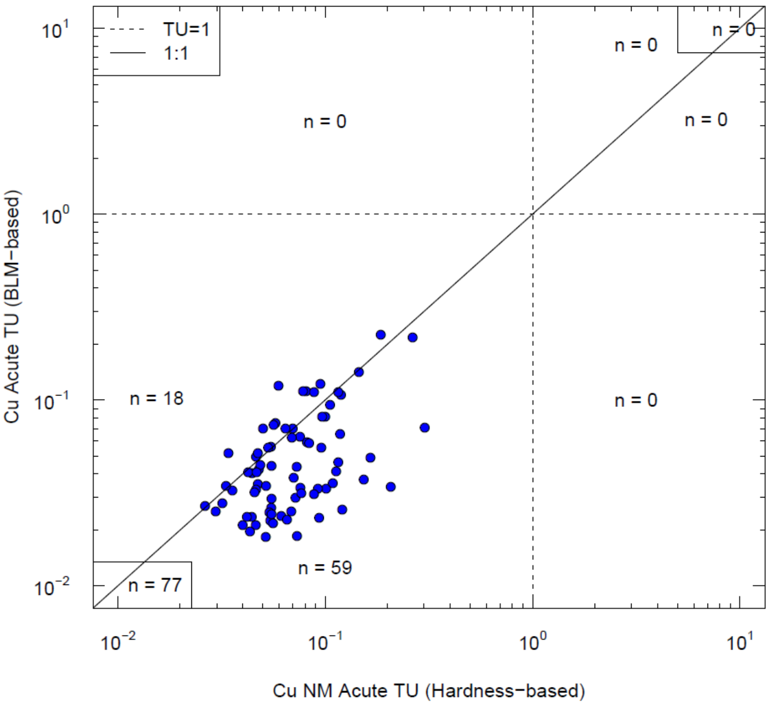


Figure 4-17. Comparison of acute dissolved copper IWQC TUs between EPA 2007 BLM and New Mexico hardness-based AWQC for the Rio Grande dataset

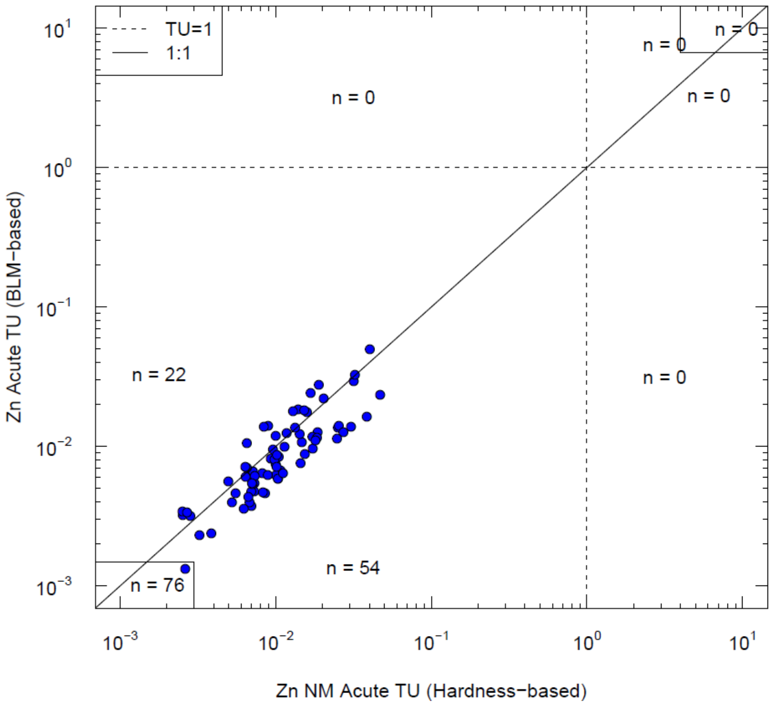


Figure 4-18. Comparison of acute dissolved zinc IWQC TUs between BLM and New Mexico hardness-based AWQC for the Rio Grande dataset

Table 4-5. Summary of acute BLM-based TUs for each Rio Grande location

	Unfiltered Aluminum				0.45-µm Filtered Aluminum				0.45-µm Filtered Copper				0.45-µm Filtered Zinc			
		No.				No.				No.				No.		
NWQMC Location ID	**% TU>1**	**TU**	**BDL**	**BDL TU>1**	**% TUs>1**	**TU**	**BDL**	**BDL TU>1**	**% TUs>1**	**TU**	**BDL**	**BDL TU>1**	**% TUs>1**	**TU**	**BDL**	**BDL TU>1**
Rio Grande below Taos Junction Bridge near Taos, New Mexico					0	12	6	0	0	12	7	0	0	12	10	0
Rio Grande at Otowi Bridge, New Mexico					0	13	7	0	0	13	7	0	0	13	11	0
Rio Grande below Cochiti Dam, New Mexico					0	18	0	0	0	18	9	0	0	18	16	0
Rio Grande at San Felipe, New Mexico	100	1	0	0	0	8	7	0	0	8	7	0	0	7	7	0
Rio Grande at Alameda Bridge at Alameda, New Mexico	88	26	0	0	0	26	6	0	0	26	14	0	0	26	24	0

BDL – below detection limit
BLM – biotic ligand model
ID – identification
NWQMC – National Water Quality Monitoring Council
TU – toxic unit

Also for the supplemental NWQMC dataset, Figures 4-19 and 4-20 show comparisons between acute BLM- and hardness-based IWQC TUs for unfiltered- and 0.45-µm-filtered aluminum concentrations. Similarly, Figures 4-21 and 4-22 show comparisons of EPA draft MLR- and hardness-based acute TUs for unfiltered- and 0.45-µm-filtered aluminum concentrations. Generally, the BLM generates higher TUs than the New Mexico hardness-based IWQC, indicating that for the Rio Grande dataset, the BLM generates lower IWQC. The MLR-based TUs are often higher than the hardness-based TUs, although the MLR-based TUs are more similar to the hardness-based TUs than are the BLM-based TUs. As described above, interpreting the patterns for aluminum is complicated and subjective given the uncertainty in appropriate sample preparation, criteria basis, and contribution from natural background.

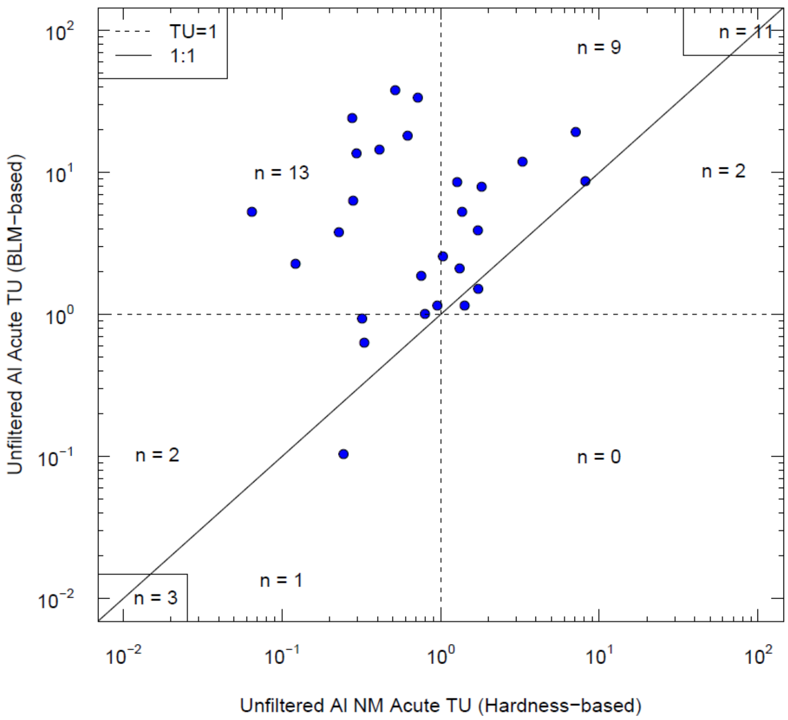


Figure 4-19. Comparison of acute aluminum IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of unfiltered aluminum) for the Rio Grande dataset

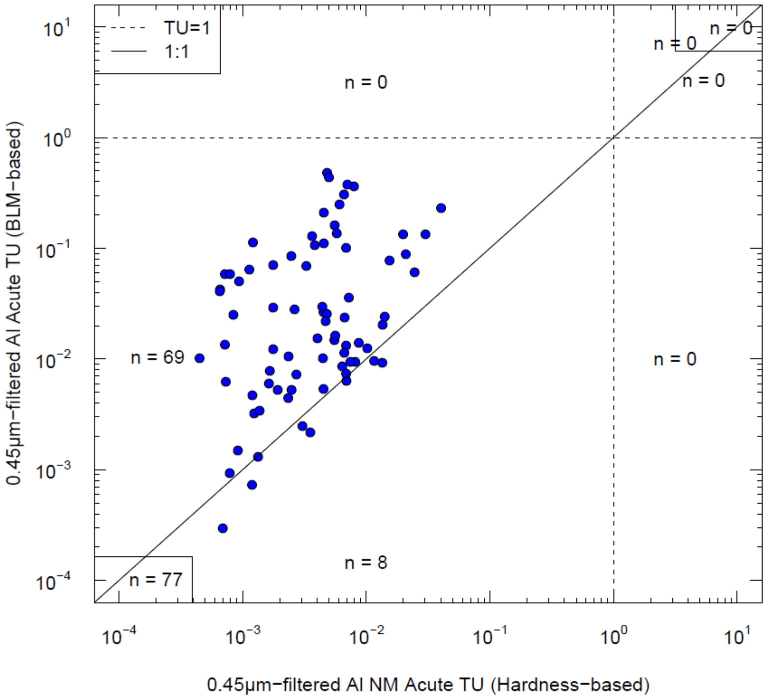


Figure 4-20. **Comparison of acute aluminum IWQC TUs between BLM and New Mexico hardness-based AWQC (on basis of 0.45 µm filtered aluminum) for the Rio Grande dataset**

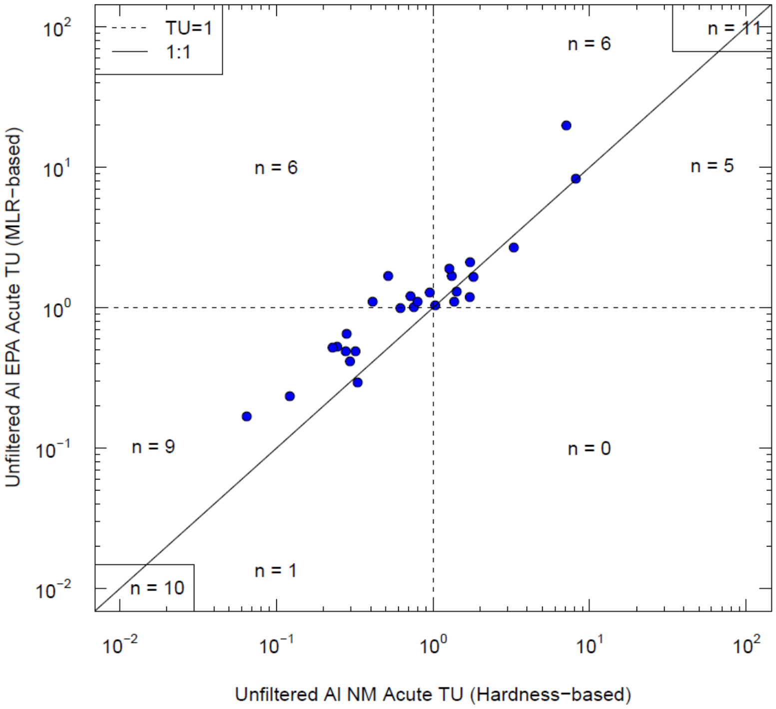


Figure 4-21. **Comparison of EPA draft MLR-based acute TUs and New Mexico hardness-based TUs for aluminum (for unfiltered aluminum) for the Rio Grande dataset**

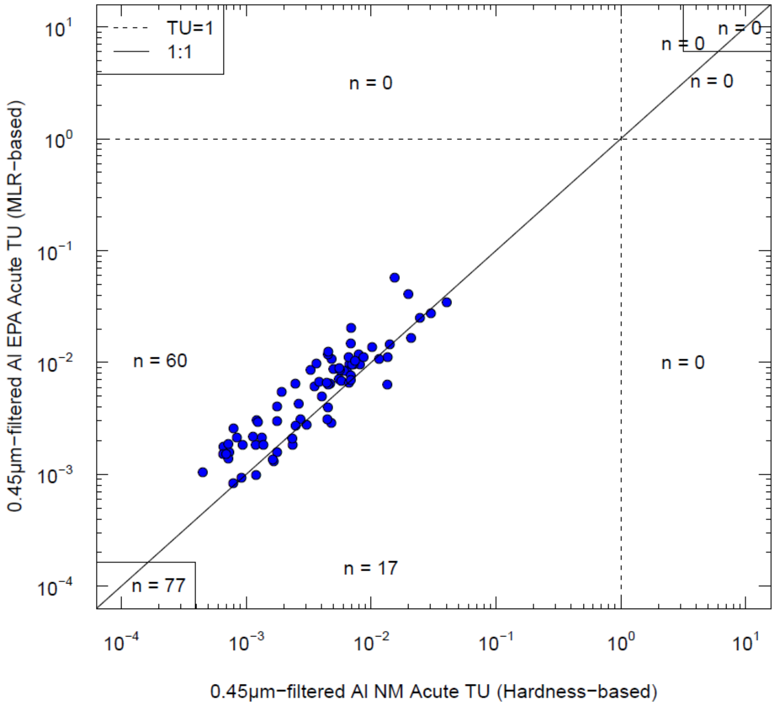


Figure 4-22. Comparison of EPA draft MLR-based acute TUs and New Mexico hardness-based TUs for aluminum (for 0.45-µm filtered aluminum) for the Rio Grande dataset

4.4 SPATIAL PATTERNS IN ACUTE IWQC

Figure 4-23 provides a longitudinal summary of acute BLM-based copper TU results for the Los Alamos watershed (mainstem and two tributaries). This type of data visualization can help illustrate the spatial distributions of the large differences between the acute TUs for BLM-based and hardness based IWQC. In Figure 4-23. One can see that all three DP canyon locations exhibit similar results, illustrating the significant false positive concern for hardness-based copper IWQC pointed out in Section 4.3. Similar longitudinal series of boxplots for the minor watersheds are provided in Appendix A.

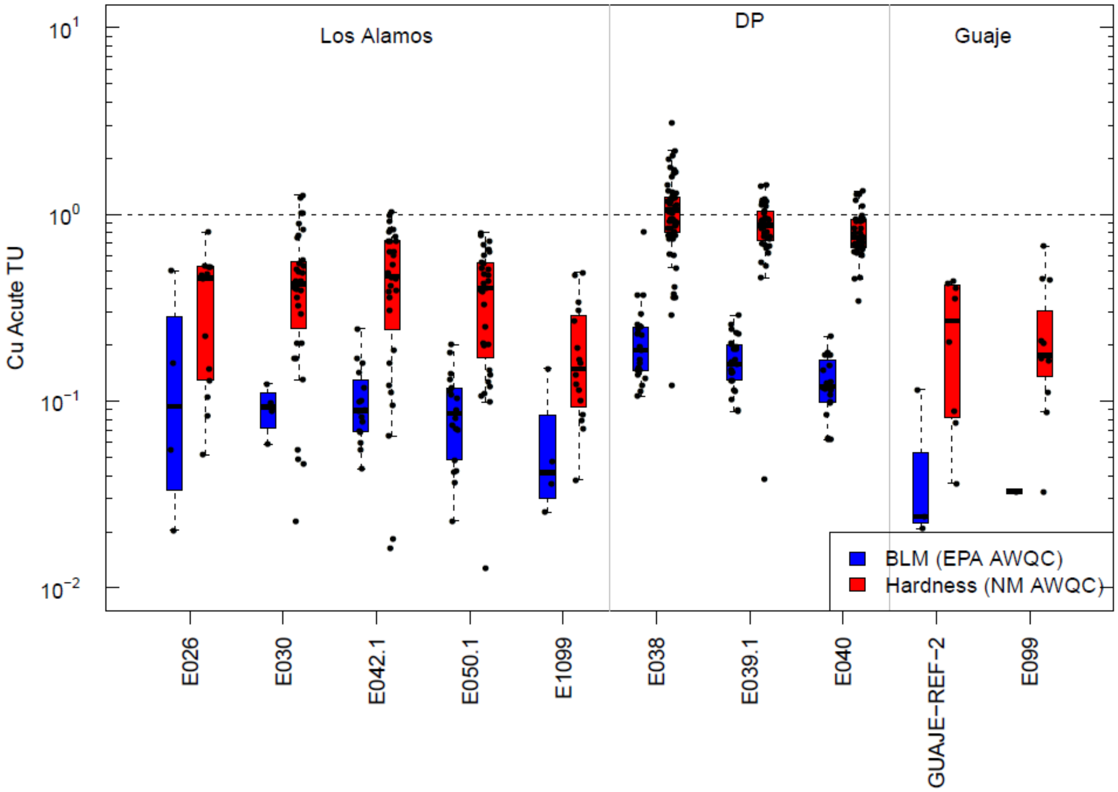


Figure 4-23. Los Alamos Watershed longitudinal summary of acute dissolved copper IWQC TUs based on BLM and New Mexico (NM) IWQC

For copper, BLM-based IWQC exceedances (TUs > 1, n=11) were limited to 5 locations:E056, E243, E122.LFatAP (Sandia Left fork at Asph plant), E121 and E252 (Water canyon above SR-501). It is important to note that 7 of the IWQC exceedances were attributable to BDL copper results where the copper detection limits were 10 μg/L, which exceeded the respective BLM-based IWQC. These occurrences were most pronounced at E252 and should be regarded as artifactual results and not relied up given the copper DL was approximately 3-fold higher than typical DLs reported in the dataset (~ 3 μg/L). The four remaining IWQC exceedances were limited to two locations in Upper Sandia canyon (E121 and E122.LFatAP).

Another potential concern for the acute copper BLM IWQC results is apparent in the Sandia Canyon watershed for E122.LFatAP. See Figure 4-24. This location had only WT (storm water) sample types which were associated with lower BLM-based IWQC (n=11) than the 22 baseflow (WS or WP) sample events at this same gage station coordinates (E122) but that were identified by EIM with different nomenclature (South Fork of Sandia at E122, i.e. E122.SF Windward ID). The stormflow E122 (WT) events had lower average pH (7.0) than the average pH of 8.5 in the E122 baseflow (WS, WP) events, while DOC was similar across all events at E122 (average 12 mg/L for WT, and 12.2 mg/L for WS, WP events).

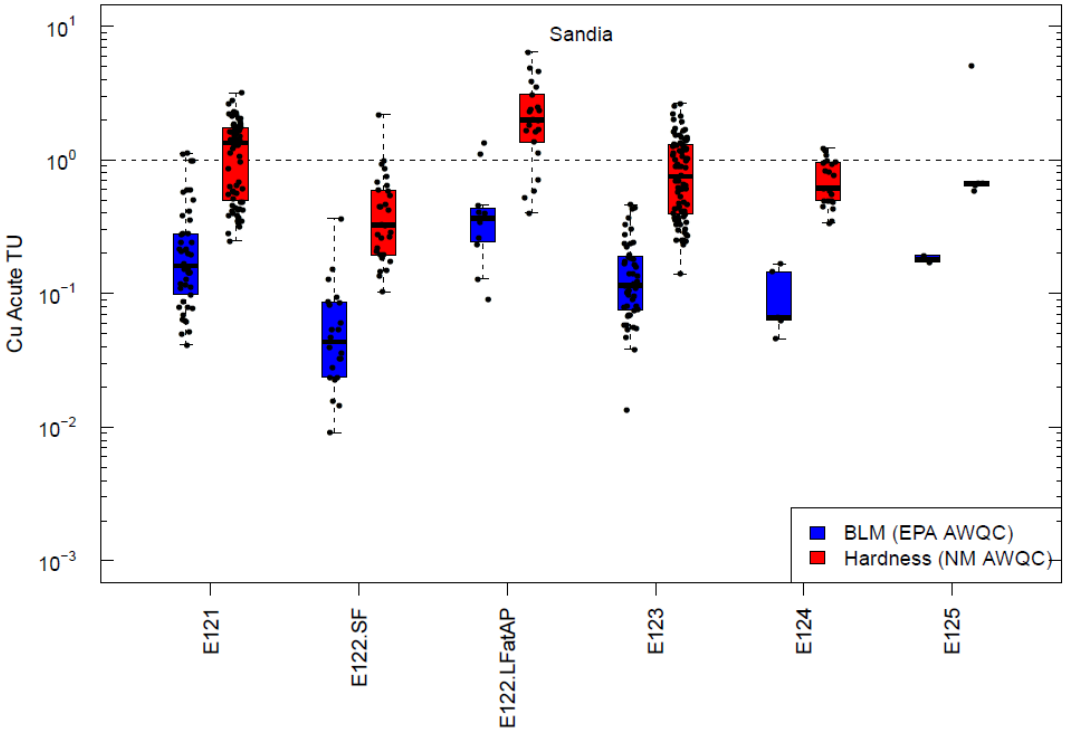


Figure 4-24. Sandia Canyon longitudinal summary of acute dissolved copper IWQC TUs based on BLM and New Mexico (NM) IWQC

Given the BLM sensitivity to pH it is apparent that the lower pH of the stormflow samples at E122 is a significant consideration, which is not surprising given the runoff from the significant impervious surface area in the associated watershed (rainfall is naturally acidic with pH~5.5). Considering spatial patterns in the Upper Sandia perennial waters, not far downstream from E122, BLM events from gage station E123 (Sandia below wetland) exhibited no BLM-based IWQC TUs>1 across a large dataset (n=49 BLM events) nearly evenly distributed between stormflow (n=22) and baseflow (n=27). See Figure 4-24, which again helps to illustrate the significant false positive rate of the hardness-based copper IWQC. Additional longitudinal summaries based on chronic IWQCs are provided in Appendix B.

A longitudinal summary of BLM- and hardness-based acute copper TUs for the supplemental NWQMC dataset for the Rio Grande is shown in Figure 4-25. While BLM-based acute copper TUs are generally lower than hardness-based TUs, the TUs for the Rio Grande are generally lower than those calculated for the LANL dataset. This pattern is likely due to differences in copper concentrations and/or water chemistry (e.g., DOC, pH, and hardness) between the Rio Grande perennial waters and the ephemeral/intermittent surface waters of the Pajarito Plateau. Additional longitudinal summaries based on both acute and chronic IWQCs are provided for the Rio Grande in Appendix C.

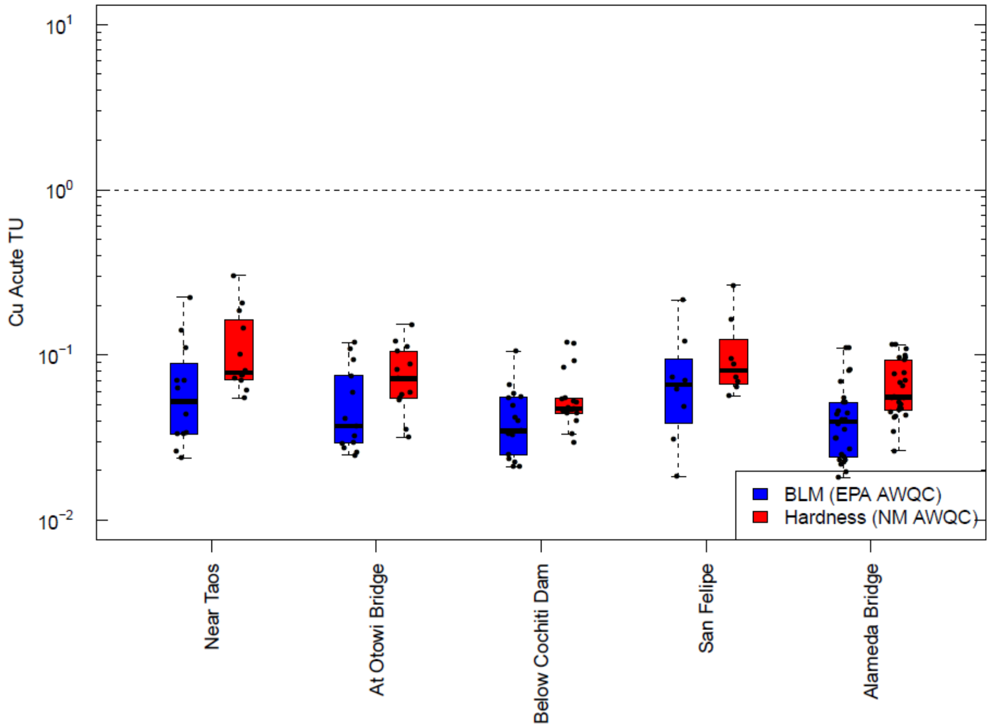


Figure 4-25. Longitudinal summary of acute dissolved copper IWQC TUs based on BLM and New Mexico (NM) IWQC from the Rio Grande dataset

4.5 EVALUATION OF TIME-VARIABLE ACUTE IWQC FOR FMBS AND OTHER POTENTIAL SSWQC OUTCOMES

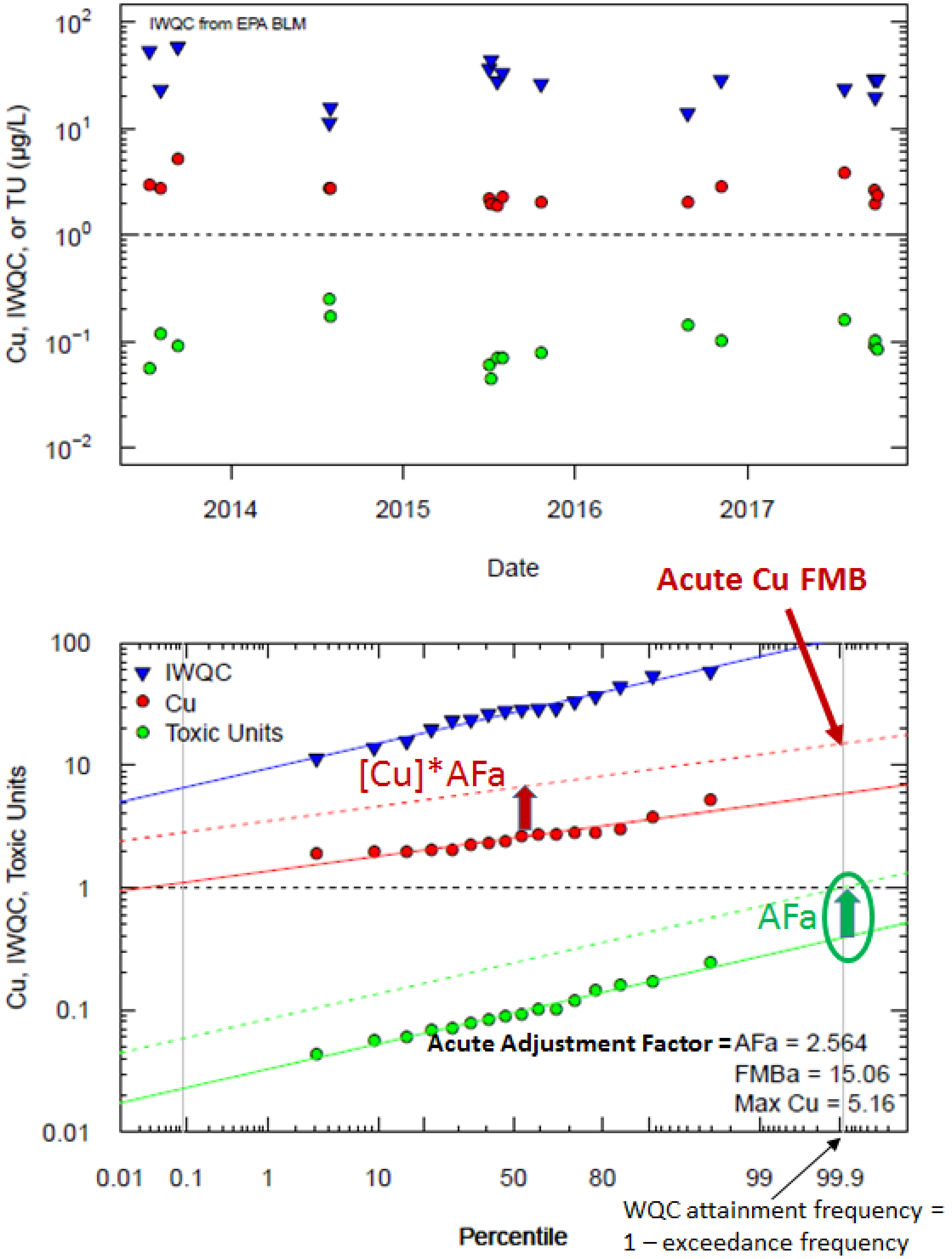
Location-specific acute BLM-based FMBs were calculated for each metal for locations containing at least 10 BLM-based TUs. A summary of acute FMBs for copper, lead, and zinc by sampling location is provided in Table 4-6; FMBs for minor watersheds are described in Section 4.6. Figure 4-26 provides a graphical representation of the BLM-based copper FMB derived for E042.1 as an example. In this figure, "AFa" is the acute adjustment factor applied to the distribution of copper TUs (green dashed line) such that the projected IWQC exceedance frequency is equal to once in three years (the 99.9th percentile). In this case, the AF is 2.56, which is applied to shift the dissolved copper distribution (red dashed line) upwards so that it intersects a value of 15.06 µg/L, which is the FMB. Appendix D provides comprehensive plots of acute IWQC and TUs over time and the corresponding plots used to derive the FMBs for each metal for each location and by minor watershed groups of locations. Plots are also included for aluminum FMBs based on the various filter size sample preparations.

Table 4-6. Acute BLM-based FMB results for copper, lead, and zinc by location

Location ID	Windward ID	Copper (µg/L)	Lead (µg/L)	Zinc (µg/L)
Acid above Pueblo	E056	5.7	175	294
Canon de Valle below MDA P	E256			218
DP above Los Alamos Canyon	E040	12.2	270	356
DP above TA-21	E038	14.2	275	338
DP below grade ctrl structure	E039.1	19.6	177	368
Los Alamos above low-head weir	E042.1	15.1	161	253
Los Alamos below low-head weir	E050.1	14.1	275	305
Mortandad below Effluent Canon	E200	11.5	263	415
Pajarito above Threemile	E245.5	11.2	217	497
Pajarito above Twomile	E243		237	306
Pueblo above Acid	E055	9.6	155	308
Sandia below Wetlands	E123	11.3	276	341
Sandia left fork at Asph Plant	E122.LFatAP	35.3	101	2100
Sandia right fork at Pwr Plant	E121	4.8	58	218
South Fork of Sandia at E122	E122.SF	84.8	1110	787
Twomile above Pajarito	E244	5.1	252	195
Water above SR-501	E252 up			

Note: 1) results shown for locations with more than 10 available TUs, 2) FMBs are based on 0.45µm filtered ("dissolved") metal concentrations and BLM-based IWQCs which are also on a dissolved basis.

BLM – biotic ligand model
FMB – fixed monitoring benchmark
ID – identification
IWQC – instantaneous water quality criteria
TU – toxic unit
Windward – Windward Environmental LLC



Acute Cu FMB

Acute Adjustment Factor = AFa = 2.564
FMBa = 15.06
Max Cu = 5.16

WQC attainment frequency =
1 – exceedance frequency

Figure 4-26. Example BLM-based acute copper FMB for E042.1

Table 4-7 provides a summary of acute BLM- and MLR-based FMB results for aluminum by location, and Table 4-8 provides a summary of acute BLM- and MLR-based FMB results for aluminum by minor watershed. The resulting FMBs vary considerably between the six permutations possible (three filter preparations x two AWQC basis). Care must be taken in interpreting the aluminum FMBs given the uncertainty in 1) the EPA MLR-based AWQC are draft subject to finalization, 2) the BLM has broader bounds than the MLR-based AWQC for DOC and pH as indicated in EPA 2017 and associated literature, 3) the criteria implementation basis (UF, vs F10 vs F0.45), and the significance of impacts from aluminum in the natural background conditions(LANL 2017b, 2016, 2015, 2014, 2013, 2010a, b, 2007).

Table 4-7. Acute aluminum BLM- and MLR-based FMB results based on filter size preparation by location

Location ID	Windward ID	BLM (µg/L)			MLR (µg/L)		
		UF	F10	F0.45	UF	F10	F0.45
Acid above Pueblo	E056	1307		998	1493		1550
Canon de Valle below MDA P	E256	659		503	4204		4988
DP above Los Alamos Canyon	E040	862	991	832	4699	4282	3893
DP above TA-21	E038	695	714	1002	2355	3373	2850
DP below grade ctrl structure	E039.1	1314	636	819	2911	4634	2818
Los Alamos above low-head weir	E042.1	1027		622	2091		2317
Los Alamos below low-head weir	E050.1	2405		1194	2300		2019
Mortandad below Effluent Canon	E200	1398		1384	3588		3564
Pajarito above Threemile	E245.5	2041		1337	830		944
Pajarito above Twomile	E243	1525		1009	3042		2294
Pueblo above Acid	E055	1531		861	1735		1931
Sandia below Wetlands	E123	1339	648	972	2273	3020	2063
Sandia left fork at Asph Plant	E122.LFatAP	339		172	2020		1694
Sandia right fork at Pwr Plant	E121	572	210	689	1770	2602	1467
South Fork of Sandia at E122	E122.SF	1216		611	2972		3360
Twomile above Pajarito	E244	3130		1015	914		1630
Water above SR-501	E252 up	2426		775	3380		883

Note: Results based on 10 or more IWQC and TU results.

BLM – biotic ligand model
F – filtered
FMB – fixed monitoring benchmark
ID – identification
IWQC – instantaneous water quality criteria
MLR – multiple linear regression
TU – toxic unit
UF – unfiltered
Windward – Windward Environmental LLC

Table 4-8. Acute aluminum BLM- and MLR-based FMB results based on filter size preparation by minor watershed

Canyon	2015 Draft IP MTAL (µg/L)	BLM (µg/L)			MLR (µg/L)		
		UF	F10	F0.45	UF	F10	F0.45
Acid	442	1360		1064	1461		1625
Canon de Valle	974	659		503	4204		4988
DP	688	899	913	970	3040	4651	3489
Los Alamos	1042	3038	783	837	3727	3866	2234
Mortandad	554	2029		1283	3215		2718
Pajarito	1069	3305	1579	1266	1354	3517	1738
Pueblo	985	1058		907	1673		1721
Sandia	1490	1377	299	901	2310	3397	1784
Twomile	628	3130		1015	914		1630
Water	965	737		430	4281		1408

Note: Blank cells indicate that there were no data, or insufficient data for calculating FMBs
Results based on 10 or more IWQC and TU results.

BLM – biotic ligand model
F – filtered
FMB – fixed monitoring benchmark
IWQC – instantaneous water quality criteria
MLR – multiple linear regression
MTAL – maximum target action level
UF – unfiltered
TU – toxic unit

Additionally, 10th, 25th and 50th percentiles of acute BLM-based IWQCs for copper, lead, and zinc are provided for the LANL dataset in Table 4-9 (for locations with at least 10 calculated TUs). Table 4-10 provides a similar summary of acute BLM- and MLR-based IWQC percentiles for aluminum by location for the LANL dataset, and Table 4-11 provides a summary of IWQC percentiles calculated for the Rio Grande dataset.

Where data are absent or insufficient to generate BLM-based IWQC for a location of interest, using conservative percentile IWQC results from other, representative locations that have BLM-based IWQC datasets may be a useful initial approach for screening observed metals concentrations. For example, the State of Idaho's guidance recommends NPDES permit writers use the minimum 10th percentile of BLM-based IWQC for 189 locations characterized in 2016 as part of that state's initial BLM rulemaking effort (IDEQ 2017).

Additionally, as an alternative for reconciling time-variable IWQC when data are insufficient for calculating FMBs, conservative percentiles have been proposed for initial screening purposes (McConaghie and Matzke 2016). EPA has gone so far as to indicate that the 2.5th percentile IWQC may need to be used for conservatism (EPA 2016), although caution must be exercised when using such an approach to evaluate any unintended over-conservatism. The 10th, 25th, and 50th BLM-based IWQC percentiles were also evaluated by Oregon DEQ in its 2016 Technical Support Document used for statewide copper criteria evaluations using the BLM (McConaghie and Matzke 2016). Lastly, the 50th percentile (median) is provided as a general measure of central tendency that can be compared with the hardness-based IP MTALs that have been based on geometric mean or average hardness.

Careful consideration of the key differences between FMBs and IWQC are needed while interpreting the time-variable outcomes provided herein. Significant differences in BLM IWQC and TU results among multiple locations may affect FMBs derived for multiple locations within a particular canyon or AU grouping. Similarly, certain locations may contain BLM events dominated by certain sample types, e.g., WT – stormflow versus WM/WP/WS baseflow that may have experienced significantly different water quality that might lead to correspondingly different IWQC and/or FMBs.

Specifically, the copper BLM-based FMBs for the four sampling locations in the Upper Sandia AU varied across an order of magnitude between 4.8 and 85 µg/L (see Table 4-6, copper FMBs, for locations "Sandia right fork at Pwr Plant (E121)" and "South Fork of Sandia at E122 (E122.SF)"). Meanwhile, an overall copper FMB of 8.5 µg/L for all four locations in the AU grouped together (Table 4-12) was approximately an order of magnitude lower than the highest individual Sandia location FMB. Interestingly, among the four locations (n=127 BLM datasets), copper would exceed an FMB in 16 samples, while 6 of those results would not have exceeded BLM-based acute IWQC. In practice, exceedances of an IWQC (or lack thereof) should take precedence over exceedances of an FMB for a particular sample result. Some of this contrast may reflect significant differences between baseflow and stormflow water quality that will require further consideration, especially where pH measurements are concerned as described in Section 4.4. This situation is applicable to lead and zinc BLM-based FMBs for Sandia as well, which is not surprising because those metal BLMs behave similarly to the copper BLM.

Table 4-9. Acute copper, lead and zinc BLM IWQC percentiles by location

Location ID	Windward ID	Median Hardness (mg/L as calcium carbonate)	Copper (μg/L)			Lead (μg/L)			Zinc (μg/L)		
			10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile
Acid above Pueblo	E056	20	7.4	8.9	16	160	180	210	240	250	290
Canon de Valle below MDA P	E256	66	10	12	18	130	160	180	190	210	250
DP above Los Alamos Canyon	E040	28	16	20	26	220	260	330	230	270	300
DP above TA-21	E038	28	8.1	11	13	120	150	210	160	180	220
DP below grade ctrl structure	E039.1	25	12	16	20	160	200	280	200	220	290
Los Alamos above low-head weir	E042.1	34	15	22	28	260	280	310	270	290	330
Los Alamos below low-head weir	E050.1	45	17	23	33	290	340	370	280	310	350
Mortandad below Effluent Canon	E200	28	16	23	26	240	270	350	310	350	360
Pajarito above Threemile	E245.5	24	8.3	16	25	170	230	310	280	320	370
Pajarito above Twomile	E243	35	10	20	24	160	210	250	210	230	270
Pueblo above Acid	E055	39	23	28	32	310	340	380	320	320	360

Location ID	Windward ID	Median Hardness (mg/L as calcium carbonate)	Copper (μg/L)			Lead (μg/L)			Zinc (μg/L)		
			10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile
Sandia below Wetlands	E123	53	17	28	40	240	290	370	240	270	340
Sandia left fork at Asph Plant	E122.LFatAP	26	7.1	16	22	97	200	230	210	240	300
Sandia right fork at Pwr Plant	E121	27	9.3	14	31	130	190	250	160	210	240
South Fork of Sandia at E122	E122.SF	111	79	100	120	490	570	710	320	380	480
Twomile above Pajarito	E244	30	8.9	14	21	180	210	240	220	230	300
Water above SR-501	E252 up	46	2.1	4.2	6.5	39	78	120	160	170	200

Note: Results based on 10 or more IWQC and TU results.

BLM – biotic ligand model
IWQC – instantaneous water quality criteria
Windward – Windward Environmental LLC
ID – identification

Table 4-10. Acute total aluminum IWQC percentiles based on BLM and MLR by location

Location ID	Windward ID	Median Hardness (mg/L calcium carbonate)	Aluminum BLM (µg/L)			Aluminum MLR (µg/L)		
			10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile
Acid above Pueblo	E056	20	720	820	1100	1600	1900	2200
Canon de Valle below MDA P	E256	66	610	720	840	2800	3400	3600
DP above Los Alamos Canyon	E040	28	790	900	1000	3100	3600	3600
DP above TA-21	E038	28	570	640	880	1900	2200	2600
DP below grade ctrl structure	E039.1	25	720	810	1100	2600	2800	3100
Los Alamos above low-head weir	E042.1	34	850	1100	1200	2300	2700	3500
Los Alamos below low-head weir	E050.1	45	820	980	1400	2600	3200	3800
Mortandad below Effluent Canon	E200	28	970	1100	1300	2800	3100	3900
Pajarito above Threemile	E245.5	24	990	1200	1800	1200	1500	2100
Pajarito above Twomile	E243	35	690	800	1100	3000	3400	3900
Pueblo above Acid	E055	39	1100	1100	1200	2300	3500	3800
Sandia below Wetlands	E123	53	620	790	920	2500	3300	3800
Sandia left fork at Asph Plant	E122.LFatAP	26	640	900	1100	1400	2200	2400
Sandia right fork at Pwr Plant	E121	27	380	480	660	2200	2500	3200
South Fork of Sandia at E122	E122.SF	111	470	660	820	1700	2400	3100
Twomile above Pajarito	E244	30	590	670	1000	1600	1900	2900
Water above SR-501	E252 up	46	400	450	640	1300	1800	2500

Note: Results based on 10 or more IWQC and TU results.

BLM – biotic ligand model
ID – identification
IWQC – instantaneous water quality criteria
MLR – multiple linear regression
Windward – Windward Environmental LLC

Table 4-11. Acute copper, lead, and zinc BLM IWQC percentiles and acute aluminum BLM and MLR IWQC percentiles for the Rio Grande dataset

Location ID	Date Range	No. of Events	Median Hardness (mg/L)	Copper (µg/L)			Lead (µg/L)			Zinc (µg/L)			Aluminum BLM (µg/L)			Aluminum MLR (µg/L)		
				10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile	10th Percentile	25th Percentile	50th Percentile
Rio Grande below Taos Junction Bridge near Taos, New Mexico	2005 to 2010	12	97	12	13	26	86	104	163	93	111	159	58	214	930	1300	1300	1550
Rio Grande at Otowi Bridge, New Mexico	2005 to 2010	13	109	11	17	22	104	142	211	125	158	239	91	160	499	1400	1900	2600
Rio Grande below Cochiti Dam, New Mexico	2009 to 2015	18	120	15	17	23	163	192	223	216	231	264	120	227	826	2800	3125	3600
Rio Grande at San Felipe, New Mexico	2005 to 2008	8	114	12	15	20	122	135	175	147	149	198	66	70	374	1770	1875	2150
Rio Grande at Alameda Bridge at Alameda, New Mexico	2005 to 2015	27	122	15	20	30	173	196	254	196	227	255	84	195	1308	2000	2550	3200

BLM – biotic ligand model
ID – identification
MLR – multiple linear regression
IWQC – instantaneous water quality criteria

In contrast, most other FMBs were relatively similar between the individual locations (Table 4-6) and the pooled locations among the various canyons (Table 4-12). For example, the range of copper FMBs for individual and pooled locations for DP, Los Alamos, Mortandad and Pajarito canyons fell within a relatively narrow range of 11 to 15 µg/L, and none of the observed copper concentrations exceeded any FMB basis. The dataset for these four canyons contains nearly 200 BLM sample events across most of the past 13 years, with over 130 samples collected in the past 5 years, thus is robust and sound for considering BLM-based alternative AWQC (as IWQCs or FMBs).

4.6 POTENTIAL TARGET ACTION LEVELS FOR THE LANL INDIVIDUAL PERMIT

This section provides a summary of how some of the above-described outcomes might be used for NPDES permit compliance. In the case of LANL's NPDES individual permit (IP) for solid waste management units and areas of concern, acute hardness-based New Mexico AWQC are used as the current basis for maximum target action levels (MTALs). The MTALs are used to determine compliance activities based on storm water sampling results. In the 2010 IP, the metals MTALs were based on a 30-mg/L hardness[14], which yielded one-size-fits-all MTALs for dissolved copper, lead, and zinc of 4.3, 17, and 42 µg/L, respectively (while in effect in early 2010, MTALs based on hardness-based New Mexico AWQC for aluminum were not included in the 2010 IP by EPA). In contrast, the 2015 draft IP, in its Appendix F proposed ranges of MTALs for these metals, including aluminum across the numerous canyon watersheds; the MTALs were based on acute New Mexico AWQC using spatially aggregated average hardness results for surface water samples for each canyon.

The 2015 draft IP MTALs for copper, lead, and zinc are provided in Table 4-12, which also contains BLM-based acute FMBs for canyons for which 10 or more BLM acute IWQC and TU datasets were available, as identified in Section 4.2. Table 4-12 also provides median BLM acute IWQC for copper, lead and zinc for canyons with 10 or more BLM events. This table provides columns for each metal showing the factor difference between the acute BLM-based potential MTALs and the 2015 draft IP MTALs. The table also provides median hardness results for each canyon derived from the BLM dataset aggregated herein (10 or more samples).

In either case of the BLM application (acute FMBs or median acute IWQC), the differences with respect to the 2015 draft IP MTALs were most pronounced for lead (14- to 18-fold higher on average) and zinc (5-fold higher on average). All BLM-based acute copper FMBs were higher than the 2015 draft IP MTALs, ranging from 10% higher for Sandia to 6.2 times higher for Water canyon. Meanwhile, acute BLM IWQC ranged from 3.2 to 7.8 times higher than the 2015 MTALs. Thus, using either BLM-

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[14] A 2008 LANL report indicates an overall geometric mean hardness of 30.1 mg/L and a median of 29.2 mg/L for filtered hardness results from 423 samples collected in receiving waters across LANL watersheds(LANL 2008).

based MTAL (acute FMB or median acute IWQC) for any of these three metals would likely yield different compliance scenarios. If it is accepted that the BLM provides more accurate environmental protection than do hardness-based AWQC, especially given the level of vetting behind the EPA 2007 copper BLM-based AWQC, it follows that BLM-based MTALs also can lead to more accurate decision making for storm water compliance needs while maintaining the level of environmental protection intended by EPA.

For aluminum, the potential new MTALs are a more complex set of outcomes related to the different combinations of sample preparations (e.g., UF, F0.45, F10 and F1) and the three types of AWQC evaluated (i.e., BLM, EPA 2017 MLR, and New Mexico 2010). Tables 4-7 and 4-13 provide the summaries accordingly.

Table 4-12. Potential BLM-based IP MTALs for copper, lead, and zinc by canyon

Canyon	2015 Draft IP Hardness	Median Hardness (mg/L)	Change in Hardness (%)	Dissolved Copper (µg/L)						Dissolved Lead (µg/L)						Dissolved Zinc (µg/L)					
				2015 Draft IP MTAL	BLM FMB[a]	Factor Diff. from IP	BLM IWQC Median	Factor Diff. from IP	Acute New Mexico WQC[b]	2015 Draft IP MTAL	BLM FMB[a]	Factor Diff. from IP	BLM IWQC Median	Factor Diff. from IP	Acute New Mexico WQC[b]	2015 Draft IP MTAL	BLM FMB[a]	Factor Diff. from IP	BLM IWQC Median	Factor Diff. from IP	Acute New Mexico WQC[b]
Acid	22	20	-13%	3.3	9.1	2.8	17	5.2	3.0	12	223	18	210	17	10	41	346	8.4	310	7.5	37
South Fork Acid	21			3.1						12						39					
Ancho	40	43	7%	5.6					6.3	23					27	69					75
North Fork Ancho	30			4.3						17						54					
Arroyo de la Delfe	22			3.2						12						40					
Bayo	59			8.1						36						99					
Canada del Buey	39			5.5						23						67					
Canon de Valle	40	66	66%	5.7			18	3.2	9.5	23			180	7.7	48	69	218	3.1	250	3.6	113
Chaquehui	30	25	-18%	4.3					3.7	17					14	54					46
DP	31	26	-15%	4.5	14.5	3.3	19	4.3	4.0	18	230	13	250	14	15	55	339	6.2	280	5.1	49
Fence	68			9.4						42						113					
Graduation	31			4.5						18						55					
Los Alamos	42	47	11%	5.9	13.7	2.3	29	4.9	6.8	25	219	8.8	370	15	31	73	221	3.0	350	4.8	82
Mortandad	26	30	12%	3.8	12.7	3.3	30	7.8	4.5	15	290	19	400	27	17	48	325	6.8	410	8.6	54
Pajarito	43	32	-24%	6.0	14.8	2.5	24	4.0	4.8	25	237	9.3	290	11	19	74	395	5.3	360	4.9	59
Potrillo	21			3.1						12						39					
Pratt	26			3.8						15						48					
Pueblo	40	39	-4%	5.7	9.7	1.7	35	6.1	5.7	24	173	7.3	410	17	24	70	423	6.0	370	5.3	69
Rendija	115			15.3						75						181					
Sandia	55	48	-12%	7.6	8.5	1.1	40	5.3	7.0	33	172	5.2	350	11	32	92	282	3.1	320	3.5	84
Ten-Site	16			2.4						8.3						30					
Threemile	29			4.2						17						52					
Twomile	29	30	4%	4.2	5.1	1.2	21	5.0	4.5	16	252	15	240	15	18	52	195	3.8	300	5.8	55
Walnut	23			3.3						13						42					
Water	40	43	8%	5.6	35.1	6.2	19	3.4	6.3	23	1479	63	260	11	28	69	303	4.4	230	3.3	76

Note: Median based on 10 or more results unless indicated by *.

Blank cells indicate that there were no data or insufficient data for calculating FMBs.

[a] FMBs shown only for locations with 10 or more IWQC and TU results.

[b] New Mexico WQC are based on median hardness.

BLM – biotic ligand model
FMB – fixed monitoring benchmark
IP – individual permit
IWCQ – instantaneous water quality criteria
MTAL – maximum target action level
WQC – water quality criteria

Table 4-13. Potential BLM- and MLR-based IP MTALs for total aluminum by canyon

				Total Aluminum (µg/L)				
	2015 Draft IP		Median Hardness (mg/L)	Acute FMB[a,b]		Acute IWQC Median Values[c]		
Canyon	Hardness	MTAL (µg/L)		BLM	EPA 2017 MLR	BLM	EPA 2017 MLR	New Mexico 2010
Acid	22	442	20	1360	1461	1200	2200	365
South Fork Acid	21	414						
Ancho	40	966	43					1060
North Fork Ancho	30	658						
Arroyo de la Delfe	22	427						
Bayo	59	1649						
Canada del Buey	39	926						
Canon de Valle	40	974	66	659	4204	840	3600	1948
Chaquehui	30	667	25					501
DP	31	688	26	899	3040	1000	3200	549
Fence	68	2026						
Graduation	31	692						
Los Alamos	42	1042	47	3038	3727	1400	4000	1200
Mortandad	26	554	30	2029	3215	1300	4200	650
Pajarito	43	1069	32	3305	1354	1400	3000	731
Potrillo	21	409						
Pratt	26	554						
Pueblo	40	985	39	1058	1673	1300	3900	935
Rendija	115	4122						
Sandia	55	1490	48	1377	2310	890	3300	1250
Ten-Site	16	274						
Threemile	29	639						
Twomile	29	628	30	3130	914	1000	2900	664
Walnut	23	452						
Water	40	965	43	737	4281	600	2500	1072

Note: Blank cells indicate that there were no data or insufficient data for calculating FMBs.

[a] FMBs shown only for locations with 10 or more available IWQC and TU results.

[b] FMBs based on TUs for unfiltered aluminum.

[c] Median IWQC based on 10 or more results.

BLM – biotic ligand model
EPA – US Environmental Protection Agency
FMB – fixed monitoring benchmark
IP – individual permit
IWQC – instantaneous water quality criteria
MLR – multiple linear regression
MTAL – maximum target action level
TU – toxic unit

4.7 APPLICATION OF BLM CHRONIC IWQC TO PERENNIAL SURFACE WATERS

Chronic IWQC were generated for all sample events, but only evaluated for specific LANL waters currently designated in §126 NMAC as perennial waters (e.g., upper Sandia, and specific AUs in Water Canyon and Canon de Valle). Although chronic IWQC are technically applicable to §98 NMAC waters (i.e., default intermittent) such as the greater Pueblo Canyon, chronic IWQC were not evaluated for these waters, partly to avoid potential confusion, since it is understood that some of these waters are being (or will be) evaluated under the NMED Hydrology Protocol use attainability analysis approach to determine whether habitat and hydrology support an aquatic life use that may or may not be subject to chronic AWQC.

Figures 4-27 to 4-29 portray comparisons of chronic IWQC TUs for §126 NMAC perennial waters in the LANL dataset. Similar patterns emerge consistent with those for the acute IWQC comparisons in Section 4.2, although the false positive rates for chronic IWQC based on hardness are now significant for lead (49%) and zinc (12%). For copper, the hardness-based chronic IWQC exhibited resulted in false positives over the BLM-based chronic IWQC in nearly half the samples (49%). Chronic aluminum IWQC TU plots for the LANL dataset are provided in Appendix E, and chronic copper, zinc, and aluminum IWQC TU plots for the Rio Grande dataset are also provided in Appendix F.

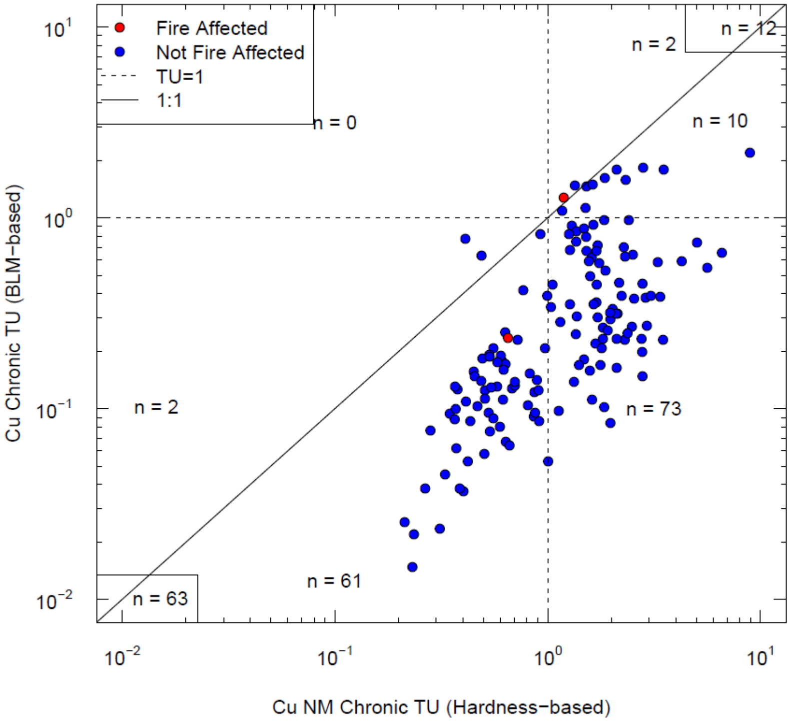

Figure 4-27. Comparison of dissolved <u>copper chronic IWQC</u> TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters

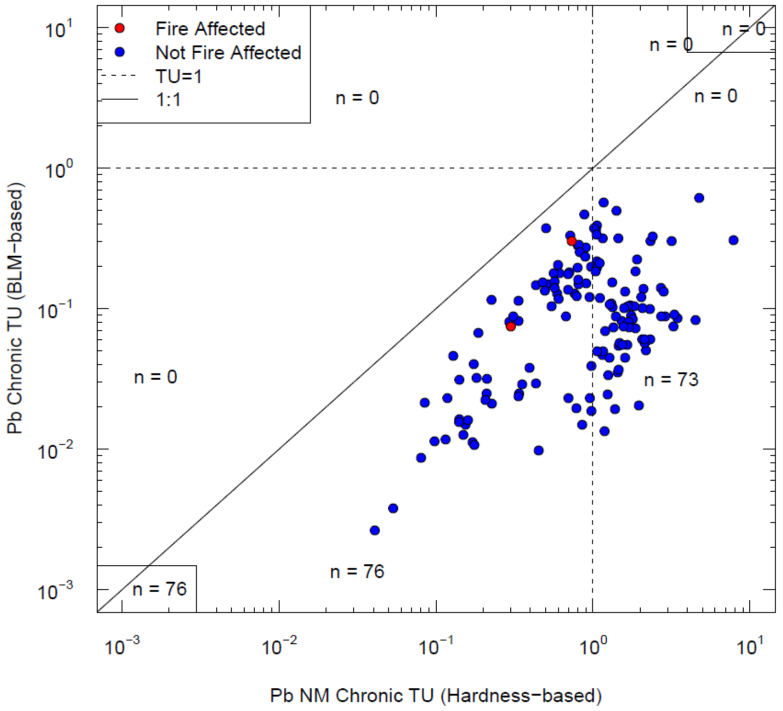

Figure 4-28. **Comparison of dissolved <u>lead chronic IWQC</u> TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters**

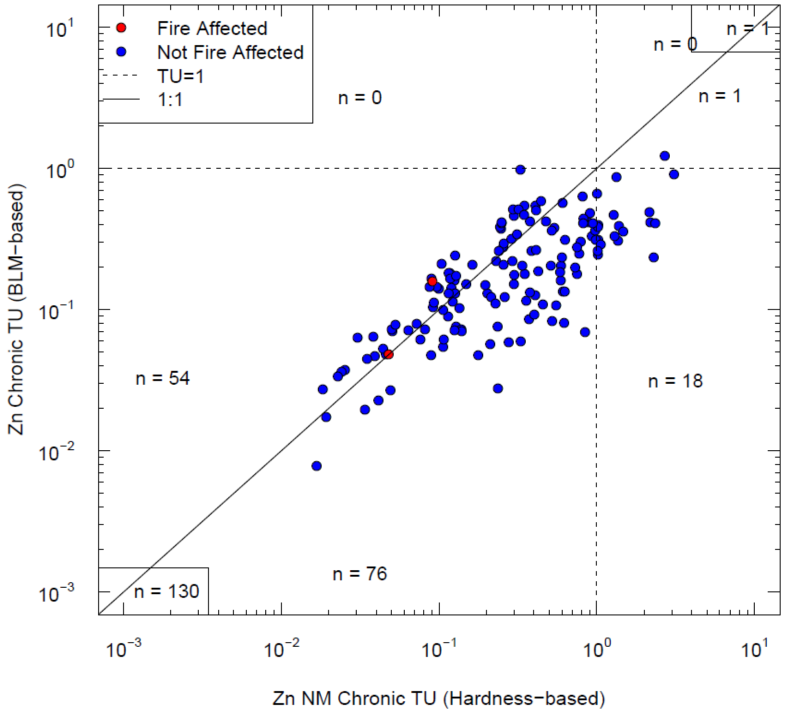

Figure 4-29. **Comparison of dissolved <u>zinc chronic IWQC</u> TUs based on BLM and New Mexico AWQC for NMAC Class 126 waters**

4.8 IMPLICATIONS OF BLM-BASED IWQC FOR 303(D) LISTINGS

As mentioned in Section 4.3, application of BLM-based AWQC for copper can be expected to result in potentially significant differences for water quality standards compliance determinations versus using hardness-based AWQC, whether for acute or chronic criteria considerations. Such differences for lead and zinc are likely to be less significant for acute criteria but of potential concern for chronic criteria. To illustrate the potentially different outcomes, Table 4-14 compares LANL BLM dataset outcomes for the current and proposed New Mexico §303(d) listings for copper (NMED 2018). For the five new AU segments proposed for Category 5 listings for impairments by copper (acute), results for hardness-based New Mexico TUs support the new listings, while BLM-based TUs show zero incidence of acute BLM-based IWQC exceedances.

Similarly, for the three of seven previously §303(d)-listed AUs, BLM datasets indicate no acute copper IWQC exceedances. Two of the seven listed AUs would probably also pose little to no risk based on the BLM after consideration of BDL copper results used to calculate the TU values. BLM datasets were not available for the remaining two AUs. The Acid Canyon AU previously §303(d)-listed for impairment by zinc is proposed for delisting in 2018, which is supported by results for New Mexico hardness-based and BLM-based IWQC from the current LANL dataset.

As discussed in Sections 4.4-4.6, the Upper Sandia Canyon water quality patterns bear further consideration with regard to BLM outcomes (IWQC and FMBs). The relatively frequent exceedances (48%) of New Mexico acute copper IWQC are in sharp contrast to infrequent (4%) BLM-based IWQC exceedances, which may be limited to particular flow regimes. The acute criteria averaging period for the EPA 2007 BLM-based copper AWQC is 24 hours, which bears consideration for the interplay between the relatively stable baseflow and intermittent, short duration storm water runoff that Upper Sandia canyon experiences, a fairly unique situation with respect to other Pajarito Plateau waters.

Table 4-14. Comparison of IWQC attainment based on BLM and New Mexico IWQC generated for 303(d) Impaired Waters Listings in the LANL vicinity

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_ID	AU Name	WQS Reference	IMPAIRMENT	IR Category (by AU)	CYCLE FIRST LISTED	n	TU>1	exc freq (%)	n	TU>1	exc freq (%)	Locations
NM-128.A_06	Pajarito Canyon (Two Mile Canyon to Arroyo de La Delfe)	20.6.4.128	COPPER, ACUTE	5/5C	2016	9	7*	78%	9	1*	11%	E243
NM-9000.A_042	Mortandad Canyon (within LANL)	20.6.4.128	COPPER, ACUTE	5/5C	2010	17	7	41%	17	0	0%	E200, E201, E204
NM-9000.A_047	Sandia Canyon (Sigma Canyon to NPDES outfall 001)	20.6.4.126	COPPER, ACUTE	5/5B	2010	128	61	48%	127	4	3%	E121, E122 (2), E123
NM-97.A_002	Acid Canyon (Pueblo to headwaters)	20.6.4.98	COPPER, ACUTE	5/5C	2010	27	1*	4%	27	1*	4%	E055.5, E056
NM-97.A_004	Walnut Canyon (Pueblo Canyon to headwaters)	20.6.4.98	COPPER, ACUTE	5/5C	2014	no data						
NM-97.A_005	Graduation Canyon (Pueblo Canyon to headwaters)	20.6.4.98	COPPER, ACUTE	5/5C	2010	no data						
NM-97.A_029	South Fork Acid Canyon (Acid Canyon to headwaters)	20.6.4.98	COPPER, ACUTE	5/5A	2014	7	0	0%	7	0	0%	E055.5
NM-97.A_029	South Fork Acid Canyon (Acid Canyon to headwaters)	20.6.4.98	ZINC, ACUTE	5/5A	2014	7	0	0%	7	0	0%	E055.5
NM-128.A_14	DP Canyon (Grade control to upper LANL bnd)	20.6.4.128	Copper, Dissolved	5/5C	2018	49	15	31%	49	0	0%	E038, E039.1
NM-9000.A_043	Pueblo Canyon (Acid Canyon to headwaters)	20.6.4.98	Copper, Dissolved	5/5C	2018	13	5	38%	13	0	0%	E055
NM-128.A_16	Arroyo de la Delfe (Pajarito Canyon to headwaters)	20.6.4.128	Copper, Dissolved	5/5C	2018	4	3	75%	4	0	0%	E242.5
NM-128.A_08	Pajarito Canyon (Lower LANL bnd to Two Mile Canyon)	20.6.4.128	Copper, Dissolved	5/5C	2018	18	5	28%	18	0	0%	E245.5, E250
NM-128.A_15	Two Mile Canyon (Pajarito to headwaters)	20.6.4.128	Copper, Dissolved	5/5C	2018	10	5*	50%	10	0	0%	E244

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

5 Discussion, Uncertainty and Other Considerations for Further Use of the BLM DQA Results

This section describes the types of uncertainty encountered and how they may affect key considerations going forward, including but not limited to:

1. Status of BLMs and their acceptance for generating AWQC that meet EPA guidelines
2. IWQC uncertainty with respect to key water quality variables
3. Existing or upcoming New Mexico water quality assessments
4. Spatial groupings of data for FMBs
5. Use of percentiles versus FMBs
6. Potential new IP MTALs

5.1 STATUS OF BLMS AND THEIR ACCEPTANCE FOR GENERATING AWQC THAT MEET EPA GUIDELINES

To date, EPA has recommended the BLM for use only in generating copper AWQC for freshwater aquatic life, and two states have adopted the BLM as a statewide replacement of hardness-based copper AWQC.[15] However, the BLMs for aluminum, lead, and zinc applied herein have been developed in a manner similar to that used to develop EPA's 2007 nationally recommended copper AWQC. In addition, the aluminum, lead, and zinc BLMs applied herein have been developed and evaluated for the purpose of generating AWQC according to EPA guidelines (e.g., DeForest and Van Genderen 2012; DeForest et al. 2017; Santore et al. 2018). It is not clear if or when EPA will recommend BLM-based AWQC for aluminum, lead, zinc, or other metals. Nonetheless, the lack of an EPA national recommendation does not preclude a state from adopting BLM-based AWQC as a uniform replacement of, or side-by-side alternative to, current hardness-based AWQC, or as SSWQC subject to state agency and EPA review and approval in each case. Additionally, EPA's initial and revised draft "missing parameters" documents (EPA 2012b, 2016) provide an approach that can be used to address not only missing data for copper BLM-based AWQC, but also for the other BLMs given consistent relationships.

Thus, the underpinnings of the BLMs applied herein are sound, state of the science understandings designed to maintain EPA's intended level of protection and provide a potential new and more accurate basis for evaluating not only LANL-area waters but others where suitable datasets exist. This DQO/DQA provides a sound framework for evaluating water quality datasets to generate BLM-based outcomes. The considerable

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[15] EPA released draft marine/estuarine AWQC for copper based on the BLM in 2016 (EPA [in prep]).

differences shown between BLM-based AWQC outcomes and those based on current hardness-based AWQC generally suggest that very different surface water quality management decisions might be reached, and that fewer causes for concern would be raised by considering the more accurate BLM-based approaches.

5.2 IWQC UNCERTAINTY WITH RESPECT TO KEY WATER QUALITY VARIABLES

While the dataset used herein to generate BLM-based IWQCs was rich, with respect to BLM input parameters, strategies to address missing values had to be used to maximize usable datasets. Data for pH, which is regarded as a highly important BLM parameter, were available for this dataset, so no estimates of pH were used. However, data for DOC, another sensitive input to the BLM, had to be estimated from TOC in cases where only TOC data were available. In general, estimating DOC from TOC for BLM purposes is a recognized approach, e.g. as used in Oregon (ODEQ 2016a) , and herein was bounded by patterns exhibited in the local dataset. While conservative decisions were made in estimating DOC concentrations, DOC is often an important limitation for application of the BLM. Future monitoring to support BLM application should plan for the collection of complete datasets.

No data existed for temperature in the dataset considered herein, but a temperature sensitivity analysis demonstrated that a conservative assumption of 10°C was appropriate (lower bound of BLM calibration range for temperature input). Temperature has little impact on BLM predictions for copper, lead, and zinc, but it can be important for aluminum (Figure 4-3). To gain a better understanding of the potential broader impacts on decision making from using estimated temperature values for aluminum, further evaluations are needed. The differences in BLM-based acute aluminum IWQC computed at 10°C versus those computed at 15°C appear to be significant and most Pajarito Plateau surface waters are likely to be warmer than 10°C most of the year (e.g., summer monsoonal runoff). The water temperature variable is not included in the MLR proposed by EPA in its 2017 draft aluminum AWQC, so if such AWQC are eventually adopted, the temperature sensitivity issue for aluminum may be moot.

5.3 EXISTING AND UPCOMING NEW MEXICO WATER QUALITY ASSESSMENTS

Employing the BLM to evaluate acute copper IWQC was shown to yield potentially significant differences in assessment outcomes compared to using the current New Mexico hardness-based criteria. The evaluations showed a 36% false positive rate: using hardness-based IWQC would yield an incorrect decision on the status of water quality standard attainment in 36% of the samples. This finding suggests that the 305(b)/303(d) status of current or proposed listings of impairment caused by copper in the LANL area waters may need to be reconsidered in light of the copper BLM-based AWQC. Indeed, based on the proposed 2018 303(d) listings, five additional AUs have been identified as impaired by copper, yet none of the observed copper concentrations exceeded BLM-based acute IWQC for associated locations in the LANL BLM dataset.

The difference was less pronounced for acute zinc IWQC (2% false positive rate), and no errors were apparent for acute lead IWQC. However, the New Mexico hardness-based acute IWQC for lead and zinc tended to yield TUs that were approximately an order of magnitude higher than TUs for BLM-based acute IWQC for these metals (Figures 4-6 and 4-7). These patterns suggest a tendency that might yield significant potential false positives for acute IWQC in other cases where higher observed lead and zinc concentrations might occur. In contrast, chronic IWQC for lead and zinc exhibited pronounced differences between TUs for BLM-based and New Mexico hardness-based IWQC with 49% and 12% false positives, respectively.

Based on visual inspections of the plots contained herein, potentially fire-affected data appear to fall within the overall distributions in the TU quadrant plots and so probably pose little if any impact on potential conclusions that might be reached. However, spatial groupings of BLM datasets should be carefully considered.

5.4 SPATIAL GROUPINGS OF DATA FOR FMBS

For purposes of generating single target values analogous to NPDES WQBELs or sampling benchmarks, like those of the EPA MSGP and LANL IP, the FMBs and median IWQC have merit to the extent that they are sufficiently representative of the key variables involved and projected for the future. The FMB provides an advantage because it explicitly examines observed and projected metal concentrations and exceedance frequencies, while median IWQC are based solely on observed IWQC without regard to observed metals levels or projections. The relatively large datasets for certain canyons yielded robust FMBs and median IWQC that could readily be considered as a new basis for MTALs in the forthcoming LANL IP. The copper acute FMBs for DP, Los Alamos and Pajarito canyons were very similar (13.7 to 14.9 µg/L) and based on relatively large BLM datasets collected over more than a decade and so pooling data for a single FMB for these canyons appears reasonable. However, further consideration of FMBs for Upper Sandia is warranted based on the patterns observed between FMBs and IWQC across the four sampling locations discussed in Section 4.5. An FMB based on data pooled for the four locations appears to be overshadowed by the distinctly different patterns in water quality between baseflow (WS or WP samples representative of stable effluent flow from LANL NPDES outfall 001) versus storm water runoff (WT samples). Further evaluations of pH during the two distinct flow regimes is recommended, as well as considerations for accounting for the acute BLM-based AWQC averaging period (24-hours).

5.5 USE OF HARDNESS-BASED MTALS FOR THE IP

Because the MTALs in the 2015 draft IP depend on hardness results available at the time, i.e. through circa 2014, new hardness data should be evaluated to update those MTALs if BLM-based MTALs or other consideration for use of the BLM is not provided via the IP. For example, compared with the 2015 draft IP hardness basis, median hardness is 66% higher in the current dataset for Canon de Valle, while it is

24% lower for Pajarito canyon. However, the hardness data evaluated herein were limited to those samples that had available BLM datasets so it is not clear if potentially available additional hardness data might further influence updated hardness-based MTALs for copper, lead, zinc and aluminum. In addition, it is not clear whether data richness might affect such considerations (median hardness-based MTALs calculated herein were based on 10 or more samples, while it is not clear for the 2015 draft IP whether sample numbers were taken into account). A relative change in the hardness basis of an MTAL will result in a proportional change in the MTAL calculated on that hardness value and so the uncertainty could have potentially significant impacts on IP compliance decision making.

5.6 POTENTIAL NEW IP MTALS BASED ON THE BLM

The potential impact of the BLM on setting new IP MTALs for copper, lead and zinc is clear (Table 4-12). For copper, BLM-based acute FMBs averaged nearly 3-fold higher, and BLM-based median acute IWQC averaged 5-fold higher than the hardness-based 2015 draft IP MTALs. Similarly, for zinc, both BLM-based alternatives averaged 5-fold higher. And for lead, the BLM-based MTAL alternatives had even greater differences than hardness-based MTALs; averaging 14- to 18-fold higher than the 2015 IP MTALs. In these cases, the FMB-based BLM scenarios may have more merit than median IWQC-based scenarios as IP MTALs because of the greater degree of realism provided by the FMB in terms of its inclusion of exceedance frequency patterns. However, as mentioned above, the sensitivity of the FMB to variability in IWQC and/or TUs for certain locations and spatial groupings appears important and warrants further evaluation. Potential new IP MTALs for aluminum will have to consider the broader issues and considerations posed by 1) sample preparation methods (measurements of unfiltered aluminum are clearly inappropriate for determining compliance), 2) choice of BLM versus the MLR approach proposed by EPA 2017 aluminum AWQC, and 3) aluminum from natural background contributions.

In conclusion, the relatively rich datasets evaluated herein, and the improved accuracy of environmental protection that results from using the BLM appropriately, suggest a distinct ability to make more appropriate decisions and resource allocations than those permitted by hardness-based AWQC, whether for state 305(b)/303(d) assessment purposes or for NPDES permits like the LANL IP.

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Appendices

A. Acute IWQC TU Longitudinal Plots
B. Chronic IWQC TU Longitudinal Plots
C. Acute and Chronic IWQC TU Longitudinal Plots for the Rio Grande
D1. Acute FMBs for Individual Locations
D2. Acute FMBs for Watersheds
E. Chronic IWQC Comparisons in TU Quadrant Diagrams
F. Chronic IWQC Comparisons in TU Quadrant Diagrams for the Rio Grande Dataset

Attachment 2

Total Aluminum: Not Totally Relevant for Water Quality Standards

Total Aluminum: Not Totally Relevant for Water Quality Standards

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ABSTRACT

A large surface water dataset from more than 100 locations on the Pajarito Plateau, Northern New Mexico and spanning 10 years, was evaluated for aluminum concentrations in both unfiltered samples and samples filtered through 10, 1, 0.45, and 0.2 µm filters. Comparisons of aluminum concentrations in the unfiltered and filtered samples to EPA and New Mexico state ambient water quality criteria (AWQC) revealed that aluminum concentrations often exceeded criteria regardless of filter size and sample location. Aluminum concentrations in surface waters downstream of developed areas within and around Los Alamos National Laboratory (LANL) and Los Alamos County town site were similar to aluminum concentrations in surface waters collected from reference watersheds that represent natural background locations, indicating that exceedances occur naturally. Solubility calculations showed that the vast majority of aluminum concentrations were over-saturated with respect to amorphous $Al(OH)_3(s)$, regardless of filter size. Finally, aluminum concentrations in samples collected during storm events were strongly associated with suspended sediment concentrations, suggesting that naturally-occurring aluminosilicates in suspended particulate material contribute to AWQC exceedances.

While the toxicity data upon which State and EPA AWQC are based are generally expressed as measured (or nominal) total aluminum concentrations, the source of aluminum in all AWQC cases is a soluble aluminum salt prepared under laboratory conditions. Therefore, the only potential contributors to observed toxicity in the AWQC toxicity database are dissolved or precipitated (e.g., freshly precipitated amorphous $Al(OH)_3$) forms of aluminum. Aluminosilicates were not considered in the derivation of aluminum AWQC, and therefore should not be considered when quantifying toxicologically relevant aluminum concentrations in natural surface water samples for comparison to AWQC. It has been demonstrated that aluminosilicate particles smaller than 1 μm can be present in natural samples. These types of particles would be expected to be non-toxic and serve only to contribute to false positive determinations of criteria exceedances in surface water samples from upstream, i.e., natural background and downstream of developed areas. Thus, aluminum concentrations in surface waters from developed and background locations cannot be accurately evaluated for attainment of AWQC due to the presence of naturally occurring, non-toxic aluminosilicates.

Therefore, application of the 2017 EPA proposed AWQC for aluminum that are based on total aluminum synthetic test solutions in an unfiltered sample would incorrectly identify natural background conditions as impaired in a majority of occasions . Using 10-µm or even 0.45-µm filters to remove aluminosilicates prior to assessing attainment of the New Mexico 2010 hardness-based aluminum AWQC produces fewer AWQC exceedances than total aluminum measurements, but likely retain aluminosilicates that contribute to AWQC exceedances. Preparation of environmental samples for evaluation of aluminum AWQC attainment needs to be able to differentiate potentially bioavailable forms of aluminum (i.e., dissolved and precipitated forms) from non-bioavailable forms (e.g., aluminosilicates), or meaningless

AWQC exceedances in surface waters will continue to be problematic. The relevant issue for aluminum is that the size range of potentially bioavailable aluminum precipitates and non-bioavailable particles overlaps. A sample preparation protocol that solubilizes potentially bioavailable amorphous $Al(OH)_3(s)$, but does not solubilize aluminosilicates, could be utilized prior to filtration with 0.45- or 0.2-μm filters to more accurately represent potentially bioavailable forms of aluminum, while minimizing aluminum from non-bioavailable forms in environmental samples. Further development of such criteria implementation protocols is needed and verification through toxicity testing of environmental and empirical laboratory samples may be helpful in that endeavor.

INTRODUCTION

There are fundamental differences between the types of exposure conditions used to evaluate aluminum bioavailability and toxicity in laboratory experiments and exposure conditions that are prevalent in natural surface water environments. These differences are generally acknowledged, but not adequately addressed, during development of ambient water quality criteria (AWQC) for the protection of aquatic life. In the context of developing aquatic life criteria, US EPA controls for exposure conditions include duration, frequency, and magnitude of exposure. But even within the specified targets for those conditions, there may be differences between laboratory and field exposures. For example, acute toxicity tests for fish usually have an exposure duration of four days, but acute criteria are typically applied to field conditions by comparison with 1-hour average concentrations (US EPA, 1995). To some extent this difference provides a level of reasonable conservatism. For aluminum (and perhaps iron) there is an additional difference that is neither anticipated by or controlled for in the development of the water quality criteria, and that is that the predominant chemical or physical form(s) of aluminum to which organisms are exposed can be very different in laboratory and field settings to such an extent that application of the criteria is not representative and is problematic.

In laboratory exposures, soluble aluminum salts or acid stock solutions are used to achieve target nominal total[1] aluminum concentrations. These forms of aluminum are highly reactive, and highly bioavailable (Gensemer and Playle 1999; Teien et al 2006). Aluminum toxicity frequently occurs at concentrations that exceed solubility, and so the laboratory exposure conditions are further complicated by the fact that the test organisms are exposed to a mixture of soluble and precipitated aluminum (Santore et al, 2018).

In contrast, aluminum in natural surface water environments is often predominately in the form of aluminum-bearing minerals such as aluminosilicates in the suspended sediment load. When suspended sediment is exposed to acid in the preservation and pre-analytical digestion process, aluminum from aluminosilicates is liberated and subsequently quantified as part of the total aluminum concentration. The bioavailability of aluminum from aluminosilicates is minimal, in contrast to the bioavailability of aluminum from soluble aluminum salts. As a result, total aluminum concentrations in natural surface water samples that exceed aluminum water quality criteria by one or more orders of magnitude little to no toxicological relevance. Therefore, the application of water quality criteria for aluminum at sites

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[1] Analytical measurements of aluminum in laboratory exposures typically include total, total recoverable, or “dissolved” (i.e., operationally defined as passing through 0.45 μm filter) concentrations. From the perspective of understanding the amount of potentially bioavailable aluminum to which organisms are exposed in the laboratory, measurement of these concentrations is a common strategy

where mineral forms of aluminum dominate is likely to generate water quality criteria exceedances where there is no impairment from aluminum.

It has been demonstrated in laboratory toxicity tests that toxicity is often correlated with measurements of total aluminum (e.g., (Cardwell, Adams et al. 2018, Gensemer, Gondek et al. 2018)). Several laboratory experiments have demonstrated that dissolved aluminum and freshly precipitated aluminum can both contribute to toxicity. Therefore, total aluminum may be a reasonable way to quantify aluminum in toxicity tests since it will include both dissolved and freshly precipitated forms of aluminum. Indeed, many of the toxic effect concentrations (ECx) included in recent aluminum toxicity databases from which AWQC were derived exceed solubility limits for aluminum, based on the formation of amorphous $Al(OH)_3(s)$ (Gensemer 2009, EPA 2017). This provides a clear indication that total aluminum is important to consider when evaluating aluminum toxicity in laboratory toxicity tests.

However, there is an important difference between measurement of total recoverable aluminum in a laboratory toxicity test and actual bioavailable aluminum in a natural surface water sample. The biggest problem with using total aluminum as a way to characterize aluminum exposure is that it will also include non-bioavailable forms of aluminum minerals that have been liberated in the pre-analytical sample preparation process. In a toxicity test, these non-bioavailable forms of aluminum are absent and so this deficiency with measurements of total aluminum is not a problem. However, in an environmental sample, naturally-occurring aluminum forms can be included when measuring total aluminum in surface water samples containing suspended sediments: mineral-bound aluminum (e.g., aluminosilicates such as feldspars, sanidine, and clays) associated with suspended material naturally present in the aquatic environment. Aluminum, after oxygen and silica, is the third most common element in the earth's crust (8.1% by weight on average) with aluminum oxide (Al_2O_3) the second most prevalent of the oxides (approximately 16%). Hence, environmental samples of water with suspended sediments will have a significant potential for including natural background concentrations of aluminum associated with rocks and minerals. Much of the aluminum associated with mineral solids is tightly bound within the crystalline mineral matrix of solids, and therefore is not bioavailable. Thus, the use of total aluminum measurements in environmental samples will be predominantly characterizing non-bioavailable forms of aluminum (Santore et al, 2018). Comparison of total aluminum measurements from environmental samples with laboratory-derived water quality criteria will likely lead to false positive exceedances, where no impairment from aluminum occurs naturally.

Given that aluminum comprises ~8% by weight of the Earth's crust, and assuming that naturally sourced suspended solids are similarly composed, water samples containing suspended sediment concentrations (SSC) as low as 9.4 mg/L and 1.1 mg/L, will exceed EPA's 1988 nationally recommended aluminum acute and chronic AWQC, respectively, if based on total aluminum. Therefore, samples from natural waters with measurable TSS would be expected to contain aluminum primarily from mineral forms associated with suspended clays and silts. The occurrence of freshly precipitated amorphous aluminum hydroxides in natural water samples in most aquatic environments is unlikely. An exception may be in areas impacted by acid rock drainage where a metal-rich acidic seep mixes with a higher pH water body. In these conditions, there could be formation of amorphous aluminum hydroxide precipitates in the mixing zone (USEPA, 2000).

EPA is in the process of updating its nationally recommended aluminum AWQC to incorporate not only hardness effects, but also other parameters like pH and dissolved organic carbon (DOC) that control bioavailability (USEPA, 2017). EPA has considered these and other toxicity modifying factors in the copper AWQC by using the biotic ligand model (BLM; EPA 2007). These factors should also be incorporated in the aluminum AWQC since they have also been demonstrated to influence aluminum bioavailability and toxicity (Gensemer and Playle 1999; Gensemer et al. 2018). Toxicity modifying factors for aluminum can be considered by using multiple linear regression models (MLRs; DeForest et al. 2018) and the BLM (Santore et al. 2018) which have been developed to predict aluminum toxicity in natural waters. The consideration of toxicity modifying factors in the EPA's updated nationally recommended aluminum AWQC is a significant improvement over the previous aluminum AWQC, but the 2017 draft AWQC do not address how it should be applied to environmental samples dominated by non-bioavailable forms of aluminum, e.g., aluminum bearing minerals.

Only certain states have adopted EPA's 1988 nationally recommended AWQC for aluminum, and of these states, New Mexico and Colorado have recognized the issues associated with comparing total aluminum concentrations to AWQC. Both states have incorporated modifications with respect to aluminum bioavailability in their AWQC and also understand that the presence of natural background aluminum can contribute to false positives. In contrast with the static values of the EPA 1988 aluminum AWQC the New Mexico 2010 aluminum AWQC depend on hardness, much like state and EPA AWQC for several other metals, e.g., cadmium, lead, and zinc.

According to guidance provided by the New Mexico Environment Department (NMED 2010, WQCC 2010, NMED 2013, NMED 2015), assessments of surface water quality data against the State's AWQC are based on analysis of aluminum in a filtered sample. NMED recommends using a 10-µm filter for samples with turbidity exceeding 30 NTU. However, the 10-µm filter size may be too large to determine toxicologically appropriate aluminum concentrations because it will allow the inclusion of naturally occurring clay and silt-sized sediment particles that contain non-bioavailable aluminum forms that are non-toxic. Mineral forms of aluminum will be liberated from these particles when the filtered samples are acidified and digested before analysis according to standard laboratory protocols. Therefore, retaining the aluminum from these naturally occurring minerals in sample filtrate will overestimate bioavailable aluminum and may result in spurious exceedances of AWQC (i.e., false positives).

The New Mexico filtration step is in recognition that natural samples will likely contain materials such as clay, silt, and sand. The important conundrum with respect to aluminum in natural samples is to remove nontoxic sources of aluminum, but to retain potentially toxic precipitated forms, such as amorphous aluminum hydroxide, which has been implicated as a form of aluminum that contributes to toxicity in laboratory toxicity tests in cases where aluminum exceeds solubility limits. Because of the uncertainty associated with the relevant size of precipitated amorphous aluminum hydroxide, and the potential for overlap in size with clay particles, filtration alone may not be sufficient to address this issue simultaneously.

The goal of this paper is to present a case study that provides evidence that the current practices used in sample preparation for measurement of aluminum in surface water samples may not provide aluminum concentration data that are appropriate for comparison to AWQC derived from laboratory toxicity tests. Specifically, the forms of aluminum that may be present in samples collected following typical protocols will be evaluated from the context of what is known about aluminum bioavailability and forms of aluminum that contribute to toxicity. Additionally, filtration as a means to remove non-bioavailable aluminosilicates from environmental samples will also be evaluated.

MATERIALS AND METHODS

Surface water quality monitoring data within the vicinity of Los Alamos National Laboratory (LANL) were obtained and evaluated in the context of which form or fraction of aluminum is most appropriate for comparison to AWQC. Data were obtained from LANL's Environmental Information Management (EIM) database (also available to the public at www.intellusnm.com) and processed to aggregate synoptic water chemistry data for as many sampling events as possible. Sampling events were defined as unique combinations of location and sampling date. Aggregation of data by unique sampling events was intended to provide sufficient data to examine aluminum concentrations, bioavailability, and solubility in unfiltered and filtered surface water samples, as well as to calculate instantaneous water quality criteria (IWQC) based on New Mexico and EPA AWQC, using water quality measurements in the samples. In addition to surface water monitoring data from the vicinity of LANL, a limited number of analyses were conducted to evaluate particle characteristics in storm water and suspended sediment samples collected from 3 locations (1 location was downstream of an urban developed landscape, and 2 locations represent natural background landscapes). Analysis of particle characteristics was intended to provide information regarding the size and composition of particles present in natural surface water samples. Reported aluminum concentrations in surface water samples were compared to solubility limits for amorphous $Al(OH)_3(s)$ to determine if mineral phase aluminum was likely present. Similarly, aluminum concentrations were also compared to sample-specific IWQC for sampling events that had sufficient data.

Surface Water Monitoring Data from the Pajarito Plateau

Surface water chemistry, including aluminum concentrations, have been monitored by LANL at many locations across the Pajarito Plateau, the geographic area within and surrounding LANL. The predominant sediment type on the Pajarito Plateau derives from an erodible, volcanic ash substrate called Bandelier Tuff. High-flow events (e.g., those triggered by monsoonal thunderstorms) mobilize large volumes of sediment and sediment-associated elements in storm water discharges. Many of these elements including metals and major cations and anions, are naturally present in soils and sediments (McDonald, Ryti et al. 2003). For example, Al is the third most abundant elements in the Earth's crust and is incorporated into the majority of minerals found in soil and sediment. Thus, natural sources contribute to the total chemical load of streams on the Pajarito Plateau. Development on the Pajarito Plateau is moderate; the town of Los Alamos has a population density of approximately 1,100 residents per mi^2 and an area of 11 mi^2, covering roughly 31% of the plateau. LANL accounts for a relatively small portion of the total development on the Pajarito Plateau (approximately 0.06% by area). Development generally alters natural landscapes and significantly changes hydrology by increasing runoff due to impervious surfaces that have replaced natural landscapes. Runoff from developed areas is also well-known to affect storm water quality.

While the LANL monitoring dataset includes data for hundreds of monitoring locations (including surface water and stormwater discharge locations), the analyses described herein were focused on data collected from 115 surface water monitoring locations (Figure M1). These locations are described as either natural background (i.e., from undeveloped watersheds) or downstream (i.e., downstream of developed LANL, county, or town areas) surface waters. The 28 natural background locations represent surface water drainage from watersheds that have little to no human alterations and that are located either upstream, north or south of LANL (Figure M1). In contrast, the 87 downstream surface water locations are gaging stations located in stream channels within or downstream of the LANL facility or the

Los Alamos County town site, and thus during wet weather sampling represent significant storm water runoff from LANL and the town of Los Alamos. Many of the downstream surface water locations have 10 or more years of water quality and flow records. Most (i.e., 90%) of the natural background and downstream surface water locations represent ephemeral or intermittent waters that flow seasonally only in response to rainfall (ephemeral) or snowmelt (intermittent). A few locations represent isolated perennial waters sourced to springs or treated wastewater effluent, or entire watersheds (i.e., Rito de Frijoles in Bandelier National Monument).

Unfiltered and filtered aluminum concentration data for surface water samples span a time range from January, 2005 to November, 2017. Filtered aluminum concentrations correspond to samples analyzed after passing through filter pore sizes of 10-, 5-, 1-, 0.45-, 0.2-, and 0.02-µm. After aggregation of data by sampling event, a total of 1,659 individual sampling events were identified for the 115 surface water monitoring locations. In addition to aluminum concentrations, data for other surface water quality characteristics (e.g., pH, suspended sediment concentration [SSC], DOC concentrations, and concentrations of major cations and anions) were also aggregated by sampling event. The purpose of data aggregation by sampling event was to facilitate comparisons of aluminum concentrations for unfiltered and filtered (multiple filter pore sizes considered) samples, and to compare aluminum concentrations to calculated IWQCs. Sampling event-specific IWQCs were calculated only where sufficient data were available for a particular AWQC basis (New Mexico 2010, EPA 2017, BLM). For example, calculation of New Mexico hardness-based IWQC require that hardness data are available, while calculation of EPA (2017) draft IWQC require that hardness, pH, and DOC data are available. Calculation of BLM-based pseudo[2]-IWQC (pWQC) for aluminum (Santore et al. 2018) require that data for pH, DOC, alkalinity, major cations, and major anions are available. Data analyses were focused on the unfiltered, 10-, and 0.45-µm filtered aluminum concentrations because those were the most common sample preparations, and because they are potentially most relevant from the perspective of AWQC.

Aggregation of the LANL dataset involved summarizing data for each water chemistry parameter by unique sampling events, and in some cases data for particular water chemistry parameters were not available. Data used for IWQC and solubility calculations were preferentially based upon operationally defined “dissolved” (i.e., passing through a 0.45-µm filter) concentrations for water quality parameters such as pH, DOC, major cations, major anions, and alkalinity. For cases where dissolved concentrations for water chemistry parameters were not available, relationships between total (unfiltered) and dissolved concentrations were examined using the entire dataset to determine if dissolved concentrations could be estimated from total concentrations. Notable estimates that were made during data aggregation include: estimates of DOC from total organic carbon (TOC), where DOC was estimated by calculating 0.704*TOC (based on the lower confidence limit of the regression between DOC and TOC, assuming an intercept = 0; $n = 182$, $p < 2.2 \times 10^{-16}$ and $r^2 = 0.781$), substitution of total alkalinity for dissolved alkalinity, and use of location-specific averages for sulfate and chloride, where data were missing.

Review of Toxicity Test Data Used to Develop AWQC

The recent EPA (2017) draft aluminum AWQC are based on updated acute and chronic aluminum toxicity datasets for freshwaters. These data were reviewed and the database used to derive NM 2010

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[2] Even though EPA evaluated the BLM as part of its 2017 draft proposed Al AWQC, we consider the BLM-based IWQC generated in this manuscript as “pseudo” or “pWQC”, although we have followed EPA 1985 guidelines in applying the BLM.

AWQC were also reviewed and compared to the data used by EPA (2017). Many of the DOC concentrations used in conjunction with the EPA (2017) draft aluminum AWQC are estimated values, based upon recommendations from the copper AWQC document (EPA 2007). As DOC is an important input for both the MLR approach used by EPA and the BLM approach described in Santore, Ryan et al. (2018), these estimates represent a potentially important source of uncertainty. The water chemistry associated with the toxicity tests in these databases will be used to evaluate aluminum solubility for the purpose of understanding the potential forms of aluminum present in exposure media.

Calculation of Water Quality Criteria and Evaluation of Aluminum Solubility

Using the aggregated LANL surface water dataset, New Mexico hardness-based aluminum IWQC, EPA (2017) draft aluminum IWQC, and BLM-based aluminum pWQC (Santore et al. 2018) were calculated for each sampling event that contained sufficient data (i.e., all necessary model inputs for each AWQC approach). The draft EPA (2017) AWQC normalization approach is based upon MLR models described in DeForest et al. (2018). To perform the MLR-based EPA (2017) draft aluminum IWQC calculations, the companion calculator workbook provided by EPA was used directly. The BLM-based pWQC calculations were performed using the BLM executable file (version 2.41) provided with the BLM download from the Windward Environmental website (i.e., http://www.windwardenv.com/biotic-ligand-model/).

The aggregated surface water dataset did not contain data for temperature or percent humic acid (%HA); both are required BLM inputs. Temperature was assumed to be 10°C, and %HA was set at the EPA recommended default value of 10% (HydroQual 2007, Windward 2015). A detailed description of aluminum BLM parameters and calculations is provided in Santore et al (2018). BLM-based pWQC were calculated using the toxicity database described by Gensemer et al. (2018), which represents chronic toxicity data. Because the pWQC are directly calculated using the aluminum BLM reflect chronic AWQC, a conservative acute-to-chronic ratio (ACR) of 5.0 was applied to convert the chronic IWQC to acute IWQC. In EPA's 2017 proposed aluminum AWQC EPA (2017) a final ACR of 8.068 was used. Although the ACR is generally intended to convert a final acute value (FAV) to a final chronic value (or chronic criterion), using it conversely to convert chronic to acute criteria is reasonable for purposes of these evaluations, especially at conservative value. Using the lowest normalized genus mean chronic value for *Salmo* (508.5 µg/L) and the FAV of 2741 µg/L described by EPA (2017) for a water with pH =7, hardness = 100 mg/L as $CaCO_3$, and DOC = 1 mg/L, a conservative ACR would be 2741/508.5 = 5.39. For added conservatism here, calculation of acute BLM-based pWQC used an ACR of 5.0. To facilitate comparison of observed surface water aluminum concentrations with the various IWQC calculations described above, toxic units[3] (TUs) were calculated as the quotient of the observed aluminum concentration with the IWQC calculated from that sample's water chemistry data.

The aluminum BLM was also used in speciation mode so that aluminum solubility, or saturation with respect to amorphous $Al(OH)_3(s)$, could be evaluated for samples with sufficient chemistry data. The log solubility constant (log(Ksp)) used for amorphous $Al(OH)_3(s)$ was 9.76 (Sposito 1995). To perform saturation index (SI) calculations, the ion activity product (IAP) for $Al(OH)_3$ was calculated as:

$$IAP = \{Al^{3+}\}\{OH^{-}\}^{3},$$

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[3] A TU>1 indicates the observed concentration exceeded the IWQC magnitude and does not necessarily indicate a "violation" of water quality standards, which must also take into account exceedance frequency, as well as other considerations such as representativeness, data quality, etc.

and SI is calculated as:

$$SI = log10\left(\frac{IAP}{K_{sp}}\right).$$

Saturation index calculations were performed for all samples with sufficient chemistry data (i.e., BLM inputs), using unfiltered and filtered aluminum concentrations. Speciation calculations were performed using ambient pH (i.e., pH associated with the original environmental sample) and reported aluminum concentrations. Because aluminum concentrations were determined following the protocol for total recoverable aluminum (i.e., samples were acidified and digested), it was expected that SI would be greater than zero for the majority of unfiltered and 10-µm filtered samples. This expectation is driven by the likely liberation of aluminum from aluminosilicates during sample preparation/preservation. In addition to evaluating aluminum solubility status in the LANL dataset, aluminum solubility status was also investigated in the AWQC datasets (e.g., New Mexico 2010 and EPA 2017).

Particle Characterization

In addition to collecting surface water samples for water quality parameters described above, LANL has also evaluated samples with more sophisticated techniques to characterize dissolved solids and particulates. In a 2018 LANL report (LANL 2018), particles from surface waters naturally high in suspended sediments and mineral-bound aluminum from the Pajarito Plateau in New Mexico were evaluated using a variety of quantitative and qualitative techniques, including x-ray diffraction (XRD) and scanning electron microscopy with electron dispersive spectroscopy (SEM-EDS). These evaluations concluded that dissolved or precipitated aluminum hydroxides were absent and that fine particles passing a 1µm filter were dominated by aluminosilicates.

RESULTS

The LANL dataset contained >3,600 sampling events (i.e., combination of location and date) for three types of surface water samples: baseflow, stormflow, and snowmelt. This dataset has more than 3,057 measurements of aluminum concentrations corresponding to unfiltered water samples and samples filtered using filters of pore sizes ranging from 10 µm to 0.02 µm. Regarding aluminum concentrations, measurements from unfiltered and those filtered through 0.45 µm filters were most common. In addition to aluminum concentrations, the dataset contains synoptic measurements of suspended sediment concentration (SSC), pH, organic carbon concentrations (i.e., either total or dissolved), and major ions. These additional water quality characteristics allowed for calculation of IWQC using the hardness-based New Mexico AWQC, the proposed draft EPA AWQC, and a BLM-based calculation analogous to AWQC. A summary of the dataset is provided in Table R1.

Toxic units (TUs) were calculated as the quotient of observed aluminum concentration and corresponding IWQC for a given sample. Figure R1 provides a summary of TUs for different aluminum sample preparations (i.e., unfiltered or filtered through 10- and 0.45-µm filters) and the three different AWQC bases. From Figure R1, it is clear that observed aluminum concentrations exceeded IWQC in many samples, regardless of the sample preparation approach, the basis for AWQC, or whether a natural background or LANL surface water location. Figure R2 shows it is also clear that stormflow aluminum concentrations more frequently exceeded IWQC, especially in unfiltered and 10-µm filtered samples. When considering only 0.45-µm filtered samples, stormflow samples and baseflow/snowmelt samples are more similar in their level of exceedances.

A likely explanation for the high percentage of IWQC exceedances in stormflow samples in the unfiltered and 10-µm filtered sample preparations is that particulate material in SSC is contributing to the aluminum concentration. Indeed, it is clear that natural background aluminum concentrations are significantly correlated with SSC (Figure R3). Figure R4 shows the aluminum and SSC associations in broader context of the three water sample types across all 115 locations. The solid and dashed lines in Figure R4 provide estimates of the amount of aluminum that may be contributed by suspended sediment, assuming that suspended sediment contains 8.1% and 100% aluminum by weight, respectively. Thus, aluminum concentrations in stormflow samples can be attributed to aluminum in suspended sediment, although the contribution from suspended sediment is generally less than 8.1% (i.e., the average aluminum content of the Earth's crust). This is not necessarily unexpected, because suspended sediment contains organic material, in addition to weathered minerals.

Figure R4 also shows that the range of aluminum concentrations in the baseflow and snowmelt samples does not appear to indicate an association with SSC, and in some cases, aluminum concentrations are higher than would be expected even if suspended sediment was entirely composed of aluminum. A subset of the samples shown in Figure R4 have sufficient water chemistry data such that solubility can be evaluated (with respect to amorphous $Al(OH)_3(s)$) (Figure R5). Generally, our calculations indicate that aluminum concentrations in excess of 200 to 300 µg/L are over-saturated with respect to amorphous $Al(OH)_3(s)$, indicating that the high aluminum concentrations in samples with low SSC are not attributable to "dissolved" aluminum.

While solubility exceedances may be expected when evaluating total aluminum concentrations (i.e., contributions of aluminum from suspended sediments), aluminum concentrations in a majority of the 10- and 0.45-µm samples also exceeded solubility (Figure R6). It is not necessarily unexpected that aluminum concentrations in 10-µm filtered samples would exceed solubility, because silt and clay particles can pass through a 10-µm filter. It is however, not expected that aluminum concentrations in 0.45-µm filtered samples will exceed solubility, given that 0.45-µm filtration is generally taken as the operational definition for dissolved solutes. However, in the LANL dataset, 70% of the 0.45-µm filtered aluminum concentrations exceeded the solubility limit for amorphous $Al(OH)_3(s)$. These results suggest that particulate aluminum is capable of passing through a 0.45-µm filter, which suggests that using a 0.45-µm filter to define dissolved aluminum in environmental samples in this locale may be erroneous. Some uncertainty may exist in the solubility calculations (discussed below), but it should be noted that aluminum concentrations exceeded solubility limits by as much as 3 orders of magnitude in some 0.45-µm filtered samples.

To evaluate the nature of mineral forms of aluminum present in natural surface waters, LANL analyzed particles in stormflow samples from two natural background locations as well as one downstream gaging station to determine if amorphous $Al(OH)_3(s)$ could be identified (LANL 2018). The XRD and SEM/EDS analyses results did not identify amorphous $Al(OH)_3(s)$ in any of the samples evaluated, suggesting that aluminum-containing particles did not include the potentially bioavailable, and reportedly toxic amorphous $Al(OH)_3(s)$ precipitate (Figure R7). Furthermore, SEM/EDS showed that fine particles passing a 1µm filter contained aluminosilicates (Figure R8).

Comparison of SI calculations with acute TU calculations (based on New Mexico hardness-based AWQC), demonstrates very similar patterns in solubility exceedances and IWQC exceedances for natural background and downstream surface water locations (Figure R9). For unfiltered samples (n=495), all samples exceeding the New Mexico acute aluminum IWQC are over-saturated with respect to amorphous Al(OH)$_3$(s) in samples from both natural background (n=53) and downstream surface waters (n=260) . However, not all samples that are over-saturated exceed New Mexico hardness-based IWQC. For 10-µm filtered samples (n=34), only one sample exceeding acute aluminum IWQC did not exceed solubility limits. The pattern is similar for 0.45-µm filtered samples, but there are 3 samples in natural background locations that exceed IWQC without exceeding solubility limits. These results are not surprising, because it is generally true that higher concentrations of aluminum are needed to exceed either the solubility limit or the IWQC. Although some of the factors that influence aluminum solubility also affect bioavailability, and these factors (e.g., pH and DOC) are not considered with hardness-based IWQC, but are taken into account in both the EPA 2017 proposed AWQC and BLM-based pWQC.

Results summarized in Figures R2 and R6 indicate that stormflow samples are highly likely to exceed IWQC and solubility limits simultaneously, and Figures R2 and R4 strongly suggest that aluminum concentrations in these samples are associated with SSC. The potential reasons for elevated aluminum concentrations in the baseflow and snowmelt samples with low SSC are unknown, but the data can be evaluated to determine if similar concentrations are observed in samples from natural background and downstream locations.

For unfiltered samples, the distributions of aluminum concentrations from natural background and downstream locations (considering all sample types pooled) are essentially identical (Figure R10), with similar geometric means and standard deviations (standard deviations calculated with log10-transformed values). When the data are separated by sample type, similar concentrations are observed for natural background and downstream locations, suggesting that the sources of aluminum are similar regardless of the level of landscape development near a sampling location or in its greater watershed. Results for 10- and 0.45-µm filtered samples are similar (Figures R11 and R12). Statistical comparisons of aluminum concentrations in natural background and downstream locations is provided in Table R2.

DISCUSSION

Aluminum concentrations in the majority of surface water samples evaluated as part of this study exceeded the solubility limit for amorphous Al(OH)$_3$(s). However, some further consideration for uncertainties associated with solubility calculations may be important. Aluminum concentrations in many samples also exceeded New Mexico hardness-based AWQC, draft EPA (2017) MLR-based AWQC, and BLM-based pWQC. Generally, IWQC exceedances occurred in the majority of samples that exhibited aluminum concentrations in excess of amorphous Al(OH)$_3$(s) solubility. This is not necessarily surprising, given that most of the toxicity tests used to derive both the New Mexico hardness-based AWQC and the EPA (2017) MLR-based AWQC exhibited toxicity effect concentrations that were also in excess of amorphous Al(OH)$_3$(s) solubility (Figure D1).

A major difference between the aluminum concentrations reported here, and the aluminum exposure concentrations used in the laboratory toxicity tests used to derive AWQC is the contribution of aluminum from suspended sediment. Figures R2 and R4 provide a clear indication that total aluminum concentrations in Pajarito Plateau surface water samples collected during storm events are associated with suspended sediment. This relationship between total aluminum and SSC is also evident in nationwide surface water data retrieved from the National Water Quality Monitoring Council data portal (https://www.waterqualitydata.us/portal/), representing the entire United States (Figure D2). It is interesting to note that the data for New Mexico in Figure D2 show a similar pattern as those in Figure

R4, including the relatively high total aluminum concentrations at low SSC. Furthermore, much like Figure D1 shows for the AWQC datasets, Figure D3 shows that aluminum in the majority of the natural background and downstream surface water samples exceeded solubility limits, regardless of considerations for pH and DOC effects on solubility as well as filter size used to prepare the samples.

Suspended sediment concentrations in Pajarito Plateau surface waters range from approximately 10 mg/L to more than 100 g/L (approximately 10% solids!) during storm events, resulting in total aluminum concentrations of up to 1 g/L or higher. In contrast, the exposure waters used in the toxicity tests from which aluminum AWQC were derived did not contain any environmental suspended sediments (i.e., many tests used reconstituted lab waters, Lake Superior water, tap water, or well water; see EPA 2017). Further, the toxicity tests would have included an acceptable dilution water control, with no added aluminum. Therefore, by design, the exposure waters in the toxicity tests upon which aluminum AWQC are based could have only become over-saturated with amorphous $Al(OH)_3(s)$ by addition of a soluble aluminum salt. As a consequence, any solid phase aluminum present in the toxicity tests would have formed during or prior to initiation of the toxicity tests. This solid phase aluminum would likely be much different in characteristics than the aluminum contributed from heterogeneous suspended sediment particles in the environment.

In other words, the likely dominant contributor to total aluminum concentrations in Pajarito Plateau stormflow water samples is non-bioavailable aluminosilicates. The aluminosilicates represent a very different, non-bioavailable form of aluminum than is used in laboratory toxicity tests. Therefore the toxicity database used to derive current AWQC is not appropriate for evaluating potential impairment due to aluminum in Pajarito Plateau surface waters. As such, total aluminum concentrations from environmental samples high in suspended sediment should not be compared to aluminum AWQC that were derived from total aluminum measurements in clean laboratory waters. As a point of emphasis, even the most *insensitive* organism in the EPA (2017) acute toxicity database, *Physa sp*[4]., would not be able to tolerate the elevated aluminum concentrations in natural background surface waters, especially waters with elevated aluminum associated with suspended sediment concentrations higher than approximately 20 g/L, if the form of aluminum present were toxicologically relevant. Many surface water samples in the natural background locations have exhibited total aluminum concentrations in excess of 100,000 ug/L, which corresponds to roughly the 70th percentile (e.g., Figure R10).

Pre-filtration of water samples prior to analyzing for aluminum, with the goal of minimizing contribution of mineral phase aluminum (i.e., aluminosilicates – which are dissolved prior to analysis during sample preparation) while retaining potentially toxic precipitated amorphous $Al(OH)_3(s)$ (i.e., the likely form of solid phase aluminum in laboratory toxicity tests) is one approach that has been proposed for dealing with water samples high in suspended sediment concentrations (NMED 2012). While this approach is well-intentioned, with respect to limiting the mineral phase contribution to aluminum concentrations prior to comparison to IWQC, using a 10 µm filter is not capable of separating contributions from clays and fine silts (i.e., particles smaller than 8-µm; Wentworth 1922) from amorphous $Al(OH)_3(s)$. Figure R6 indicates that the majority of 10-µm filtered surface water samples exceed $Al(OH)_3(s)$ solubility, but there is no way of knowing if the source is aluminosilicates or precipitated $Al(OH)_3(s)$. Similarly, Figure R6 also indicates that many of the 0.45-µm filtered surface water samples exceed $Al(OH)_3(s)$ solubility,

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[4] Excluding unbounded effect concentrations in the toxicity database; and based on data for *Physa* sp from {Call, 1984 #10430}; EC50 = 55,500 ug/L; pH = 7.5, hardness = 47.4 mg/L, and DOC estimated at 1.1 mg/L.

but the form of the solid phase(s) present is not known. Further complicating this is the uncertainty of whether aluminum hydroxide phases are even present in natural background surface waters, or in stormwater runoff generated by typical urban development.

With respect to identifying a simple filtration approach that minimizes aluminosilicates, but simultaneously retains amorphous $Al(OH)_3(s)$, if such an aluminum form is even present, the issue may not be resolvable. For example, Lai et al. (2007) demonstrated that $Al(OH)_3(s)$ particles in experimental laboratory waters exhibited a size range of 1.1- to 1.14-µm, and that particle size increased across this range during aging from 4 weeks to 20 weeks. Aging during formation of these particles is important to consider, as Teien et al. (2004; 2006) demonstrated that bioavailable aluminum particles are transient, and that bioavailability (toxicity) decreases upon aging (i.e., within minutes) as particles grow from a size of approximately 0.0025-µm to larger colloids. These studies suggest a size range of $Al(OH)_3(s)$ of less than 1.2-µm, and both studies mention a decrease in bio-reactivity as particles age and grow.

Regarding aluminosilicate particles, Baalousha et al. (2006) demonstrated that natural suspended particulate matter in the size range 0.01- to 0.45-µm was composed primarily of aluminosilicates and iron oxyhydroxides. Presence of very small aluminosilicate particles provides a reasonable explanation for the high percentage of the 0.45-µm filtered natural background and LANL surface water samples that exceed the amorphous $Al(OH)_3(s)$ solubility limit (Figure R6). Given these considerations, it appears that there is potential for both amorphous $Al(OH)_3(s)$ and aluminosilicates to be present in samples filtered with a 10-µm filter, but that only amorphous $Al(OH)_3(s)$ may be excluded by a 0.45-µm filter. However, as filter size increases above 0.45-µm, it is also likely that aluminosilicates will increasingly contribute to higher aluminum concentrations that may also be smaller than 0.45-µm.

A recently proposed pH 4-extraction method for determining bioavailable aluminum and iron concentrations in environmental samples may solve the problem that filtration alone does not appear capable of addressing (William Adams, personal communication [or in prep]). The idea behind this approach is to decrease pH in a water sample to pH 4 prior to filtering through a 0.45-µm filter. The pH 4 treatment is aggressive enough to solubilize amorphous $Al(OH)_3(s)$ while not dissolving aluminosilicates. As stated above, aluminosilicates may be capable of passing through a 0.45-µm filter, which may contribute some aluminum, but any aluminum in the form of $Al(OH)_3(s)$ that may have been excluded by a 0.45-µm filter would be solubilized by the pH 4 adjustment, and will be accounted for as a potentially bioavailable form of aluminum. Compared with 10-µm filtration, this approach, has the potential to minimize (not eliminate) contributions from aluminosilicates, while simultaneously accounting for amorphous $Al(OH)_3(s)$.

Regardless of the sample preparation issues described above, the striking similarity of unfiltered and various size-filtered aluminum concentrations in samples from natural background and LANL surface water locations seems to indicate that current aluminum AWQC are not appropriate for natural surface waters on the Pajarito Plateau. The summary statistics in Table R2 and Figures R10 - R12 demonstrate that aluminum concentrations in unfiltered, 10-µm filtered, and 0.45-µm filtered surface water samples from natural background and LANL surface water locations are remarkably similar. Despite the fact that there are many more samples in LANL surface water locations compared to natural background locations, the geometric mean aluminum concentrations and log10 standard deviations essentially suggest that the data come from similar distributions.

CONCLUSIONS

Many surface water samples from both natural background and LANL surface water locations on the Pajarito Plateau exceed New Mexico hardness-based WQC, EPA (2017) draft MLR-based WQC, and BLM-based pWQC. In a majority of the surface water samples evaluated, aluminum concentrations in unfiltered and filtered (10- and 0.45-µm) also exceed the solubility limit for amorphous Al(OH)3(s). A strong association between total aluminum concentrations and SSC suggests that much of the aluminum present is in the form of aluminosilicates, which are not considered bioavailable. The similarity of aluminum concentrations in filtered and unfiltered surface water samples from natural background and surface water locations indicates that exceedance of AWQC based upon toxicity data generated with laboratory waters would be expected to occur in natural environments with little to no human influence.

The presence of aluminosilicates in environmental samples, and the lack of aluminosilicates in laboratory exposures used to evaluate aluminum toxicity and to derive AWQC, presents a conundrum with respect to evaluating attainment of AWQC on the basis of total aluminum concentrations. Results of laboratory toxicity tests indicate that precipitated forms of aluminum are contributors to observed toxicity, because dissolved aluminum concentrations alone are often not sufficiently high to cause toxicity. As a consequence, AWQC are based upon toxic effect concentrations that are expressed as total aluminum. As discussed above, the size ranges of precipitated amorphous $Al(OH)_3(s)$ and small aluminosilicate particles overlap. Therefore, a filtration approach to minimize the contribution of aluminum from aluminosilicates, while retaining the contribution of aluminum from amorphous $Al(OH)_3(s)$, is therefore not capable of resolving the issue.

A sample preparation approach that solubilizes amorphous $Al(OH)_3(s)$, while not solubilizing aluminosilicates, and then followed by filtration (0.45- or 0.2-µm) has potential to address this conundrum (i.e., the pH 4 extraction approach described above). Measurement of total aluminum in surface water samples that have the potential to contain suspended sediment is totally inadequate, and potentially irrelevant. As little as 10 to 20 mg/L of typical naturally sourced SSC can contribute enough aluminum to exceed EPA's current AWQC for aluminum (i.e., 750 µg/L), and Figures R4 and D2 demonstrate that the majority of waters on the Pajarito Plateau and in the United States exhibit SSC far greater than 20 mg/L. An improved approach for quantifying toxicologically relevant or potentially bioavailable forms of aluminum in environmental samples is absolutely necessary for purposes of evaluating attainment of aluminum AWQC. If this issue is not addressed, samples from any surface waters exhibiting similar ranges of aluminum concentrations may be needlessly characterized as impaired.

Additionally, aluminum concentrations in surface waters from natural background and downstream locations cover very similar ranges and exhibit very similar distributions, suggesting that aluminum AWQC are not appropriate for natural surface waters of the Pajarito Plateau. As discussed above, this may also be true for other surface waters in the United States. The results described here provide substantial evidence that total aluminum concentrations in natural surface waters are likely irrelevant with respect to evaluating potential impairments due to aluminum, especially in waters containing suspended sediment.

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Tables

Table R1. Summary of dataset

Parameter	Date Range	Numbers of Samples Total	Numbers of Samples Estimated	Numbers of Samples BDL	Numbers of Locations
Unfiltered Al	2005-01-24 to 2017-11-28	1357	0	42	117
10-µm filtered Al	2013-08-09 to 2017-10-05	159	0	0	36
5-µm filtered Al	2013-08-09 to 2015-10-22	24	0	0	8
1-µm filtered Al	2013-08-09 to 2017-10-05	39	0	0	12
0.45-µm filtered Al	2005-01-24 to 2017-11-28	1434	0	157	117
0.2-µm filtered Al	2013-08-09 to 2015-10-22	24	0	0	8
0.02-µm filtered Al	2014-07-29 to 2015-10-22	20	0	9	9
pH	2005-04-27 to 2017-11-28	657	368	0	73
DOC	2005-03-18 to 2017-10-05	893	324	0	90
Ca	2005-01-24 to 2017-11-28	1430	0	0	117
Mg	2005-01-24 to 2017-11-28	1430	0	1	117
Na	2005-01-24 to 2017-11-28	1329	0	0	117
K	2005-01-24 to 2017-11-28	1329	0	0	117
SO_4	2005-03-18 to 2017-11-28	1415	753	118	78
Cl	2005-03-18 to 2017-11-28	1415	754	117	78
Alkalinity	2005-01-24 to 2017-11-28	935	421	1	99
SSC	2005-03-18 to 2017-10-05	1388	1388	66	106
NM AWQC	2005-01-24 to 2017-11-28	1430	0	0	117
EPA AWQC	2005-04-27 to 2017-10-05	600	0	0	65
BLM AWQC	2005-04-27 to 2017-10-05	601	0	0	65

AWQC = ambient water quality criteria, BDL = below detection limit, BLM = biotic ligand model, EPA = Environmental Protection Agency, DOC = dissolved organic carbon, NM = New Mexico, SSC = suspended sediment concentration

Table R2. Summary of statistical comparisons of aluminum concentrations by sample preparation, sample type, and location type

Sample Preparation	Aluminum Concentration (ug/L)* Natural Background	Aluminum Concentration (ug/L)* Downstream	p-value F-test (variance)	p-value t-stat (geomean)	p-value KS (dist)
UF (all)	12372 (1.01) [167]	10159 (0.99) [1184]	0.788	0.304	0.205
UF (WT)	36213 (0.73) [120]	27876 (0.70) [842]	0.498	0.111	0.077
UF (WS)	618 (0.50) [31]	575 (0.72) [238]	**0.023****	0.762	0.524
UF (WP)	1036 (0.53) [8]	686 (0.73) [37]	0.378	0.435	0.274
UF (WM)	1647 (0.37) [8]	3749 (0.52) [67]	0.367	**0.034****	0.059
10-µm (all)	2717 (0.46) [39]	2597 (0.53) [120]	0.297	0.824	0.411
10-µm (WT)	2717 (0.46) [39]	2597 (0.53) [120]	0.297	0.824	0.411
10-µm (WS)	NA	NA	NA	NA	NA

10-µm (WP)	NA	NA	NA	NA	NA
10-µm (WM)	NA	NA	NA	NA	NA
0.45-µm (all)	465 (0.47) [163]	474 (0.53) [1263]	0.062	0.843	0.069
0.45-µm (WT)	500 (0.45) [120]	590 (0.44) [904]	0.932	0.097	**0.001****
0.45-µm (WS)	365 (0.57) [31]	232 (0.65) [274]	0.385	0.078	0.079
0.45-µm (WP)	320 (0.57) [8]	243 (0.65) [37]	0.769	0.606	0.324
0.45-µm (WM)	746 (0.20) [4]	742 (0.48) [48]	0.165	0.988	0.677

* Geometric mean (standard deviation of log10-transformed values) [number of observations]

** natural background and downstream concentrations were significantly different ($p<0.05$) for the particular statistical test (KS – Kolmogorov-Smirnov non parametric test)

NA – not applicable UF – unfiltered WM – snowmelt sample WP – persistent water sample (baseflow) WS – surface water sample (baseflow) WT – storm water sample (stormflow)

Figures

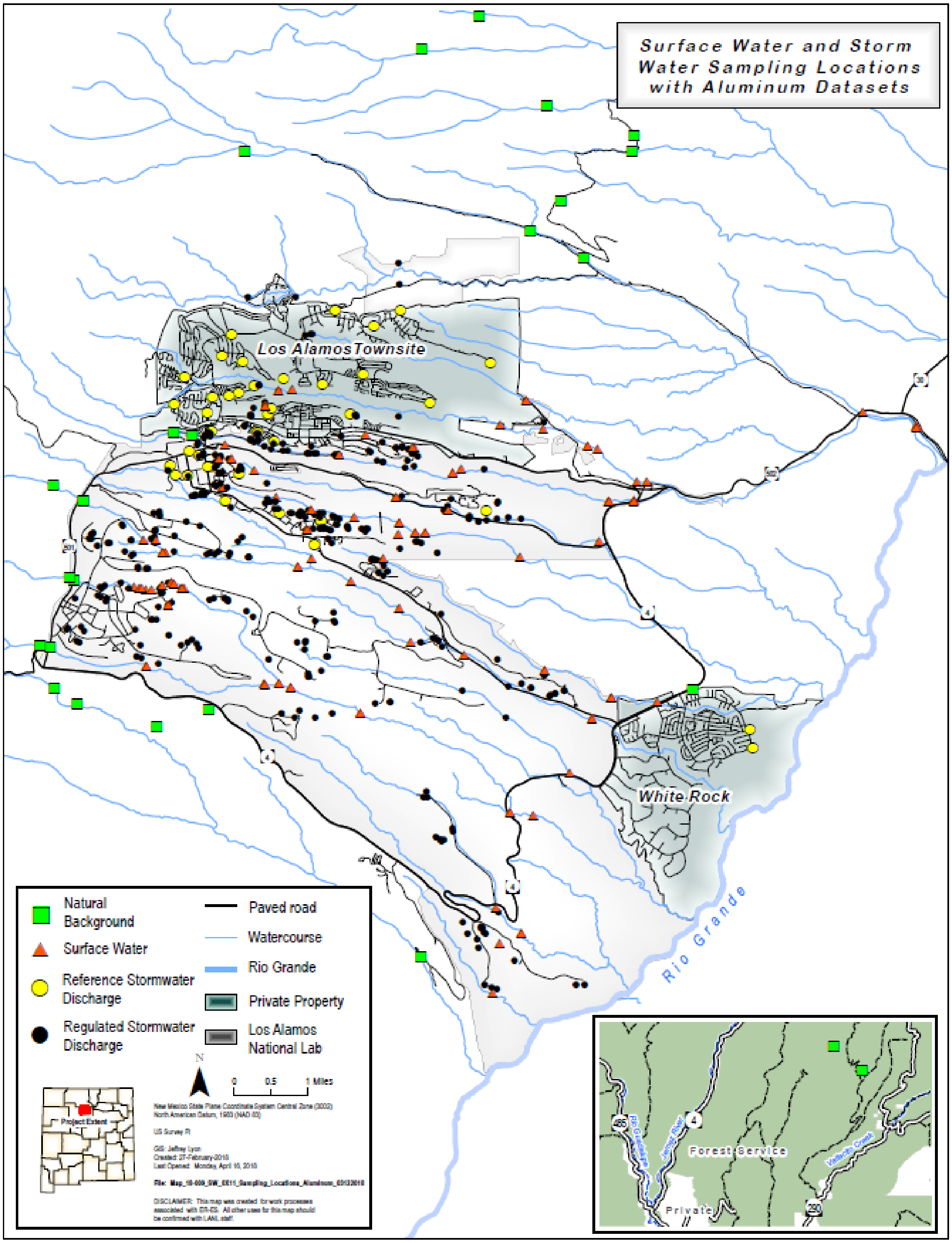

Figure M1. Map of study area.

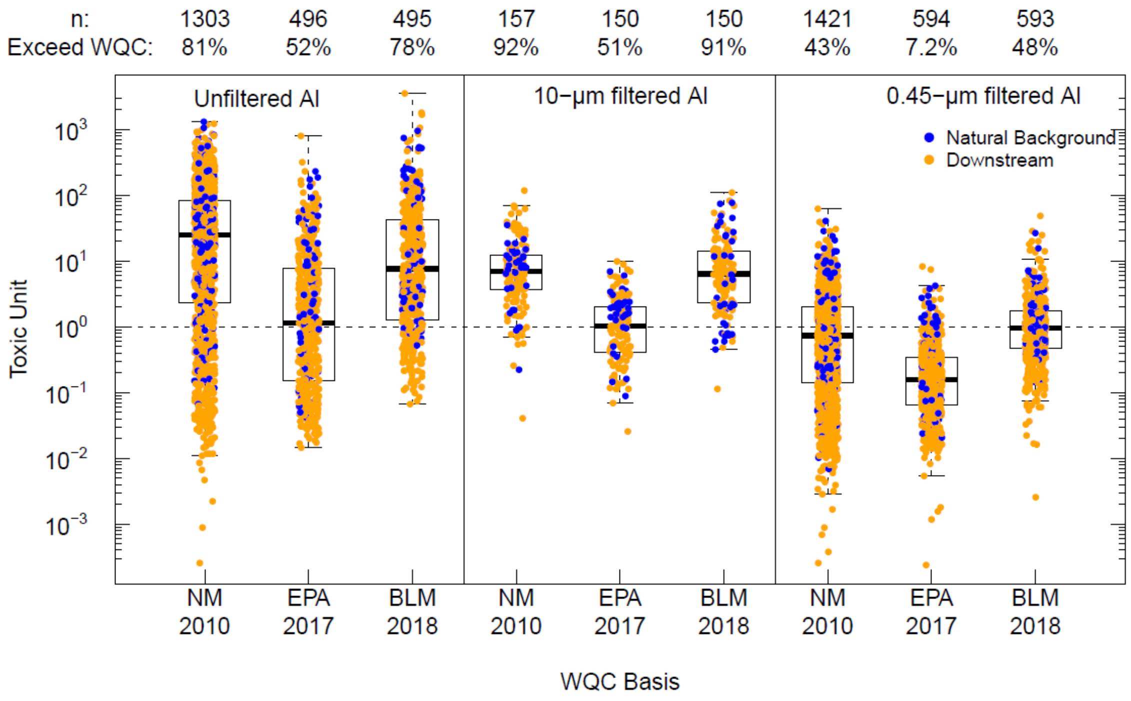

Figure R1. Aluminum toxic units (i.e., reported aluminum concentration/corresponding AWQC) for natural background and LANL surface water location samples using various sample preparations (i.e., unfiltered or filtered using specified filter pore size) are summarized for different AWQC calculation approaches. Sample types include baseflow, stormflow, and snowmelt. All results are for natural background and downstream locations.

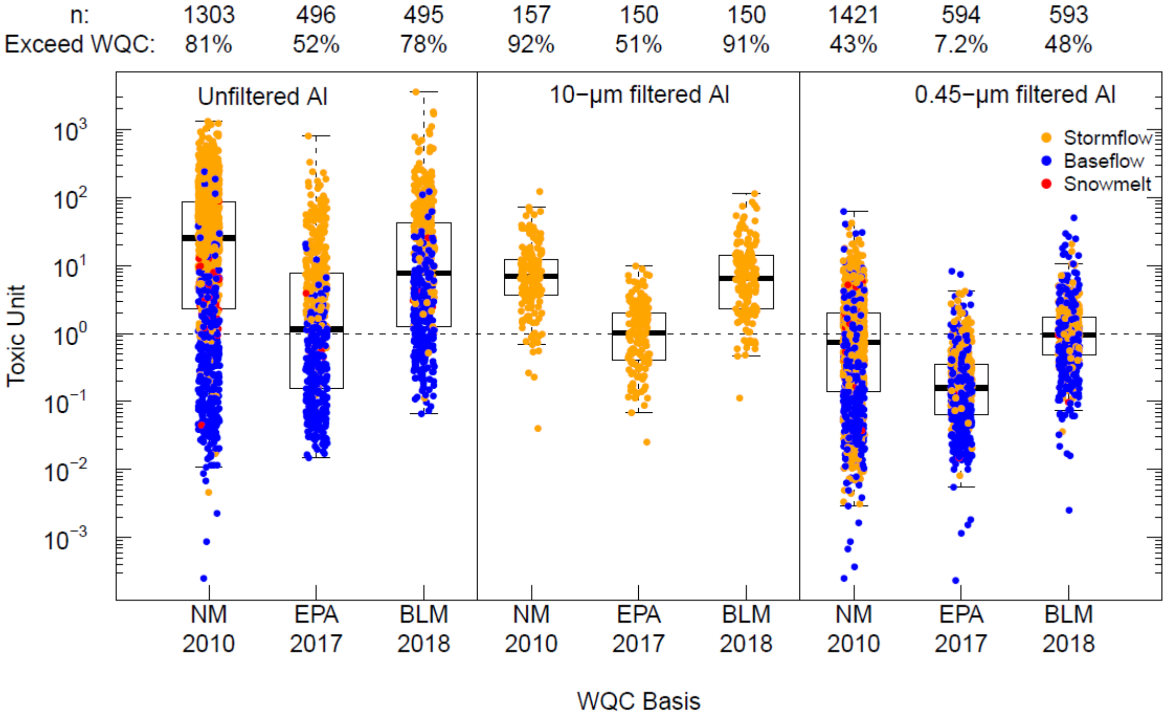

Figure R2. Aluminum toxic units (i.e., reported aluminum concentration/corresponding AWQC) for various sample types and sample preparations (i.e., unfiltered or filtered using specified filter pore size) are summarized for different AWQC calculation approaches. Sample types include baseflow, stormflow, and snowmelt. All results are for natural background and downstream locations.

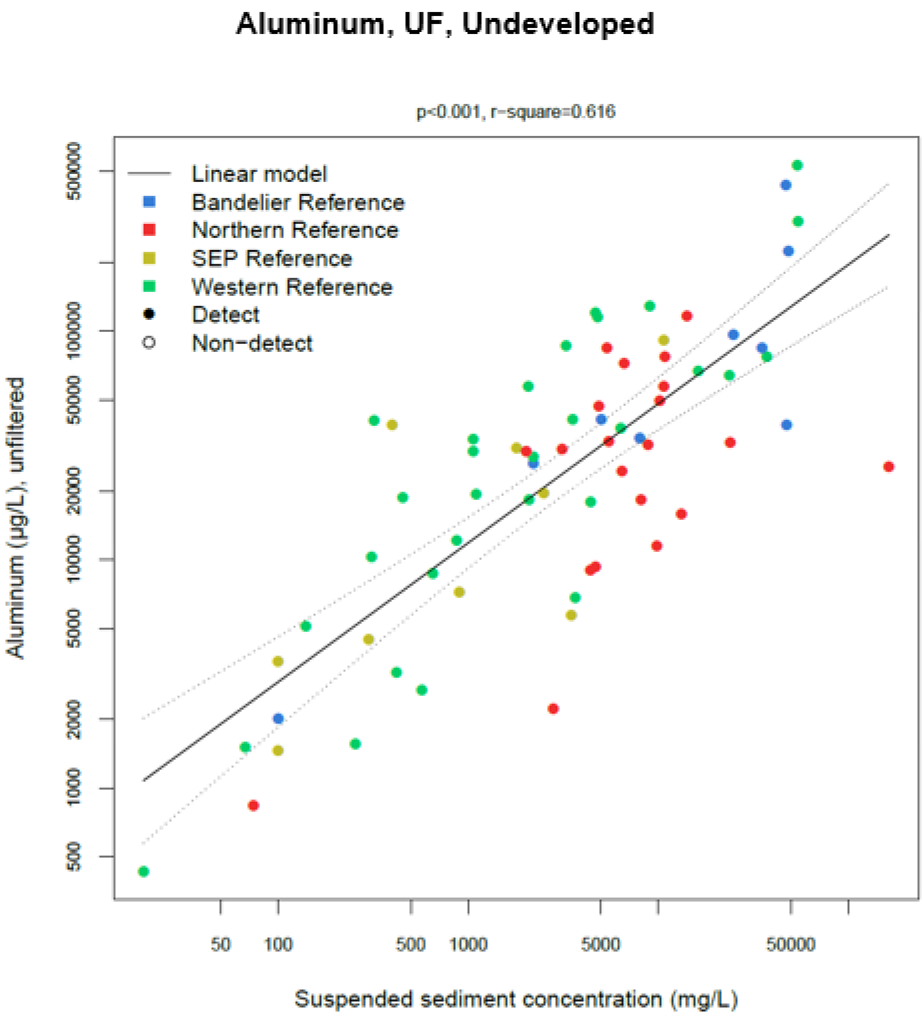

Figure R3. Aluminum (UF) and SSC correlation in natural background surface water samples.

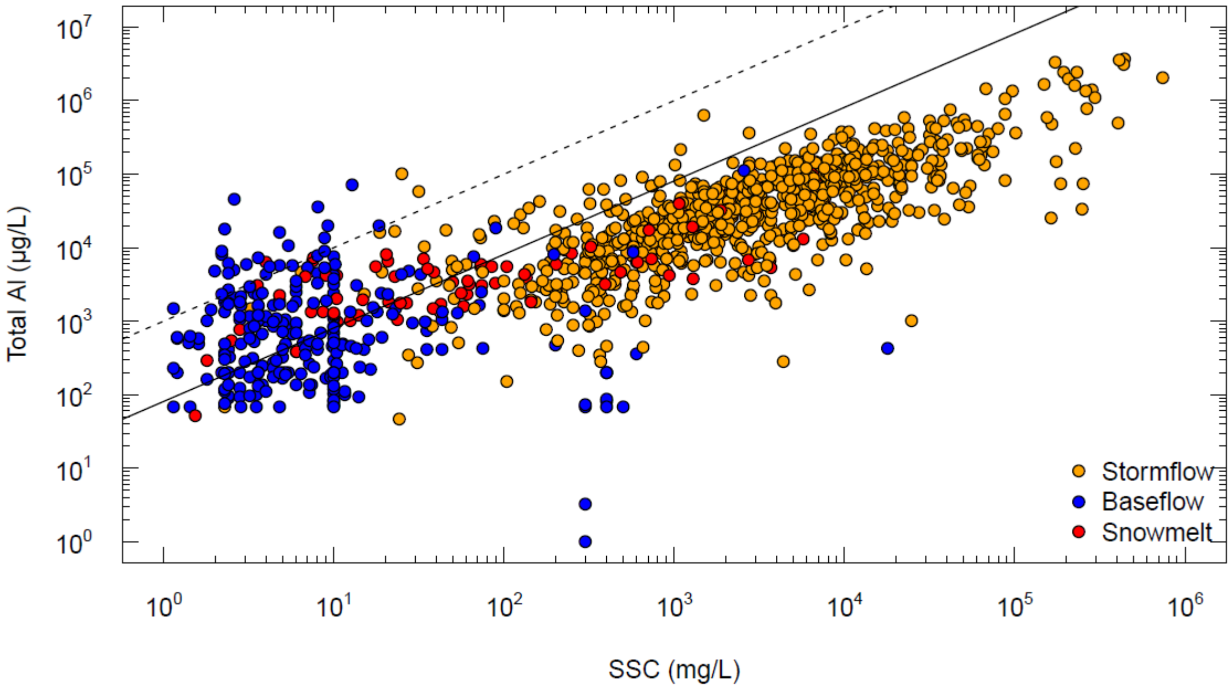

Figure R4. Aluminum concentrations vs. suspended sediment concentration, by sample type for natural background and downstream surface waters. Solid line represents 8% aluminum in SSC. Dashed line represents maximum possible 100% aluminum in SSC. Regression equation using all data: log10(Total Al) = 0.613*log10(SSC) + 2.37 [$r^2 = 0.685$]; regression equation using only stormflow data: log10(Total Al) = 0.662*log10(SSC) + 2.22 [$r^2 = 0.594$].

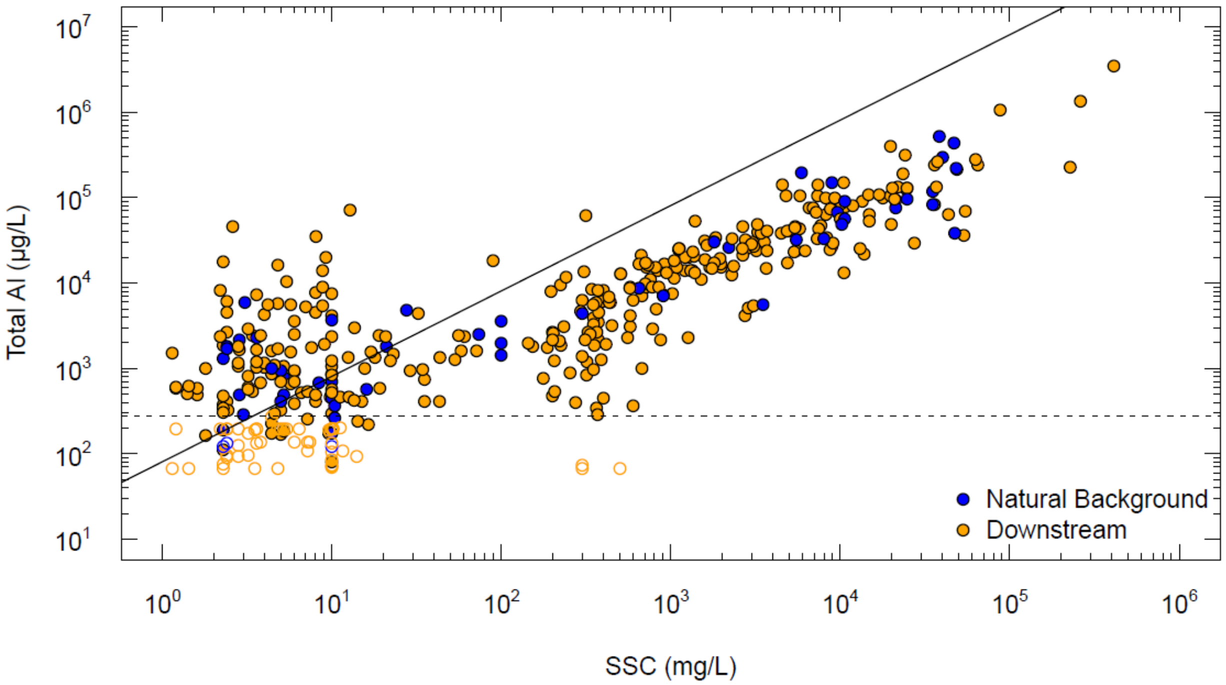

Figure R5. Solubility evaluations of aluminum, with respect to amorphous $Al(OH)_3(s)$ for natural background and downstream locations. Solid line represents 8% aluminum in SSC. Solid points represent samples oversaturated with respect to amorphous $Al(OH)_3(s)$. Horizontal dashed line approximates the solubility limit of amorphous $Al(OH)_3(s)$ in the water samples evaluated.

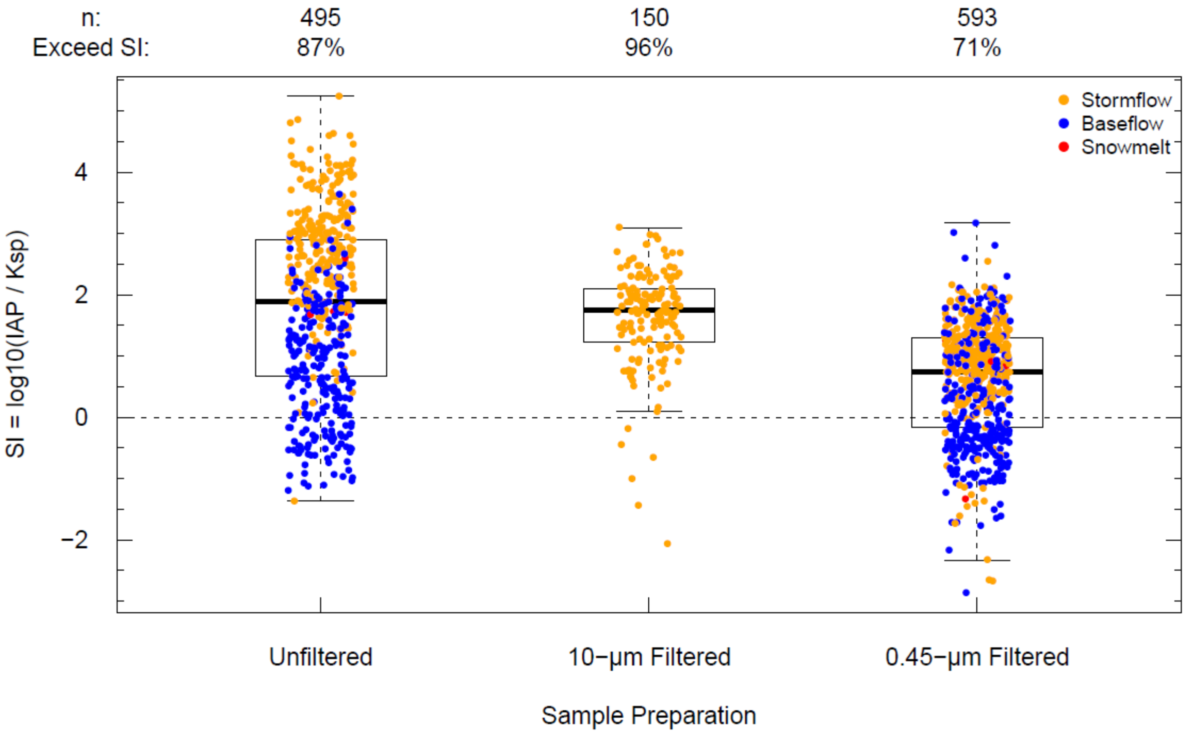

Figure R6. Saturation index calculations for amorphous $Al(OH)_3(s)$ under different sample preparation for natural background and downstream locations.

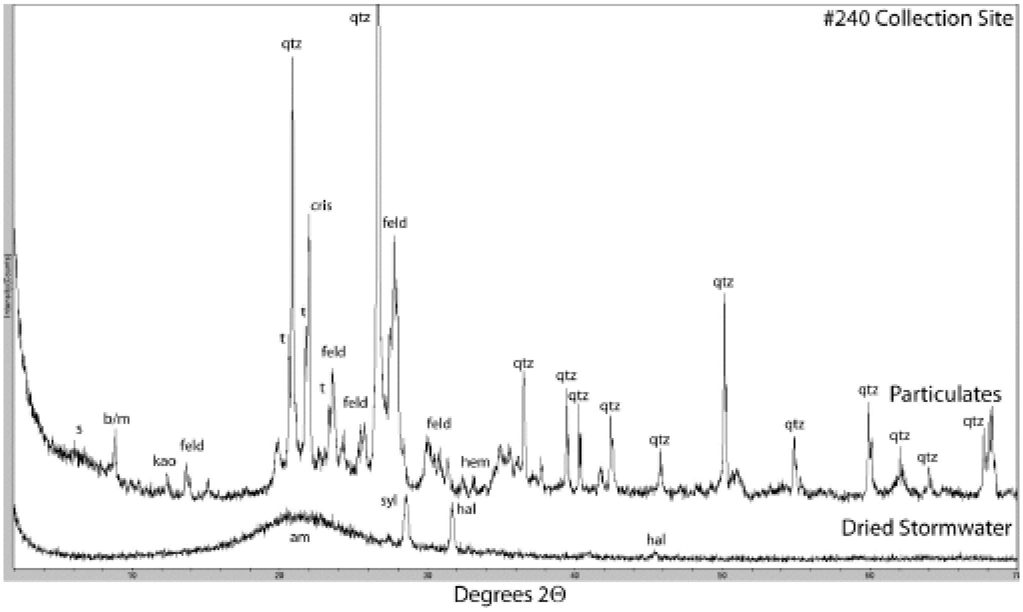

Figure A-21 **XRD patterns from dried storm water and suspended sediment particulates from the same storm water sample (E240). The dried storm water was dominated by amorphous matter (broad hump at 20–30°2θ), sylvite (syl), and halite (hal). The amorphous hump (coupled with SEM/EDS) appears to be aluminosilicate. Sylvite and halite are primarily from precipication during storm water evaporation. Suspended sediment particulates are typical of the Bandelier Formation and dominated by orthoclase/sanidine (feld), albite (feld), quartz (qtz), trydimite (t), and cristobalite (c) with minor amounts of mica (biotite or muscovite [b/m]), smectite, hematite (hem), and kaolinite (kao).**

Figure R7. XRD analysis of precipitated dissolved solids in natural background stormflow sample.

E240 Storm Water Suspended-Sediment Analysis

0.2-µm Cellulose Nitrate Filter

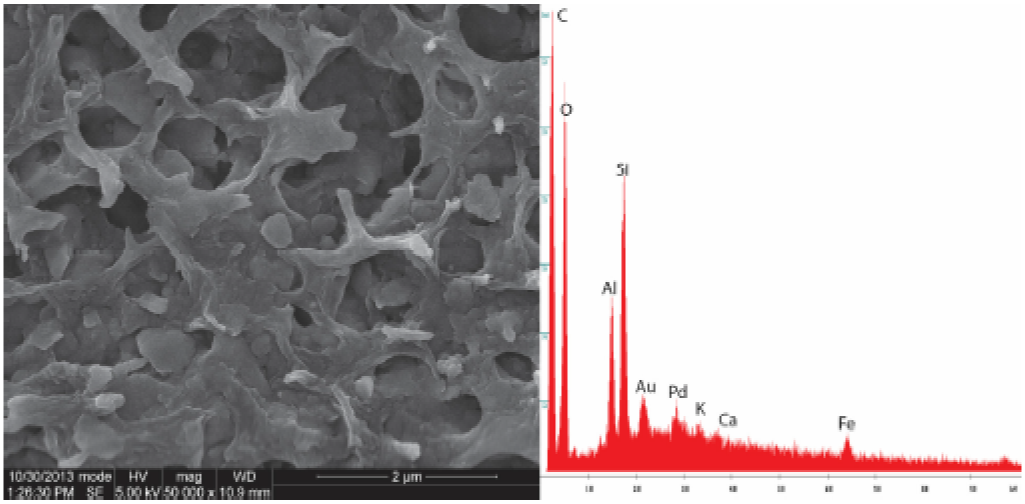

Figure A-15 Retentate exhibiting an amorphous morphology dominated by aluminum and silicon; aluminum/silicon ratio of 1/2. There are minor amounts of potassium, calcium, and iron. The particles appear to have filled most of the porosity opposed to residing on the filter surface. Particulates on the surface typically are well rounded.

Figure R8. SEM/EDS analysis results of natural background stormflow sample particles retained on 0.2µm filters after passing 1µm filter.

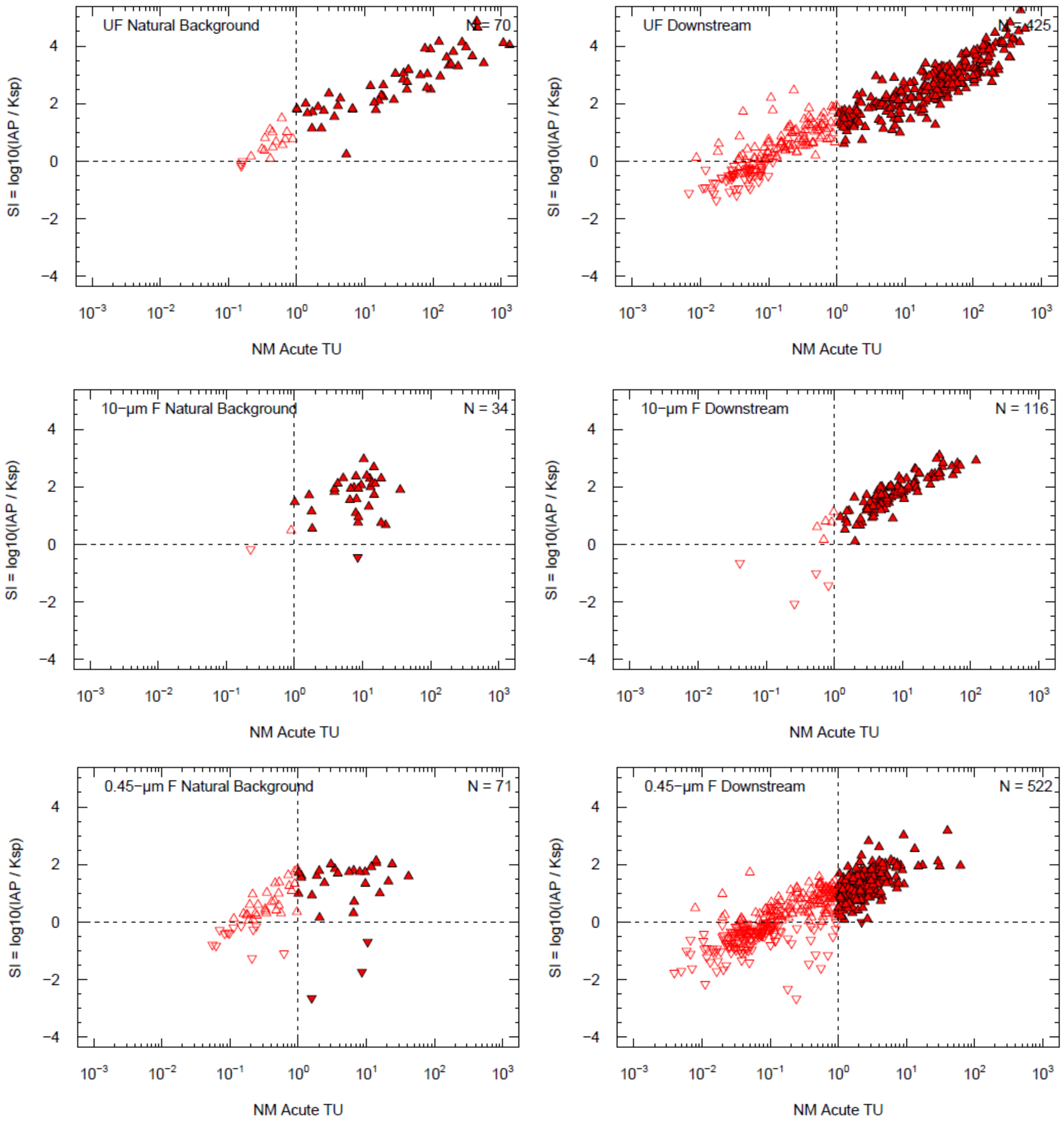

Figure R9. Comparison of solubility exceedance with New Mexico Hardness-based AWQC toxic units for aluminum concentrations from natural background and downstream locations, by filter size. Upward triangles are over-saturated and downward triangles are under-saturated, open triangles are TU<1, solid triangles are TU>1. UF = unfiltered, F = filtered.

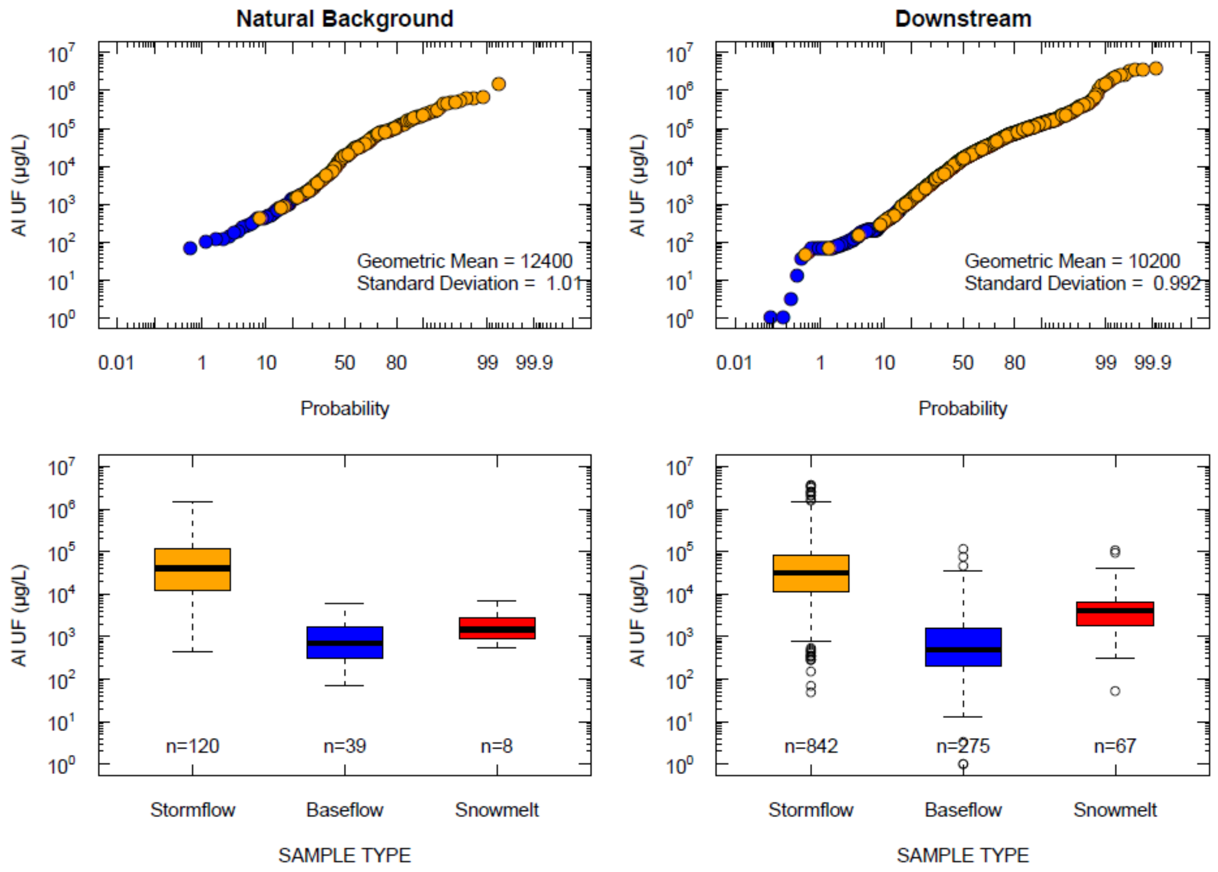

Figure R10. Comparison of total aluminum concentrations for samples from natural background and downstream locations. Boxplots characterize the range of concentrations observed in samples of different type (i.e., Stormflow; Baseflow; Snowmelt). Color of points in top panels represents the sample types, consistent with the bottom panels.

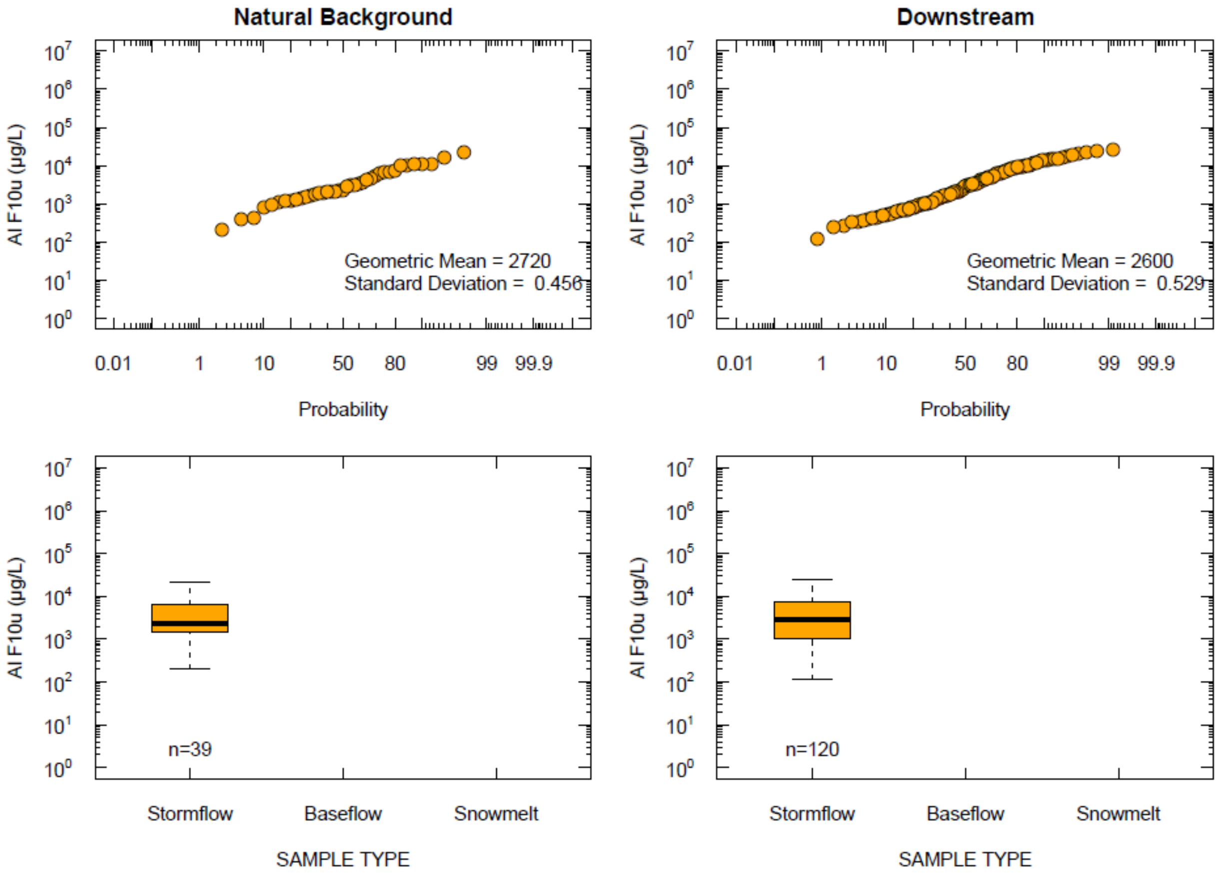

Figure R11. Comparison of 10-µm filtered aluminum for samples from natural background and downstream locations. Boxplots characterize the range of concentrations observed in samples of different type (i.e., Stormflow; Baseflow; Snowmelt). Color of points in top panels represents the sample types, consistent with the bottom panels.

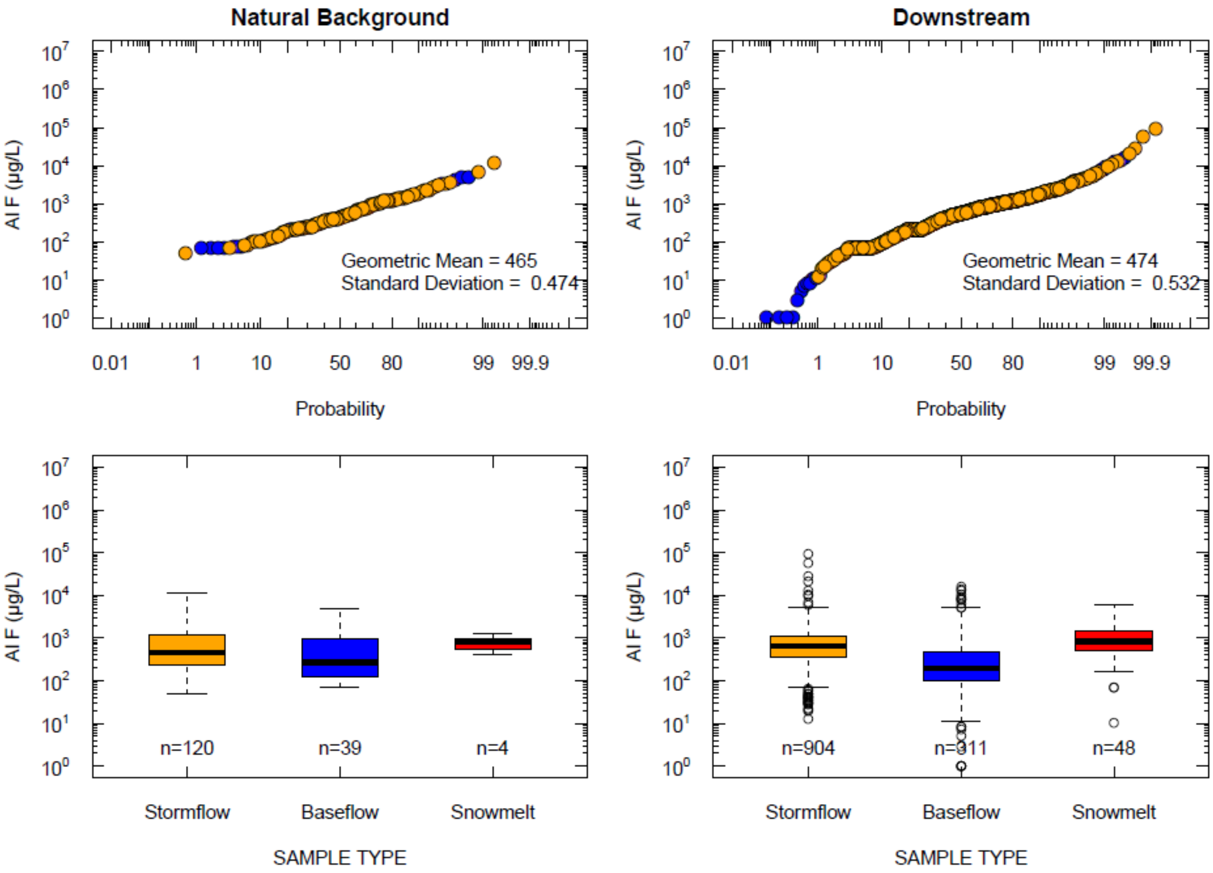

Figure R12. Comparison of 0.45-µm filtered aluminum concentrations samples from natural background and downstream locations. Boxplots characterize the range of concentrations observed in samples of different type (i.e., Stormflow; Baseflow; Snowmelt). Color of points in top panels represents the sample types, consistent with the bottom panels.

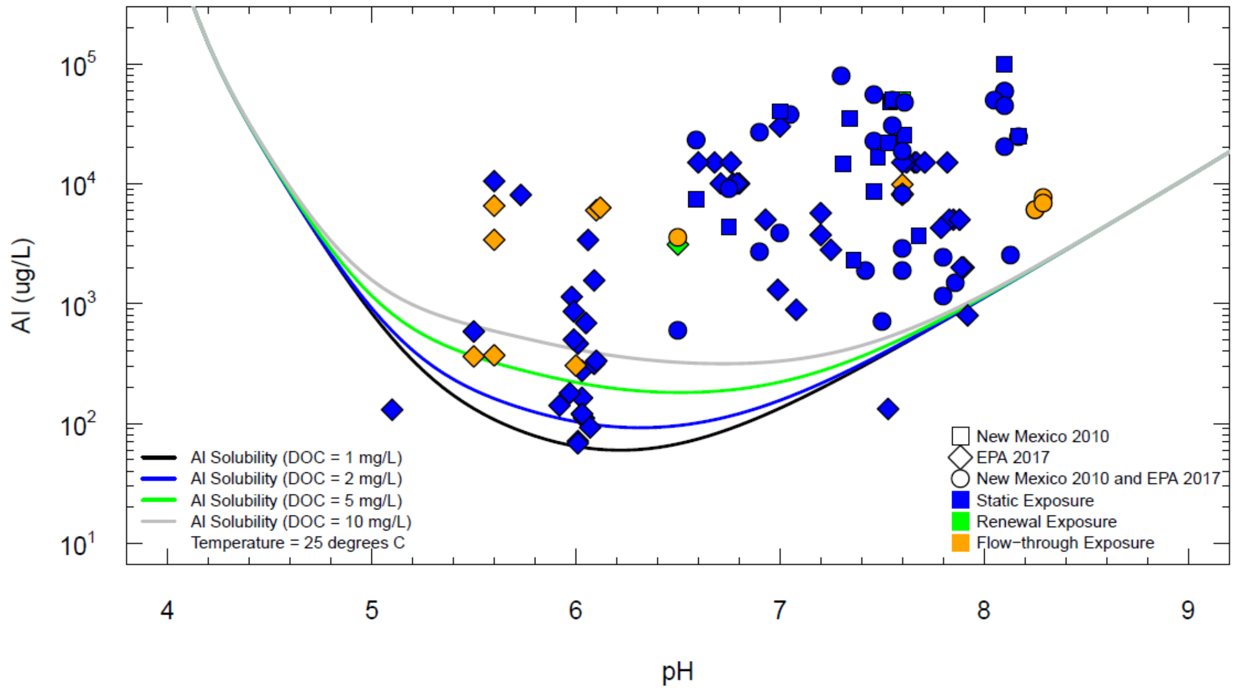

Figure D1. Aluminum effect concentrations from the toxicity database used to derive aluminum (Al) water quality criteria (AWQC) in New Mexico (GEI Consultants 2009, Gensemer 2009, Parametrix 2009) and EPA 2017 draft. Aluminum solubility limits were calculated based upon the solubility of amorphous $Al(OH)_3$ (s) over a range of pH and dissolved organic carbon (DOC) concentrations at 25° C.

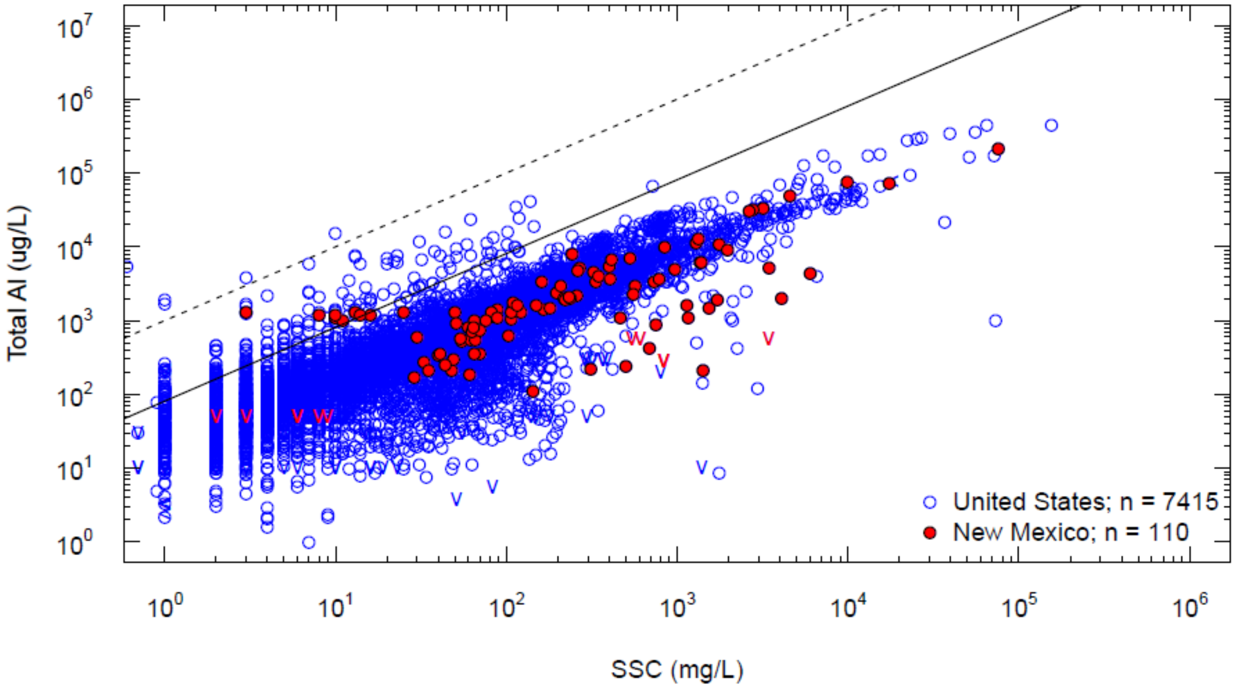

Figure D2. Total aluminum concentrations vs. suspended sediment concentration (SSC) in various surface waters of the United States. All data were obtained from the National Water Quality Monitoring Council data portal (https://www.waterqualitydata.us/portal/). Solid line represents 8% aluminum in SSC (i.e., 80,000 mg/Kg). Dashed line represents maximum possible 100% aluminum in SSC (i.e., 1,000,000 mg/Kg). V = non-detected aluminum concentration.

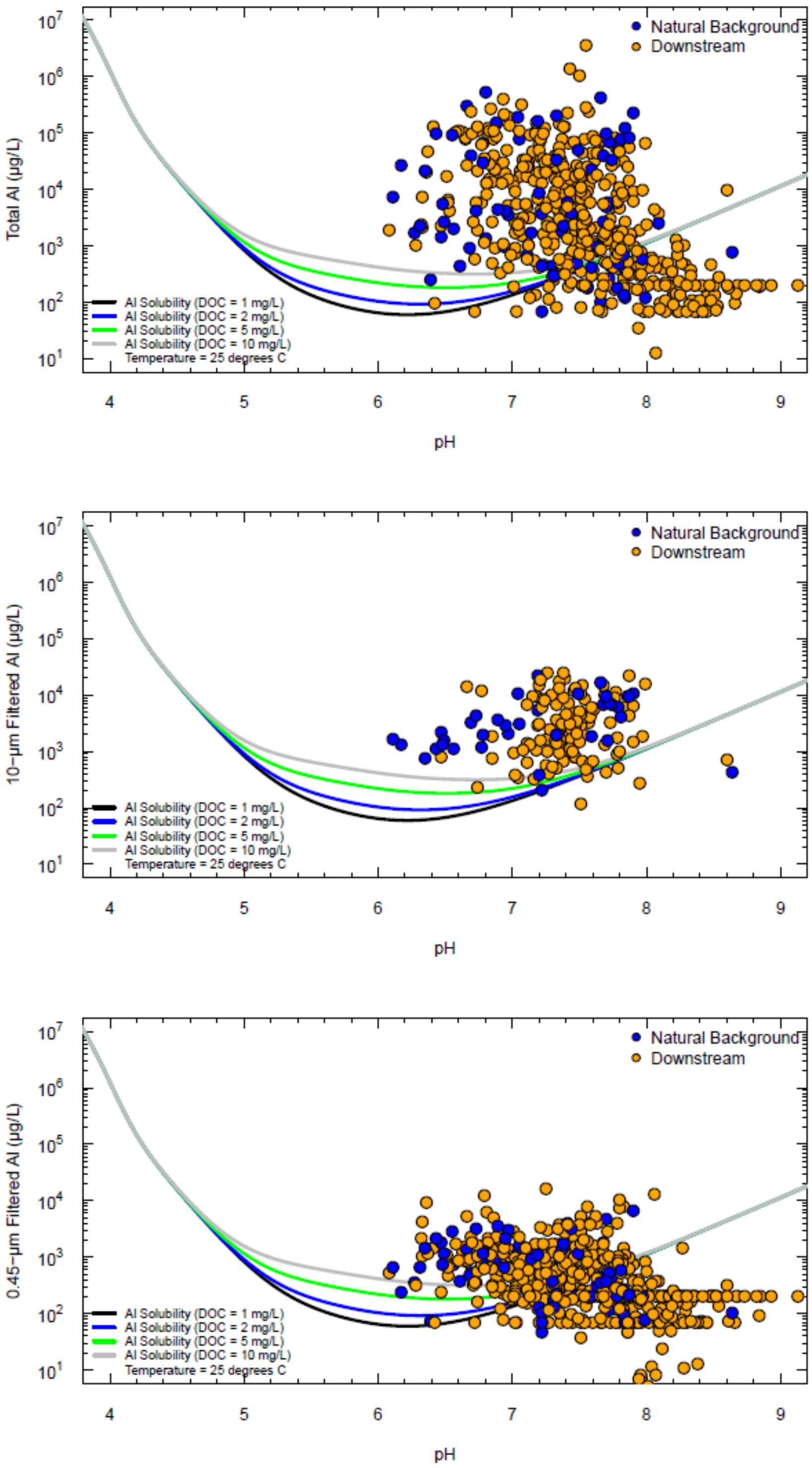

Figure D3. Observed pH and aluminum concentrations for samples from natural background and downstream locations with aluminum solubility limits calculated based upon the solubility of amorphous $Al(OH)_3$ (s) over a range of pH and dissolved organic carbon (DOC) concentrations at 25° C.