Characterizing water quality background concentrations of aluminum, PCBs, and radioactivity on the arid Pajarito Plateau, New Mexico

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Abstract

If National Pollutant Discharge Elimination System (NPDES) permit action levels are set near or below background concentrations, achieving compliance is difficult or impossible and might serve only to attempt to reduce naturally occurring constituents. In regard to an NPDES stormwater permit for Los Alamos National Laboratory (LANL), which is situated on the arid Pajarito Plateau near Santa Fe, New Mexico, studies show that aluminum and gross alpha radiation concentrations are attributable to Bandelier tuff, the major geologic medium in the area. Meanwhile, atmospheric deposition of polychlorinated biphenyls (PCBs) contributes to an anthropogenic baseline, measurable in reference watersheds. As a result, exceedances of NPDES action levels and state water quality criteria (WQC) for these constituents are erroneously attributed to LANL discharges. To address this situation, a framework was established to generate water quality background threshold values (BTVs) that characterize natural background (NBG), anthropogenic baseline, and developed background conditions using statistical methods.

Water quality data were evaluated for potential spatial and temporal dependencies, as well as relationships with suspended sediment concentration (SSC), a parameter positively correlated with storm water discharge. Data were subsetted or normalized to SSC to address dependencies prior to calculating BTVs for 18 constituents, resulting in a total of 43 BTVs. A subset of those BTVs are discussed herein.

Most recommended BTVs were calculated using ProUCL as 95-95 upper tolerance limits (UTLs) based on gamma, lognormal, normal, or nonparametric methods. The resulting anthropogenic baseline PCB BTV of 58 ng/L is 90 times higher than the New Mexico human health WQC (0.64 ng/L). The NBG gross alpha BTV is 190 pCi/g SSC, which, after back-transformation using the 25th and 75th percentiles of NBG SSC, ranges from 170 to 1,900 pCi/L, well above the New Mexico WQC (15 pCi/L). Two NBG aluminum BTVs of 17 and 76 mg/g SSC were developed (for subareas of Pajarito Plateau), which, after back-transformation, range from 15 to 1,700 mg/L and 68 to 780 mg/L, respectively; these values are much higher than the New Mexico hardness-based WQC (from 0.37 to 1.9 mg/L as total aluminum). Such results suggest that BTVs should be taken into account before concluding that exceedances of state WQC and related LANL NPDES permit action levels are attributable to LANL discharges, since such conclusions can lead to unwarranted actions such as engineered controls, 303(d) listings, and developing total maximum daily loads (TMDLs).

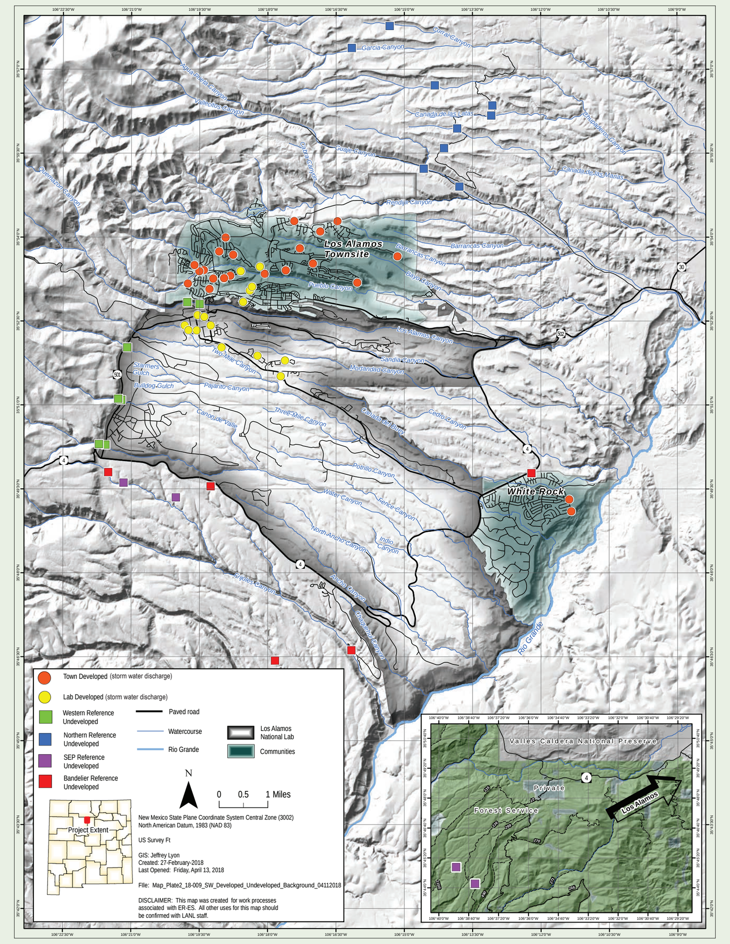
Introduction

The purpose of this study was to characterize background concentrations in storm water that runs off developed and undeveloped landscapes on the Pajarito Plateau, New Mexico, near Los Alamos National Laboratory (LANL) (Figure 1). LANL's National Pollutant Discharge Elimination System (NPDES) Individual Permit (IP) target action levels (TALs) are set near or below background concentrations, and it is impracticable for LANL to meet those IP TALs.

The Pajarito Plateau lies between the Jemez Mountains and the Rio Grande. The few perennial streams that exist on the plateau are located where effluent or natural springs provide sufficient water volume. Otherwise, streams are ephemeral or intermittent, only flowing in response to seasonal snowmelt or heavy rainfall. Storm water from the plateau infrequently reaches the Rio Grande. Figure 2 provides a conceptual site model for LANL storm water and how it relates to hydrology across the plateau, and Figure 3 provides photographic examples of typical streams on the plateau.

The key results of this study were background threshold values (BTVs), which quantify background concentrations in storm water. BTVs were developed using a background characterization framework (BCF), consistent with existing guidance for characterizing groundwater (ITRC 2013) and other media (EPA 2016). The BCF included multiple steps and decision points for developing a sufficient and "stable" or independently and identically distributed (IID) dataset, calculating BTVs, and evaluating uncertainties.

This poster focuses on key constituents of concern for LANL that have elevated background concentrations in undeveloped watersheds: aluminum, gross alpha radiation, and polychlorinated biphenyls (PCBs).



Note: "SEP" samples are associated with LANL's Supplemental Environmental Projects

Figure 1. Sampling location map for background storm water datasets

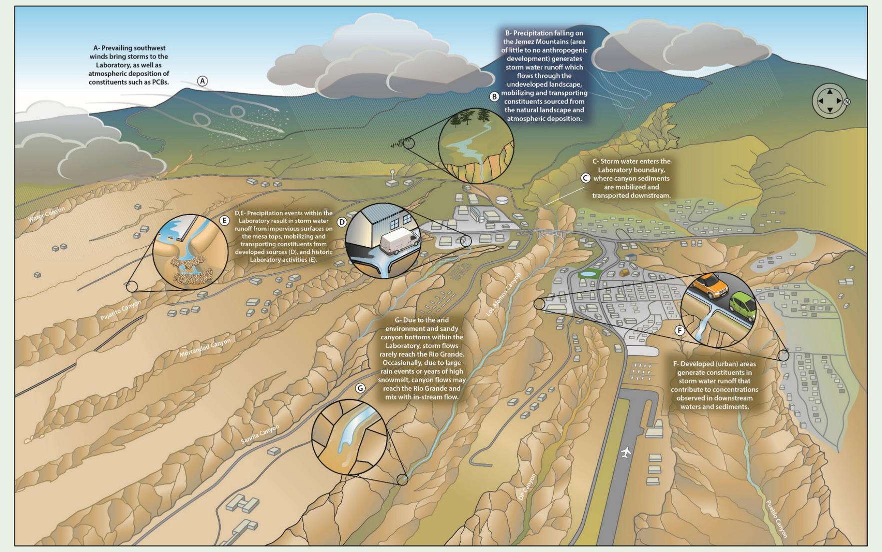


Figure 2. Conceptual site model for background storm water on Pajarito Plateau

Figure 3. Example streams on Pajarito Plateau during the early monsoonal season

Datasets

Publicly available data were downloaded from LANL's Intellus database:

- More than 750 samples collected by LANL or the New Mexico Environment Department (NMED) from 85 locations within 11 canyons (and 23 individual sub-watersheds) from 2005 to 2017 (Figure 1) were included in the dataset.
- Data collected prior to 2005 were deemed unreliable by LANL and excluded.
- Data from July 4, 2011, to January 1, 2014, were influenced by the Las Conchas Fire and were excluded per LANL guidance. (fire-affected watersheds only).
- Data for 28 constituents—corresponding to the constituents regulated by LANL's Individual Permit (IP) as well as total aluminum, total recoverable cyanide, and dissolved selenium—were included.
  – Several constituents regulated by LANL's IP were not detected in any sample, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, cyanide, benzo(a)pyrene, and silver.

LANL assigned spatial categories to each sampling location to define the major watershed (canyon), minor watershed, and "location grouping" variables. Location groupings corresponded to subareas of interest, such as undeveloped landscapes to the west of the Laboratory property (Western Reference) or undeveloped landscapes to the north of the town of Los Alamos (Northern Reference) (see Figure 1).

Suspended sediment concentration (SSC) data were paired with as many samples as possible using concurrent (same-day, co-located) samples. If only total suspended solids (TSS) data were available for a sample, SSC was estimated from TSS using a log-log linear regression ($p < 0.05$, $r^2 \sim 0.7$) developed from samples with paired SSC and TSS data.

Background Characterization Framework

The BCF is a process for evaluating background storm water data, accounting for dependencies (i.e., spatial or temporal factors affecting concentrations), and calculating BTVs. The process follows five steps (Figures 4a and 4b):

- Step 1. Identify sufficient IID populations within the dataset.
- Step 2. Explore and describe dependencies within the dataset.
- Step 3. If dependencies exist, split the dataset into subpopulations or normalize the dataset as appropriate to meet stability requirements.
- Step 4. Calculate BTVs.
- Step 5. Characterize uncertainty.

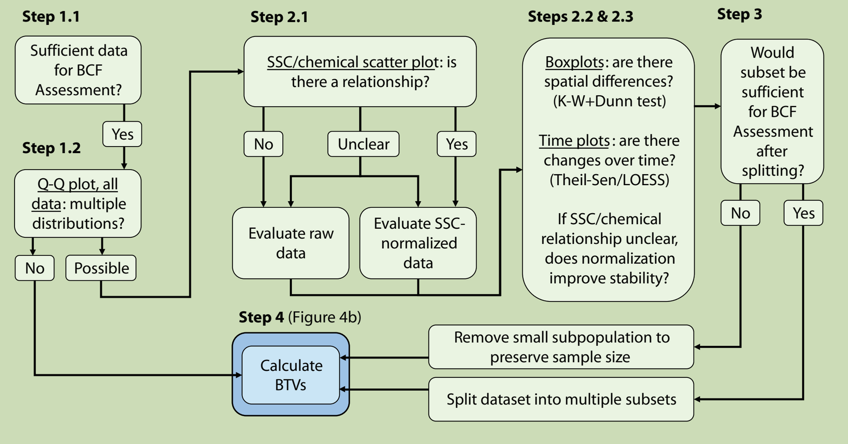


Figure 4a. Background characterization framework, Steps 1–3

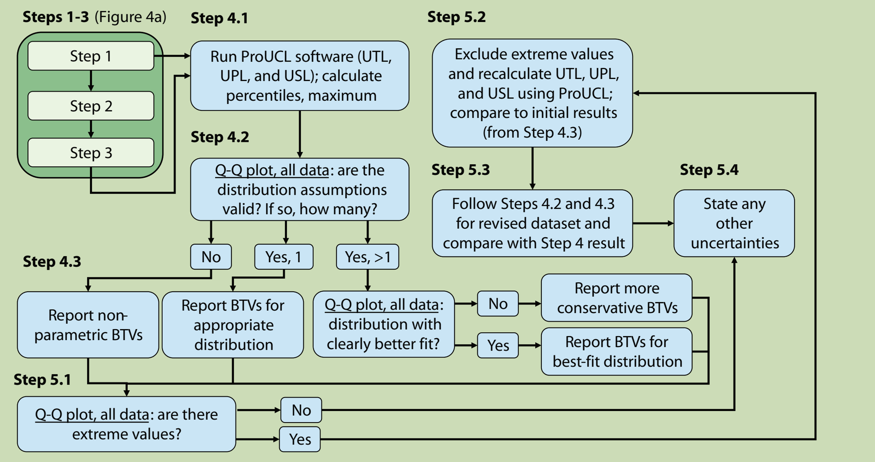


Figure 4b. Background characterization framework, Steps 4–5

Step 1 involved the initial screening out of datasets with $n < 10$ samples and detection frequencies < 20%. Quantile-quantile (Q-Q) plots (Figure 5) were also used to find possible subpopulations in the dataset for further evaluation.

In **Step 2**, spatial or temporal differences or correlations with SSC were assessed. The relationship between SSC and chemical concentration was quantified using linear regression (e.g., Figure 6); a significant slope (Student's t-test, $p < 0.05$) and reasonably strong linear fit ($r^2 \geq 0.5$) indicated a dependency that should be dealt with, whereas a significant but relatively weak slope was evaluated further (e.g., Figure 7). SSC is a covariate of stream discharge and is a useful proxy for "storm intensity." Spatial factors included major and minor watersheds and major and minor location groupings. Differences were determined with box plots and nonparametric Kruskal-Wallace and post-hoc Conover-Inman tests (two-tailed, Bonferroni-corrected familywise alpha = 0.05) (e.g., Figure 8). Temporal trends were evaluated using Theil-Sen median regression and local regression (LOESS) (e.g., Figure 9).

In **Step 3**, dependencies were removed, either by splitting the full datasets into smaller subsets of similar concentrations by spatial grouping(s) or by dividing storm water concentrations by sample-specific SSC (normalization). Temporal trends were found to be consistently related to differences in spatial sampling over time; thus, splitting data by spatial groupings also controlled for observed temporal trends. Data subsets and normalized values were re-evaluated using Steps 1 through 3.

In **Step 4**, BTVs were calculated. Various censored statistics (i.e., UTLs, upper prediction limits [UPLs], and upper simultaneous limits [USLs]) were generated using ProUCL (EPA 2016), and upper percentiles and maxima were calculated using R software. Parametric statistics were preferred, when valid based on goodness-of-fit test results and visual inspection of Q-Q plots (e.g., Figure 10).

In **Step 5**, uncertainties associated with the data and BTVs were summarized.

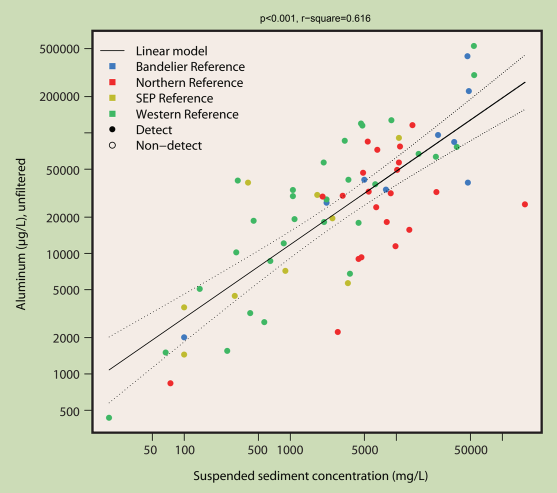


Figure 6. Scatter plot with linear regression used during BCF Step 2.1

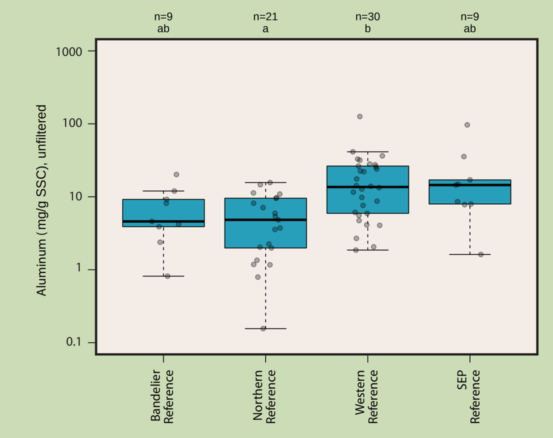


Figure 8. Box plot used during BCF Step 2.2

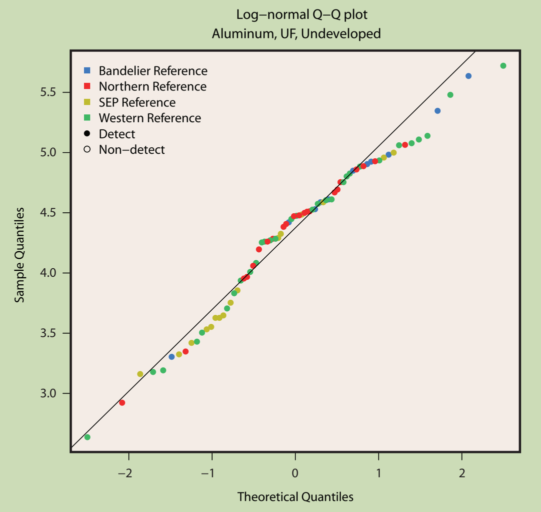


Figure 5. Q-Q plot used during BCF Step 1.2

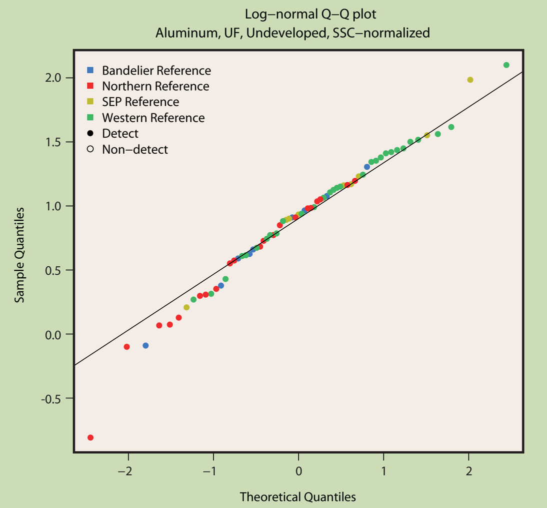


Figure 7. Q-Q plot used during BCF Step 2.1

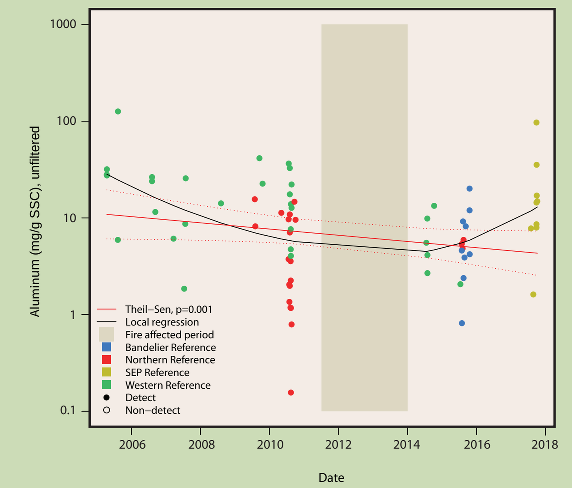


Figure 9. Time plot used during BCF Step 2.3

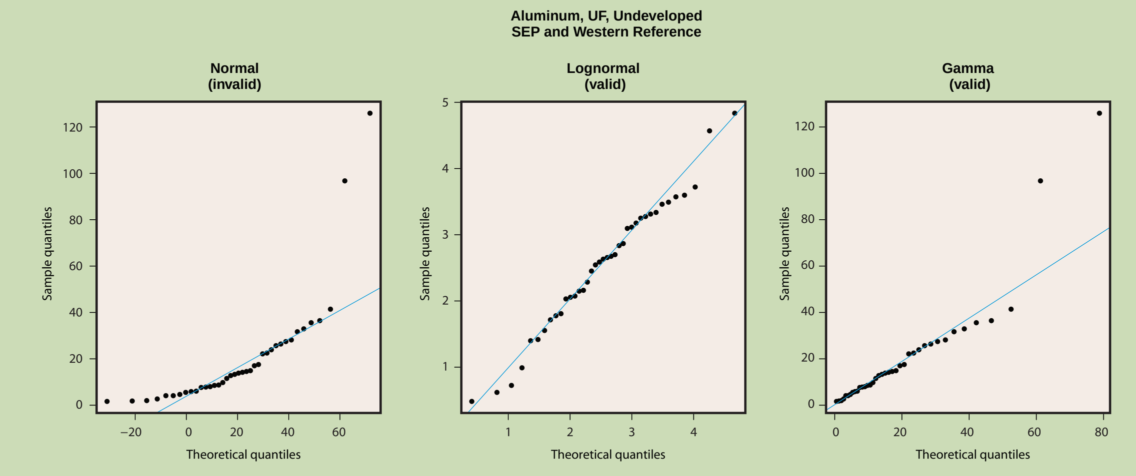
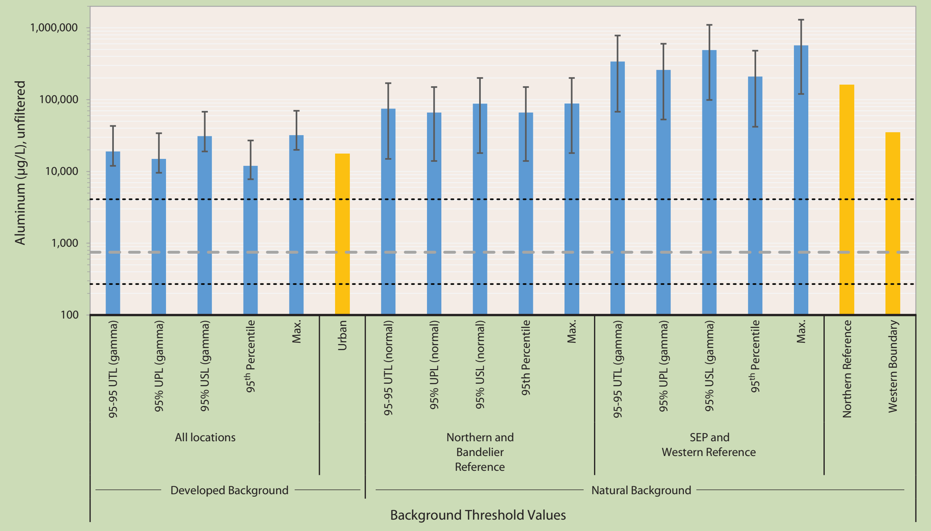


Figure 10. Q-Q plots used during BCF Steps 4.2 and 4.3

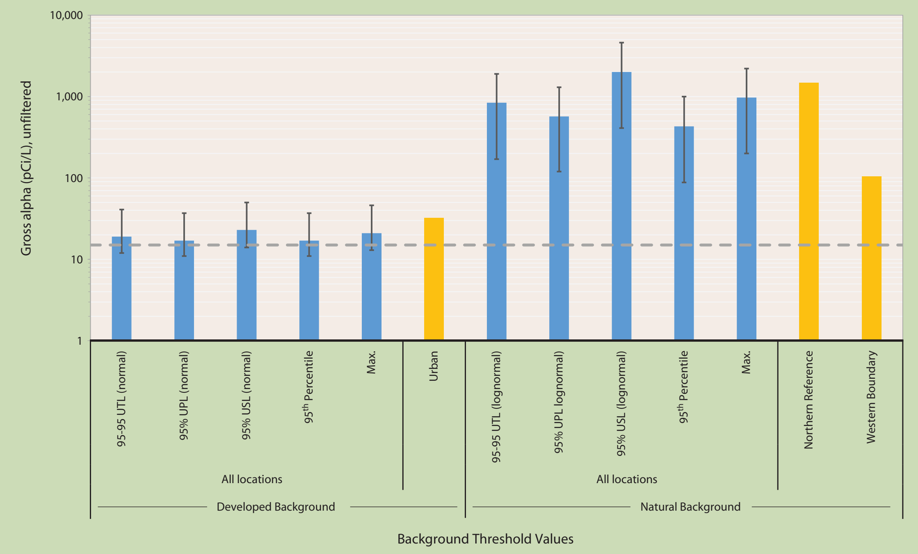
Results and Discussion

- Using the BCF, 43 sets of BTVs were developed for 18 constituents. BTVs for unfiltered aluminum, gross alpha, and total PCBs are presented in Figures 11, 12, and 13, along with LANL's current and draft permit benchmarks (average or maximum target action levels [ATALs or MTALs]).



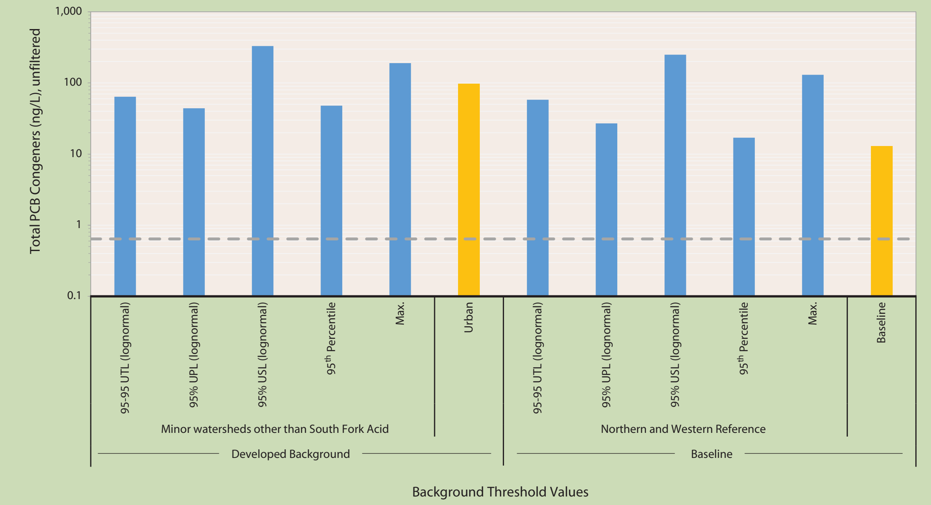
Gray dashed line is 2010 MTAL (750 µg/L), and dotted black lines are the range of watershed-specific (hardness-adjusted) 2015 draft MTALs (274 to 4,122 µg/L). Blue bars are 2018 BTVs, and orange bars are 2013 BTVs (95-95 UTLs). Whiskers and blue bars represent a likely range of back-transformed BTVs calculated by multiplying the SSC-normalized BTVs by the 25th, 50th, and 75th percentile SSC values for the respective landscape type (developed or natural). Back-transformation was used herein to allow for comparison to 2013 BTVs and permit limits.

Figure 11. Comparison of 2018 BTVs and existing LANL BTVs for unfiltered (total) aluminum



Gray dashed line is 2010 ATAL (15 pCi/L). Blue bars are 2018 BTVs, and orange bars are 2013 BTVs (95-95 UTLs). Whiskers and blue bars represent a likely range of back-transformed BTVs calculated by multiplying the SSC-normalized BTVs by the 25th, 50th, and 75th percentile SSC values for the respective landscape type (developed or natural). Back-transformation was used herein to allow for comparison to 2013 BTVs and permit limit.

Figure 12. Comparison of 2018 BTVs and existing LANL BTVs for gross alpha radiation



Dashed line is 2010 ATAL (0.64 ng/L) based on human health exposure to fish in the Rio Grande. Blue bars are 2018 BTVs, and orange bars are 2012 BTVs (95-90 UTLs).

Figure 13. Comparison of 2018 BTVs and existing LANL BTVs for total PCBs

- Few constituents were strongly related to SSC, although unfiltered aluminum and gross alpha radiation are exceptions (e.g., Figure 6).
- BTVs for natural conditions on the Pajarito Plateau exceed LANL's TALs for aluminum, gross alpha, and total PCBs (Figures 11, 12, and 13).
- For the aluminum concentrations at Supplemental Environmental Projects (SEP) Reference and Western Reference locations (Figure 1), which represent the most spatially relevant undeveloped condition for streams that receive LANL storm water, 95-95 UTLs (based on back-calculation from 76 mg/g SSC) range from 68 to 780 mg/L, approximately two to three orders of magnitude (depending on SSC) greater than the 2010 IP TAL of 0.75 mg/L. This reflects a key problem with any total aluminum standard: Aluminum is the third most abundant element in Earth's crust and a large component of any natural sediment; therefore, even low SSC will result in noncompliance with total aluminum standards.
- Gross alpha in natural waters of the Pajarito Plateau far exceeds the TAL of 15 pCi/L; estimates (based on back-calculation from SSC-normalized 95-95 UTL of 190 pCi/g SSC) range from 170 to 1,900 pCi/L, approximately one to two orders of magnitude greater than the TAL. There is not a significant spatial difference in gross alpha radiation levels across the Pajarito Plateau, which suggests that the common geology is the dominant source.
- Although PCBs are not part of the "natural" condition (PCBs are strictly man-made), they exist nonetheless in natural Pajarito Plateau waters at levels that exceed permit limits. The 95-95 UTL for total PCBs of 58 ng/L is approximately two orders of magnitude greater than the 2010 IP TAL of 0.64 ng/L, which is based on human health (via diet). Previous studies by LANL have traced PCBs to aerial deposition (LANL 2012). Thus, there is an anthropogenic "baseline" level of PCBs that should be considered.
- Aluminum and gross alpha BTVs tended to be low in developed landscapes (Figures 11 and 12) relative to BTVs for undeveloped landscapes; this is likely due to the greater amount of sediment measured in undeveloped watersheds relative to developed watersheds. Total PCBs concentrations were very similar between developed and undeveloped landscapes, possibly reflecting a similar regional source (i.e., precipitation).
- BTVs for copper and zinc from developed landscapes (not detailed herein) tended to be greater than both TALs and NBG BTVs, reflecting urban sources. Thus, urban sources should be also considered for storm water constituents when characterizing background.

Next Steps:

- LANL is continuing to collect data as part of its SEP program. Eventually, BTVs may be recalculated using a larger, updated dataset.
- BTVs will be used to evaluate LANL-influenced storm water data for LANL's forthcoming IP application.
- BTVs may be proposed as site-specific standards or as replacements for TALs.
- LANL will work with the US Environmental Protection Agency (EPA) Region 6 and NMED on options for the use of PCB BTVs in the permitting process, given that PCBs are not naturally occurring.
- LANL will establish which statistic is acceptable to both regulators and LANL for defining background conditions (i.e., protective of aquatic life without requiring unnecessary effort to control background conditions potentially unrelated to historical LANL activities).

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