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# Subject: NPDES Permit No. NM0030759 – Individual Permit Storm Water Data Background Comparisons

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Dear Mr. Herrera:

This paper provides the U.S. Environmental Protection Agency (EPA) with a statistical evaluation of storm water data collected from site monitoring areas (SMAs) under the National Pollutant Discharge Elimination System (NPDES) Permit No. NM0030759 (Individual Permit) and undeveloped and developed background data sets collected on and around Los Alamos National Laboratory (the Laboratory).

This paper was prepared in response to an EPA request made during a November 2016 meeting with staff from the Laboratory's Associate Directorate of Environmental Management (ADEM). EPA Region 6 storm water permit staff expressed an interest in seeing how background data compare directly with data generated during sampling conducted under the Individual Permit. The Laboratory collected the SMA data used in this evaluation, and the Laboratory and the New Mexico Environment Department of Energy Oversight Bureau collected the data from undeveloped and developed locations.

This paper uses box plots and three statistical test methods (Gehan, quantile, and slippage) to compare the aluminum, copper, gross alpha and total polychlorinated biphenyls (PCBs) SMA data sets to the background data sets. The box plot assessment allows for the visual comparison of the data distribution for each set. The results of the three statistical tests are used to determine if concentrations and activities of the selected chemicals at SMAs are greater than concentrations at background locations. The results show that aluminum, zinc, and gross alpha at SMAs are not greater than background. The dissolved copper and total PCBs SMA data sets are greater than the undeveloped background data set; total PCBs are also greater than the developed background data set.



If you have any questions, please contact Terrill Lemke at (505) 665-2397 (tlemke@lanl.gov) or David Rhodes at (505) 665-5325 (david.rhodes@em.doe.gov).

Sincerely,

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# Individual Permit Storm Water Data Background Comparisons



Prepared by the Associate Directorate for Environmental Management

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#### **EXECUTIVE SUMMARY**

Storm water samples collected from site monitoring areas (SMAs) at Los Alamos National Laboratory (LANL or Laboratory) may include concentrations of constituents that frequently exceed National Pollutant Discharge Elimination System Permit No. NM0030759 (hereafter, the Individual Permit, Permit, or IP) target action levels (TALs). Constituents that frequently exceed IP TALs include dissolved aluminum, copper, and zinc; gross-alpha radioactivity; and total polychlorinated biphenyls (PCBs). SMAs are storm water monitoring drainage areas that monitor storm water discharge from Sites (solid waste management units or areas of concern). However, these drainage areas also contain undeveloped and developed landscapes. Previous Laboratory studies have shown that reference drainage areas that represent background undeveloped<sup>1</sup> and developed<sup>2</sup> landscapes are sources of these constituents. Using statistical tests and plots, this paper determines if concentrations of these constituents measured in SMA storm water samples are greater than results of the same constituents measured at undeveloped and developed background locations.

These statistical evaluations resulted in the following observations concerning similarities and differences in SMA versus background constituent concentrations:

- Dissolved<sup>3</sup> aluminum and zinc SMA concentrations are not greater than either undeveloped or developed background concentrations.
- Dissolved copper SMA concentrations are greater than undeveloped background and not greater than developed background.
- Gross-alpha SMA concentrations are not greater than either undeveloped background or developed background concentrations; gross-alpha concentrations are also highly correlated to suspended sediment concentrations (SSC) and should be normalized to SSC for further statistical analysis.
- Total PCBs SMA concentrations are greater than either undeveloped or developed background concentrations; total PCBs are not correlated to SSC.

For each constituent evaluated, the IP TAL was frequently exceeded in storm water runoff results from either or both developed and undeveloped background landscapes. These results and the SMA to background comparisons confirm that undeveloped and developed background landscapes have sources of the constituents evaluated and that these landscapes may contribute to, or be the primary sources of, IP TAL exceedances at SMAs. These results indicate the importance of developing a U.S. Environmental Protection Agency–accepted method of accounting for undeveloped and developed landscape sources of these constituents for the IP.

<sup>&</sup>lt;sup>1</sup> Undeveloped landscape background sampling locations receive storm water runoff from watersheds that contain no or minimal current or former impacts from development. Constituents sourced from the undeveloped landscape are associated directly with the geology, vegetation, or other sources associated with the natural landscape.

<sup>&</sup>lt;sup>2</sup> Developed landscape background sampling locations receive storm water runoff from watersheds that contain buildings, roads, vehicles, and other common structures or activities associated with a developed landscape (residential/urban/industrial environment) and are upgradient of historical Laboratory releases of industrial material.

 $<sup>^3</sup>$  Dissolved indicates the sample was filtered through a 0.45- $\mu m$  filter.

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# Appendixes

Appendix A Analytical Results of Site Monitoring Area, Developed, and Undeveloped Data Sets (on CD included with this document)

ADEM	Associate Directorate of Environmental Management (LANL)
AOC	area of concern
DOE	Department of Energy (U.S.)
EIM	Environmental Information Management
EPA	Environmental Protection Agency (U.S.)
GIS	geographical information system
Individual Permit	National Pollutant Discharge Elimination System Permit No. NM0030759
IP	National Pollutant Discharge Elimination System Permit No. NM0030759
Laboratory	Los Alamos National Laboratory
LANL	Los Alamos National Laboratory
NMED	New Mexico Environment Department
NPDES	National Pollutant Discharge Elimination System
PCB	polychlorinated biphenyl
Permit	National Pollutant Discharge Elimination System Permit No. NM0030759
SMA	site monitoring area (EPA)
SSC	suspended sediment concentration
SWMU	solid waste management unit
TAL	target action level (EPA)
TSS	total suspended solids
UTL	upper tolerance limit

# Acronyms and Abbreviations

# 1.0 INTRODUCTION

Frequently, storm water samples collected from site monitoring areas (SMAs) at Los Alamos National Laboratory (LANL or the Laboratory) include concentrations of constituents (i.e., aluminum, copper, total polychlorinated biphenyls [PCBs] and zinc) that exceed National Pollutant Discharge Elimination System Permit No. NM0030759 (hereafter, the Individual Permit, Permit, or IP) target action levels (TALs). The same constituents frequently exceed TALs at background locations for undeveloped areas (i.e., landscapes with exposed sediments that originate from the natural geological setting) and developed areas (i.e., landscapes that are human-made from asphalt, concrete, roofing materials, etc.). The objective of this paper is to compare concentrations of these constituents measured in SMA storm water samples with concentrations found in storm water runoff from undeveloped and developed background locations.

This paper was prepared in response to a request made by the U.S. Environmental Protection Agency (EPA) during a November 2016 meeting with staff from the Laboratory's Associate Directorate of Environmental Management (ADEM). During that meeting, EPA Region 6 storm water permit staff expressed an interest in determining how background data compare directly with IP data.

The Laboratory is a multidisciplinary research facility owned by the U.S. Department of Energy (DOE) and managed by Los Alamos National Security, LLC. The Laboratory is located in north-central New Mexico approximately 60 mi northeast of Albuquerque and 20 mi northwest of Santa Fe. The Laboratory site covers approximately 39 mi<sup>2</sup>, mostly on the Pajarito Plateau, which consists of a series of mesas separated by eastward-draining canyons. The Laboratory site also includes part of White Rock Canyon along the Rio Grande to the east.

# 2.0 METHODS

#### 2.1 Data Set Preparation

Results from storm water samples collected by the Laboratory and the New Mexico Environment Department (NMED) were used as the basis for the data set evaluated in this document. The data set was developed by first screening the data to limit data relevant to this study. The data-screening steps include the following:

- Retain results for dissolved aluminum, dissolved copper, dissolved zinc, gross-alpha radioactivity, total PCBs, and suspended sediment concentration (SSC)
- Retain results for storm water (Environmental Information Management [EIM] database sample type: WT), excluding snow melt, surface water base flow, and all other sample types
- Remove quality control samples (e.g., blanks, rinsates) and waste control determination data
- Remove duplicate samples
- Remove rejected data

This data set contained 1799 sample results. The period of record for these data extends from 2000 to the 2016. All sample results in this data set are managed within the EIM database and can be publicly accessed using <u>www.intellusnm.com</u>. The data set results are also provided in Appendix A.

### 2.1.1 Data Groups

The sampling locations in this data set were divided into three groups for statistical comparisons: SMA, undeveloped background, and developed background. Sampling locations and the data group assignments are shown geographically in Figure 2.1-1. These data groups are defined as follows.

- <u>Undeveloped Background</u>—Sampling location drainage areas contain no structures, no solid waste management units (SWMUs), no areas of concern (AOCs), and few, if any, asphalt areas or dirt roads. For this paper, undeveloped background sampling locations from drainage areas north of the Laboratory were sampled and reported on in 2012 and 2013 background data reports (LANL 2012; LANL 2013). Results from the northern background drainage areas were used to calculate the upper threshold limit 95-95 percentiles the Laboratory uses to compare TAL exceedances when determining corrective action for the IP.
- <u>Developed Background</u>—Sampling location drainage areas contain developed areas, such as structures, roads, parking lots, but do not contain SWMUs or AOCs. The locations used in this evaluation include developed areas sampled and reported in background data reports (LANL 2012; LANL 2013) but also include additional locations that meet the criteria described above.
- <u>SMA</u>—This data group includes all analytical data collected from SMA locations that meet Individual Permit requirements for confirmation monitoring. SMA drainage areas contain a mix of storm water runoff from undeveloped and developed landscapes and from SWMUs or AOCs.

Developed landscapes were identified using geographic information system (GIS) aerial photography and Laboratory and Los Alamos County data sets for roads and structures. The presence or absence of SWMUs and/or AOCs was identified based on the Laboratory GIS shapefile containing this information as polygons.

For this evaluation, the SMA data group is compared independently with the undeveloped and developed background data groups, and the discussion includes the results of both comparisons. The undeveloped and developed background data groups are not compared with one another.

#### 2.2 Statistical Methods

#### 2.2.1 Box Plots

SMA to background comparisons in this study are compared using graphical displays called box plots, which show the actual values for each analyte on the y-axis. Box plots are effective for visual comparisons between data sets. Statistical methods used to further compare the data sets are discussed below. The ends of each box represent the "interquartile" range of the data distribution, which is specified by the 25<sup>th</sup> percentile and 75<sup>th</sup> percentile of the data distribution. The horizontal line above and below each box represents the extent of the whiskers, and results outside of these whiskers are considered outliers. The horizontal line within each box is the median (the 50<sup>th</sup> percentile) of the data distribution, but if the number of samples is four or fewer, the horizontal line is not displayed. Thus, each box indicates concentration values for the central half of the data sets. If extreme values occur in the data, the box may be reduced to what appears to be a single line. For such situations, these data are plotted untransformed and on a logarithmic scale. The two scales plotted side-by-side aid in visualizing the distribution of the data. The X symbols represent individual nondetected sample results (plotted as the method detection limit).

### 2.2.2 Gehan, Quantile, and Slippage Test Methods

Three statistical tests (Gehan, quantile, and slippage) were used to compare the SMA results with background. Each test compares different parts of the data set distributions. The Gehan test primarily compares differences in the central tendencies of the data sets (i.e., the position of the boxes and 50<sup>th</sup> percentile line). The quantile test evaluates differences in the upper quartile of the data (i.e., values greater than the boxes). The slippage test looks for differences in the highest values of the SMA data compared with background.

**Gehan Test**—The Gehan test is recommended when between 10% and 50% of the data sets are nondetections. It handles data sets with nondetections reported at multiple method detection limits in a statistically robust manner (Gehan 1965; Millard and Deverel 1988). The Gehan test is not recommended if either of the two data sets has more than 50% nondetections. If there are no nondetected concentrations in the data, the Gehan test is equivalent to the Wilcoxon Rank Sum test. The Gehan test is the preferred test because of its applicability to a majority of environmental data sets and it is recognized and recommended in EPA-sponsored workshops and publications.

**Quantile Test**—The quantile test is better suited to assessing shifts in a subset of the data. The quantile test determines whether more of the observations in the top chosen quantile of the combined data set come from the SMA data set than would be expected by chance, given the relative sizes of the SMA and background data sets.

If the relative proportion of the two populations being tested is different in the top chosen quantile of the data from that of the remainder of the data, the distributions may be partially shifted because it is a subset of SMA data. The quantile test is capable of detecting a statistical difference when only a small number of concentrations are elevated (Gilbert and Simpson 1992). The quantile test is the most useful distribution shift test where contaminated samples represent a small fraction of the overall data collected.

The quantile test is applied at a prespecified quantile or threshold, usually the 80<sup>th</sup> percentile. The test cannot be performed if more than 80% (or, in general, more than the chosen percentile) of the combined data set are nondetected values. It can be used when the frequency of nondetections is approximately the same as the quantile being tested. For example, in a case where 75% nondetections exist in the combined SMA and background data set, application of a quantile test comparing 80<sup>th</sup> percentiles is appropriate.

However, the quantile test cannot be performed if nondetections occur in the top chosen quantile. The threshold percentage can be adjusted to accommodate the detection rate of an analyte or to look for differences further into the distribution tails. The quantile test is more powerful than the Gehan test for detecting differences when only a small percentage of the concentrations is elevated.

**Slippage Test**—The slippage test was performed to determine if differences between two distributions appear to occur far into the tails. This test evaluates the potential for some of the SMA data to be greater than the maximum concentration in the background data set, assuming the SMA and background data came from the same distribution. This test is based on the maximum concentration in the background data set and the number of SMA concentrations, *n*, that exceed the maximum concentration in the background data (Gilbert and Simpson 1990, pp. 5–8). The result (p-value) of the slippage test is the probability that *n* or more SMA samples exceed the maximum background concentration by chance alone. The test accounts for the number of samples in each data set (number of SMA samples and number of background samples) and determines the probability of *n* or more exceedances if the two data sets came from identical distributions. This test is similar to the upper tolerance limit (UTL) comparison in that it evaluates the largest SMA measurements but is more useful than the UTL comparison because it is based on a statistical hypothesis test, not simply on a statistic calculated from the background distribution.

For all statistical tests, a p-value less than 0.05 (confidence level of 95%) will be the criterion for accepting the null hypothesis that SMA sampling results are different from background. If the results of two statistical tests indicate that SMA sampling results are not different from background, the constituent in question is assumed to not be related to releases from the SMAs.

#### 2.2.3 Relationships with SSC

Box plots and the statistical evaluations performed in this study are one method for comparing populations but do not address potential dependencies that storm water results may have. Previous evaluations of storm water data in the LANL vicinity have shown several unfiltered analytes to be dependent upon SSC (LANL 2007; LANL 2014; LANL 2016).

This paper will evaluate the correlation of SSC (as determined by American Standard of Testing and Measurement Method 3977-97) with gross alpha and with total PCBs. Dissolved metals are filtered with a 0.45-µm filter and previous evaluations have confirmed that no correlation with SSC exists (LANL 2016).

#### 3.0 RESULTS

#### 3.1 Box Plots and Statistical Tests

Figures 3.1-1 through 3.1-5 present box plot comparisons in original scale (left panel) and log scale (right panel). The box plots are ordered left to right with undeveloped background first, developed background second, and SMA farthest right. Each figure is plotted with lines showing the UTL for undeveloped and developed background landscapes and the applicable IP TAL for each parameter. In 2012 and 2013, background thresholds were calculated and reported for various constituents in storm water to support IP corrective action assessments (LANL 2012; LANL 2013). These background thresholds were generally calculated as UTLs based on the 95% upper confidence limit of the 95<sup>th</sup> percentile. (i.e., there is a 95% chance that a sample result less than this threshold is part of the background population). The UTL lines shown in the figures represent this value. In 2015, the Laboratory submitted to NMED a report entitled "Methods and Applicability for Determining Site-Specific Natural Background for Storm Water under the Clean Water Act" (LANL 2015). This report discusses the concept of using the UTL for establishing background concentrations for various environmental media, including storm water, under the Clean Water Act.

Table 3.1-1 summarizes background comparison test conclusions and also shows the number of results in each population. Note that the undeveloped background data set is substantially smaller than either the developed background or SMA data set. Recall that when the p-value is less than 0.05, the statistical test failed and the SMA data set is considered statistically greater than the background data set with which it is being compared. The following conclusions are based on the number of statistical tests that failed:

- 0 of 3 tests failed—SMA is not greater than background
- 1 of 3 tests failed—SMA is *not greater* than background (the failed test is further discussed)
- 2 of 3 tests failed—SMA is greater than background
- 3 of 3 tests failed—SMA is *greater* than background

The box plots were assessed visually in conjunction with the statistical tests, and the results are summarized below.

**Aluminum.** The position of the boxes in Figure 3.1-1 and the results of the statistical tests in Table 3.1-1 document the following results for aluminum:

- SMA to undeveloped background comparison—Fails 0 of 3 tests; SMA *not greater* than undeveloped background.
- SMA to developed background comparison—Fails 1 of 3 tests; SMA *not greater* than developed background.

The single test that the SMA to developed background comparison failed was the Gehan test with a p-value <0.001. The box plots in Figure 3.1-1 illustrate this test result, as the SMA box plot is shifted higher than the developed background box plot. The box plots show that the range of SMA results is generally within the range of the background data sets.

**Copper**. The position of the boxes in Figure 3.1-2 and the results of the statistical tests in Table 1 document the following results for copper:

- SMA to undeveloped background comparison—Fails 3 of 3 tests; SMA is greater than undeveloped background.
- SMA to developed background comparison—Fails 1 of 3 tests; SMA is *not greater* than developed background.

For the undeveloped background comparison, only the lower quartile of the SMA results are similar to the undeveloped background data set, as shown in Figure 3.1-2. For the developed background comparison, only the slippage test indicates that SMA results are greater than the developed background data set. The slippage test result could suggest some SMAs have sources of copper that are greater than the highest developed background concentrations.

**Zinc**. The position of the boxes in Figure 3.1-3 and the results of the statistical tests in Table 1 document the following results for zinc:

- SMA to undeveloped background comparison—Fails 1 of 3 tests; SMA is *not greater* than undeveloped background.
- SMA to developed background comparison—Fails 1 of 3 tests; SMA is *not greater* than developed background.

For the undeveloped background comparison, only the Gehan test indicates that SMA results are greater than background. The box plots in Figure 3.1-3 show that undeveloped background has lower concentrations of zinc than developed background. This may be because the undeveloped background data have substantially fewer samples than either developed background or SMA populations. Note that the developed UTL is not displayed on Figure 3.1-3 because this value (1120  $\mu$ g/L) is substantially larger than any of the other data plotted in Figure 3.1-3. For the developed background comparison, only the slippage test indicates that SMA concentrations are greater than background. The slippage test result could suggest some SMAs have sources of zinc that are greater than the highest developed background concentrations.

**Gross alpha**. The position of the boxes in Figure 3.1-4 and the results of the statistical tests in Table 1 document the following results for gross alpha:

- SMA to undeveloped background comparison—Fails 0 of 3 tests; SMA is *not greater* than undeveloped background.
- SMA to developed background comparison—Fails 1 of 3 tests; SMA is *not greater* than developed background.

The single test that the SMA to developed background comparison did not pass was the Gehan test with a p-value <0.001. The box plots in Figure 3.1-4 illustrate this test result because the SMA box plot is shifted higher than the developed background box plot. The box plots show that the range of SMA results is generally within the range of the background data sets.

**Total PCBs**. The position of the boxes in Figure 3.1-5 and the results of the statistical tests in Table 1 document the following results for total PCBs:

- SMA to undeveloped background comparison—Fails 3 of 3 tests; SMA is greater than undeveloped background.
- SMA to developed background comparison—Fails 2 of 3 tests; SMA is greater than developed background.

For the developed background comparison, the Gehan test indicates that SMA concentrations are greater than developed background. The box plots in Figure 3.1-5 illustrate this test result because the SMA box plot is shifted higher than the developed background box plot. The slippage test also indicates that SMA concentrations are greater than developed background. These test results could suggest some SMAs have sources of total PCBs that are greater than the highest developed background concentrations.

#### 3.2 Relationships with SSC

**Gross Alpha**. This paper presents some additional information on the highly significant relationship of gross alpha to SSC. Figure 3.2-1 shows the relationship between gross alpha and SSC, where gross-alpha results increase with increasing SSC. This relationship indicates gross-alpha activity levels are highly correlated with SSC. In this paper, gross-alpha results were not normalized to SSC before statistical tests were performed because the undeveloped background data have substantially fewer samples than either the developed background or SMA populations, and the undeveloped background data set has significantly higher SSC values<sup>1</sup>. A best-fit line was calculated for each data set with the following Pearson correlation coefficients (r<sup>2</sup>),

SMA data set

$$Log(GA) = -2.55 + 0.786 * Log(SSC), n = 47, r^2 = 0.778, p < 0.0001$$

• Undeveloped data set

$$Log(GA) = -3.33 + 0.951 * Log(SSC), n = 9, r^2 = 0.391, p = 0.07$$

• Developed data set

$$Log(GA) = -3.00 + 0.837 * Log(SSC), n = 10, r^2 = 0.938, p < 0.0001$$

These results indicate that a well-fit linear correlation exists for the SMA and developed dataset. The relationship is not well correlated for the undeveloped data set, perhaps because of the small number of samples in this data set and results with predominantly higher SSC.

<sup>&</sup>lt;sup>1</sup> Samples from undeveloped background sampling locations for this paper were collected in dry arroyos north of the Laboratory. These drainage areas typically have higher sediment yields per unit of storm water discharge, which is reflected in the higher SSC results shown in Figure 3.2-1.

**Total PCBs.** Figure 3.2-2 displays SSC versus total PCBs for all three data sets. The plot shows no visible correlation of total PCBs with SSC for any data set.

#### 4.0 CONCLUSIONS

This paper uses statistical tests and plots to compare concentrations of aluminum, copper, zinc, gross alpha, and total PCBs (constituents that frequently exceed IP TALs) measured in SMA samples with concentrations found in storm water runoff from undeveloped and developed background areas. These comparisons document the statistical similarity and differences of concentrations in the three data sets and the following conclusions for each constituent.

- **Aluminum**—The dissolved aluminum SMA data set is not greater than either background data set (undeveloped and developed), indicating that SMAs are not a source of aluminum.
- **Copper**—The dissolved copper SMA data set is greater than the undeveloped background data set but not greater the than developed background data set; visual evaluation of the box plots shows that some SMAs have higher concentrations than developed background, indicating that developed areas and some SMAs may be a source of copper.
- **Zinc**—The dissolved zinc SMA data set is not greater than either undeveloped or developed background data set; visual evaluation of the box plots shows some SMAs have higher concentrations than either background data set, indicating that undeveloped background, developed background, and some SMAs may be a source of zinc.
- **Gross Alpha**—The gross alpha SMA data set is not greater than either the undeveloped or developed background data set, but gross alpha is highly correlated to SSC; gross alpha should be normalized to SSC to determine if concentrations are SMA-related or not.
- **Total PCBs**—The total PCB SMA data set is greater than both background data sets, indicating the some SMAs may be a source of total PCBs.

These population comparisons document the similarity and differences of SMA concentrations to undeveloped and developed background levels of these constituents. When evaluated as a data set, several constituents such as aluminum, zinc, and gross alpha at SMAs are not greater than background. The dissolved copper and total PCBs SMA data sets are greater than the undeveloped background data set; total PCBs are also greater than the developed background data set. However, concentrations of copper and total PCBs in the undeveloped and developed background data sets frequently exceed the IP TAL. These results indicate the importance of developing an EPA-accepted method of accounting for undeveloped and developed landscape sources of these constituents for the IP.

#### 5.0 REFERENCES

Gehan 1965. Gehan, E.A., "A Generalized Wilcoxon Test for Comparing Arbitrarily Singly-Censored Samples," *Biometrika* 52(1–2), pp. 203–223 (June 1965).

Gilbert, R.O., and J.C. Simpson, 1990. "Statistical Sampling and Analysis Issues and Needs for Testing Attainment of Background-Based Cleanup Standards at Superfund Sites," Proceedings of The Workshop on Superfund Hazardous Waste: Statistical Issues in Characterizing a Site: Protocols, Tools, and Research Needs, U.S. Environmental Protection Agency, Arlington, Virginia (November 1990).

Gilbert and Simpson 1992. Gilbert, R.O., and J.C. Simpson, "Statistical Methods for Evaluating the Attainment of Cleanup Standards, Volume 3: Reference-Based Standards for Soils and Solid Media," prepared for the U.S. Environmental Protection Agency by Pacific Northwest Laboratory, Richland, Washington (December 1992).

LANL 2007. "Preliminary Comments Regarding Use of Statistical Methods to Evaluate Background Surface Water Quality and Identify Laboratory Impacts," Los Alamos National Laboratory document LA-UR-07-8120, Los Alamos, New Mexico (November 2007).

LANL 2012. "Polychlorinated Biphenyls in Precipitation and Stormwater within the Upper Rio Grande Watershed," Los Alamos National Laboratory document LA-UR-12-1081, Los Alamos, New Mexico (May 2012).

LANL 2013. "Background Metals Concentrations and Radioactivity in Storm Water on the Pajarito Plateau, Northern New Mexico," Los Alamos National Laboratory document LA-UR-13-22841, Los Alamos, New Mexico (April 2013).

LANL 2014. "Storm Water Performance Monitoring in the Los Alamos/Pueblo Watershed during 2013. Los Alamos National Laboratory document LA-UR-14-24516, Los Alamos, New Mexico (LANL 2014, 257592).

LANL 2015. Methods and Applicability for Determining Site-Specific Natural Background for Storm Water under the Clean Water Act. Los Alamos National Laboratory document LA-UR-15-29535, Los Alamos, New Mexico (December 2015).

LANL 2016. "2015 Monitoring Report for Los Alamos/Pueblo Watershed Sediment Transport Mitigation Project. Los Alamos National Laboratory document LA-UR-16-22705, Los Alamos, New Mexico (April 2016).

Millard and Deverel 1988. Millard, W.P., and S.J. Deverel, December 1988. "Nonparametric Statistical Methods for Comparing Two Sites Based on Data with Multiple Nondetect Limits," *Water Resources Research*, 24(12), pp. 2087–2098 (December 1988).



Figure 2.1-1 Data set sampling locations and data group assignments



Figure 3.1-1 Concentrations of dissolved aluminum at SMA versus background. Left panel: raw data; right panel: logarithmic transformed data.



Figure 3.1-2 Concentrations of dissolved copper at SMA versus background. Left panel: raw data; right panel: logarithmic transformed data.



Figure 3.1-3 Concentrations of dissolved zinc at SMA versus background. Left panel: raw data; right panel: logarithmic transformed data.



Figure 3.1-4 Gross-alpha activities at SMA versus background. Left panel: raw data; right panel: logarithmic transformed data.



Figure 3.1-5 Concentrations of total PCBs at SMA versus background. Left panel: raw data; right panel: logarithmic transformed data.



Figure 3.2-1 Log-log scatter plot showing the relationship between gross-alpha and SSC



Figure 3.2-2 Log-log scatter plot showing the relationship between total PCBs and SSC

Parameter	SMA Comparison	Number of SMA Samples	Number of SMA Detections	Number ≥UTL	Number of Background Samples	Number of Background Detections	Gehan Test p-value	Quantile Test p-value	Slippage Test p-value
Dissolved	Undeveloped	240	239	8	23	23	0.779	0.508	0.631
Aluminum	Developed	240	239	137	116	111	<0.001	0.093	1
Dissolved	Undeveloped	258	256	166	23	17	<0.001	0.005	<0.001
Copper	Developed	258	256	14	142	139	0.830	0.943	0.002
Dissolved Zinc	Undeveloped	237	181	13	23	15	<0.001	0.122	0.627
	Developed	237	181	0	140	127	1	0.979	0.038
Gross Alpha	Undeveloped	254	236	3	14	14	1	1	0.806
	Developed	254	236	118	76	62	<0.001	0.068	0.455
Total PCB	Undeveloped	93	87	55	19	19	<0.001	0.010	<0.001
	Developed	93	87	17	29	29	0.002	0.116	0.043

 Table 3.1-1

 Summary of Statistical Comparisons of SMA Results to Undeveloped and Developed Background Data Sets

Note: Gray highlighting indicates p-values less than 0.05.

# Appendix A

Analytical Results of Site Monitoring Area, Developed, and Undeveloped Data Sets (on CD included with this document)