# Response to the Notice of Disapproval for the Bandelier Tuff Unit 4 Background Study Report, Los Alamos National Laboratory, EPA ID No. NM0890010515, HWB-LANL-11-069, Dated October 11, 2011

#### INTRODUCTION

To facilitate review of this response, the New Mexico Environment Department's (NMED's) comments are included verbatim. Los Alamos National Laboratory's (LANL's or the Laboratory's) responses follow each NMED comment.

#### NMED Comment

1. The metals data for the background study are representative of leachable element concentrations, and the analytical methods used in the current study appear consistent with the methods used in the original background study report. The results for the metals, provided in Table 4.1-1, and the discussion of these data presented in Section 4.1.1 of the report, indicate that the Qbt 4 data are essentially the same as the previously established background. It is not clear how this determination was made. It appears that a statistical evaluation of the data was not conducted and, since the Qbt 4 data were not significantly above the established background levels, it was assumed that the Qbt 4 was representative of the existing background data. However, in reviewing at the data in both Tables 4.1-1 (metals) and 4.1-5 (radionuclides), the Qbt4 data appear to actually be lower than the established background levels (with the exception of the data in Tables 4.1-2 and 4.1-6). Clarify how it was determined that the new Qbt 4 data are actually reflective of the established background data. For example, did the Permittees make this determination after conducting statistical comparisons between the data sets.

## LANL Response

As described in the background study work plan for unit 4 of the Bandelier Tuff (Qbt 4) (LANL 2010, 111504), the results from the investigation of sites at Technical Area 49 (TA-49) inside the Nuclear Environmental Site (NES) indicated that concentrations of a number of inorganic chemicals in Qbt 4 samples that were higher than the composite background values (BVs) for units 2, 3, and 4 of the Bandelier Tuff (Qbt 2, 3, 4) were naturally occurring. Data from Qbt 4 samples were collected as part of this background study for comparison with the Qbt 2, 3, 4 background data set to determine whether background concentrations of inorganic chemicals in Qbt 4 were higher than Qbt 2, 3, 4 BVs. As shown in Table 4.1-1 of the work plan and as noted in NMED's comment, most inorganic chemical results for Qbt 4 samples were below Qbt 2, 3, 4 BVs.

Box plots of the new Qbt 4 data and the existing Qbt 2, 3, 4 data were reviewed during preparation of the background study report to aid in interpretation of the data but were not included in the report. These box plots and results of statistical analyses for the 11 inorganic chemicals specifically identified in the TA-49 investigation report as possibly having background concentrations above Qbt 2, 3, 4 BVs (aluminum, arsenic, barium, calcium, cobalt, copper, lead, manganese, nickel, selenium, and vanadium) are presented in Attachment 1 to this response. The statistical analyses were performed to determine whether there were statistical differences between the Qbt 4 background study data and the existing Qbt 2, 3, 4 data. Arsenic, barium, cobalt, manganese, and nickel showed no statistical differences compared with the existing Qbt 2, 3, 4 data set. Concentrations for the new Qbt 4 samples were less than the existing Qbt 2, 3, 4 data for aluminum and lead and concentrations for the new

Qbt 4 samples were greater than the existing Qbt 2, 3, 4 data for calcium, copper, selenium, and vanadium. Even for those inorganic chemicals with statistical differences, the overall range of the new Qbt 4 background samples overlaps with the existing Qbt 2, 3, 4 data. Thus, the existing Qbt 2, 3, 4 background data appear to be representative of background concentrations in Qbt 4.

# **NMED** Comment

2. In Section 5.0, there is mention of previously collected data that was analyzed using X-ray fluorescence (XRF) and that these data indicated higher concentrations than the established background. As part of the Qbt 4 study, samples at the bottom of the borings were collected and analyzed using XRF. The Work Plan for Determining Background Concentrations of Inorganic Chemicals in Unit 4 of the Bandelier Tuff (Work Plan, p 5) stated that "[s]amples will also be submitted for analysis using X-ray fluorescence (XRF) to collect data to compare with historical XRF total metal analysis data to Qbt 4." It is not clear whether a comparison was conducted between the two XRF datasets. The Permittees must discuss how the Qbt 4 XRF data compared to the past data referred to in this Section.

# LANL Response

2. As described in the work plan for the Qbt 4 background study, x-ray fluorescence (XRF) analysis was proposed to confirm the samples collected during the background study were from Qbt 4 (LANL 2010, 111504, p. 5). Although the major-element chemistry of subunits making up the Tshirege Member of the Bandelier Tuff is relatively uniform, minor ,and trace element abundances vary systematically as a function of stratigraphic position. In general, XRF whole-rock concentrations of minor and trace elements such as barium (Ba), strontium (Sr), titanium (TiO<sub>2</sub>), zinc (Zn), and zirconium (Zr) tend to increase upsection (i.e., in higher stratigraph units), whereas incompatible elements such as niobium (Nb) and rubidium (Rb) tend to increase downsection (i.e., in lower units) (Broxton et al. 1996, 054948). The most pronounced chemical changes occur across the Qbt 3/Qbt 4 contact, making the identification of Qbt 4 based on XRF analyses relatively straightforward.

Twenty-nine of the 30 XRF samples collected for the 2011 Qbt 4 background study have chemical compositions equivalent to those for historical Qbt 4 samples collected throughout the Pajarito Plateau. The XRF data for 2011 Qbt 4 background samples was used to identify one chemical outlier in the Qbt 4 background data set (sample RE67-11-9819 in borehole 67-614317); this sample was subsequently reclassified as unit Qbt 3 based on its chemistry (LANL 2011, 206327, pp. 5–6). Attachment 2 to this response presents box plots of XRF analyses for selected minor and trace elements and shows that compositions of the 2011 Qbt 4 background samples are comparable with plateau-wide Qbt 4 samples. Attachment 2 also shows that Qbt 4 samples are readily distinguishable from plateau-wide Qbt 1 through Qbt 3 samples, which occur lower in the stratigraphic section. These data indicate the 2011 Qbt 4 background study samples are representative of Qbt 4 throughout the Pajarito Plateau.

# NMED Comment

3. It is not clear how the conclusion was made that the results from XRF confirm that the Qbt 4 data are representative of the existing background data. Explain what the data were compared to in deriving this conclusion.

# LANL Response

3. Attachment 3 to this response presents box plots that compare XRF analyses for the 2011 Qbt 4 background study samples with those for Qbt 4 samples used in the Laboratory's background report (LANL 1998, 059730). Qbt 4 XRF analyses for both data sets are chemically equivalent, supporting the interpretation that 2011 Qbt 4 background study samples are representative of Qbt 4 samples used to obtain the existing background data.

## **NMED** Comment

- 4. The report indicates that in accordance with the Work Plan, selected samples would be collected from only un-weathered tuff.
  - a. In reviewing the Work Plan, there is no mention that samples will be biased to assessing only un-weathered tuff nor does the Work Plan specify any targeted sampling of tuff in various stages of weathering or how the degree of weathering was determined. Explain why only un-weathered material was sampled.
  - b. If weathered tuff was encountered frequently at Technical Area (TA) 49 and the sample results obtained from these locations are possibly elevated due to the weathering and breakdown of the tuff, explain why the Qbt 4 sampling effort did not include collecting samples representative of all stages of weathering of the tuff or at least include the collection of samples reflective of the various conditions at TA-49.
  - c. As noted in the conclusion, the background data set should bound concentrations reflective of weathered tuff. Since the Qbt 4 data are not different from the existing background data, explain how will this bounding be determined.

# LANL Response

- 4. a. The samples used to develop BVs for tuff were collected from unweathered tuff (LANL 1998, 059730, p. 30). Therefore, to allow meaningful comparison with the existing background data set, tuff samples for the Qbt 4 background study were also collected from unweathered tuff.
- 4. b. The investigation report for sites at TA-49 inside the NES concluded that the BVs for Qbt 2, 3, 4 were not suitable for comparison with the results from the Qbt 4 samples collected during the TA-49 investigation (LANL 2010, 110656.17, p. 15). This conclusion was based in large part on the results of the bivariate analyses (i.e., scatter plots) presented in the TA-49 investigation report (LANL 2010, 110656) that concluded most of the detections of inorganic chemicals in Qbt 4 samples that exceeded BVs for Qbt 2, 3, 4 appeared to be naturally occurring. The TA-49 investigation report also referred to the results of bulk rock (i.e., XRF) analysis of tuff samples that showed marked differences in the geochemistry of Qbt 4 compared with Qbt 2 and Qbt 3 (Stimac et al. 2002, 073391). Thus, the Qbt 4 background study sampling was directed toward collecting Qbt 4 data for comparison with existing Qbt 2, 3, and 4 background data. Because the existing Qbt 2, 3, 4 data set consists of results exclusively from samples of unweathered tuff, samples of unweathered Qbt 4 were collected for comparison. As explained below, the effects of weathering on the sample results from TA-49 will be addressed in the Phase II investigation for sites at TA-49 inside the NES.

Based on the results of the Qbt 4 background study, it appears the effects of weathering are more likely the reason for the results observed for the TA-49 inside NES sampling. The approved

Phase II investigation work plan for TA-49 sites inside the NES (LANL 2011, 201570; NMED 2011, 204345) proposes additional investigations to evaluate the effects of weathering. Specifically, undisturbed core samples will be collected from 0 to 3 ft below ground surface at 10 locations where inorganic chemicals were detected in shallow Qbt 4 samples above the Qbt 2, 3, 4 BVs, but bivariate analyses indicated the results to be naturally occurring. The core will be examined to determine the degree of weathering of the depth interval sampled during the previous TA-49 investigation. If the material is weathered, this condition would support the conclusions drawn from the bivariate analysis that the elevated concentrations are naturally occurring.

4. c. The conclusions of the Qbt 4 background study (LANL 2011, 206327, p. 7) state:

Development of BVs for weathered tuff would be difficult because of the variability of weathering effects and degree of weathering. The concentrations of inorganic chemicals and radionuclides in weathered tuff should, however, be bounded by soil BVs since soil represents a very high degree of weathering.

Therefore, BVs for weathered tuff should be bounded on the low end by tuff BVs, which represent no weathering, and on the high end by soil BVs, which represent a high degree of weathering and other natural variables such as deposition of wind-borne material with a range of compositions and other soil-forming processes. The use of soil BVs as a bounding condition for weathered tuff is consistent with the results of the scatter-plot analysis presented in the TA-49 inside NES investigation report (LANL 2010, 110656, pp. I-2–I-4). That is, the results not identified as outliers in the scatter-plot analysis (i.e., results identified as naturally occurring concentrations) are all below the soil BVs.

## **NMED** Comment

5. Given that the results of the Qbt 4 study are inconclusive for evaluating the elevated levels of inorganic constituents at TA-49, the Permittees must either propose additional evaluation, such as geochemical analyses, or use the previously established background levels for Qbt 4.

## LANL Response

5. The results of the Qbt 4 background study, along with the results of the previous TA-49 investigation and the additional proposed investigations at TA-49 noted in the response for Comment 4.b, should be conclusive for evaluating elevated levels of inorganic constituents at TA-49. As discussed in the response for Comment 4.b, the approved Phase II investigation work plan for TA-49 sites inside the NES specifies additional investigations to evaluate the effects of weathering. The samples collected during the previous investigation at TA-49 where concentrations of inorganic chemicals were detected above Qbt 2, 3, 4 BVs were generally collected using a hand auger. Because of sample disturbance with the hand auger, it was not possible to determine the degree of weathering of these samples. During the Phase II investigation, a representative subset of these locations will be resampled using a hollow-stem auger, and undisturbed core samples will be collected to better evaluate the nature and degree of weathering of the material previously sampled.

#### REFERENCES

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- Stimac, J.A., D.E. Broxton, E.C. Kluk, S.J. Chipera, and J.R. Budahn, July 2002. "Stratigraphy of the Tuffs from Borehole 49-2-700-1 at Technical Area 49, Los Alamos National Laboratory, New Mexico," Los Alamos National Laboratory report LA-13969, Los Alamos, New Mexico. (Stimac et al. 2002, 073391)

Attachment 1

Statistical Tests and Box Plots for Eleven Inorganic Chemicals Identified at TA-49

Statistical tests and box plots for the 11 inorganic chemicals identified in the Technical Area 49 (TA-49) inside Nuclear Environmental Site (NES) investigation report as possibly having background concentrations above Qbt 2, 3, 4 background values (BVs) are presented below. Statistical tests were used to compare the new Qbt 4 data set with the existing Qbt 2, 3, 4 background data set. The Wilcoxon rank sum test was used to determine if the concentrations reported for the new Qbt 4 background samples differ from the pooled Qbt 2, 3, 4 background data. The Wilcoxon rank sum test is a nonparametric test that evaluates the ranks of these two data sets. Box plots were used to compare the distributions of data and to identify individual results from the new Qbt 4 that exceed existing Qbt 2, 3, 4 BVs. Figures 1 to 11 display these data. The box plots in these figures indicate the interquartile range of the sample results, with the upper and lower ends defined by the 75th and 25th percentiles, respectively. Horizontal lines within the boxes indicate median values, and horizontal lines above and below the boxes represent the 5th and 95th percentiles of the data.

*Aluminum*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are less than the existing Qbt 2, 3, 4 background data (n=63). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 1).

*Arsenic*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and 24 sample results are detects) are not different from the existing Qbt 2, 3, 4 background data (n=64). Three of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 2).

*Barium.* Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are not different from the existing Qbt 2, 3, 4 background data (n=63). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 3).

*Calcium*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are greater than the existing Qbt 2, 3, 4 background data (n=64). One of the new Qbt 4 sample results is greater than the Qbt 2, 3, 4 BV (Figure 4).

*Cobalt*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are not different from the existing Qbt 2, 3, 4 background data (n=11). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 5).

*Copper*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are greater than the existing Qbt 2, 3, 4 background data (n=64). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 6).

*Lead.* Based on the Wilcoxon rank sum test the new Qbt 4 samples (n=29 and all results are detects) are less than the existing Qbt 2, 3, 4 background data (n=63). Three of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 7).

*Manganese*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are not different from the existing Qbt 2, 3, 4 background data (n=64). One of the new Qbt 4 sample results is greater than the Qbt 2, 3, 4 BV (Figure 8).

*Nickel.* Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are not different from the existing Qbt 2, 3, 4 background data (n=63). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 9).

*Selenium*. Based on the Wilcoxon rank sum test the new Qbt 4 samples (n=29 and all results are nondetects) are greater than the existing Qbt 2, 3, 4 background data (n=15). All the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 10).

*Vanadium*. Based on the Wilcoxon rank sum test, the new Qbt 4 samples (n=29 and all results are detects) are greater than the existing Qbt 2, 3, 4 background data (n=64). None of the new Qbt 4 sample results are greater than the Qbt 2, 3, 4 BV (Figure 11).



Figure 1 Box plots comparing aluminum concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are less than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.01). Dashed line is the Qbt 2, 3, 4 BV equal to 7340 mg/kg.



Figure 2 Box plots comparing arsenic concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are not different from the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p=0.48). Dashed line is the Qbt 2, 3, 4 BV equal to 2.79 mg/kg.



Figure 3 Box plots comparing barium concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are not different from existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p=0.68). Dashed line is the Qbt 2, 3, 4 BV equal to 46 mg/kg.



Figure 4 Box plots comparing calcium concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are greater than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.05). Dashed line is the Qbt 2, 3, 4 BV equal to 2200 mg/kg.



Figure 5 Box plots comparing cobalt concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are not different from existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p=0.60). Dashed line is the Qbt 2, 3, 4 BV equal to 3.14 mg/kg.



Figure 6 Box plots comparing copper concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are greater than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.01). Dashed line is the Qbt 2, 3, 4 BV equal to 4.66 mg/kg.



Figure 7 Box plots comparing lead concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are less than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.01). Dashed line is the Qbt 2, 3, 4 BV equal to 11.2 mg/kg.



Figure 8 Box plots comparing manganese concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are not different from existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p=0.11). Dashed line is the Qbt 2, 3, 4 BV equal to 482 mg/kg.



Figure 9 Box plots comparing nickel concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are not different from existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p=0.06). Dashed line is the Qbt 2, 3, 4 BV equal to 6.58 mg/kg.



Figure 10 Box plots comparing selenium concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are greater than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.0001). Dashed line is the Qbt 2, 3, 4 BV equal to 0.3 mg/kg.



Figure 11 Box plots comparing vanadium concentrations for new Qbt 4 background samples with existing pooled Qbt 2, 3, 4 background samples. New Qbt 4 results are greater than the existing pooled Qbt 2, 3, 4 data (Wilcoxon rank sum test, p<0.01). Dashed line is the Qbt 2, 3, 4 BV equal to 17 mg/kg. Attachment 2

Box Plots of XRF Analyses for Selected Minor and Trace Elements at TA-49



2-1

Attachment 3

Box Plots Comparing XRF Analyses for 2011 Qbt 4 TA-49 Background Investigation Samples to 1998 LANL Qbt 4 Background Report Samples



