Environmental Restoration
University of California
Environmental Restoration Project, MS M992
Los Alamos, New Mexico 87545
505-667-0808/FAX 505-665-4747

U. S. Department of Energy
Los Alamos Area Office, MS A316
Environmental Restoration Program
Los Alamos, New Mexico 87544
505-667-7203/FAX 505-665-4504

Date: November 18, 1997
Refer to: EM/ER:97-490

ENTERED

NOV 1997

Dr. Robert Dinwiddie
NMED-HRMB
P.O. Box 26110
Santa Fe, NM 87502

SUBJECT: RESPONSE TO REQUEST FOR SUPPLEMENTAL INFORMATION ON DOCUMENT "*NATURAL BACKGROUND GEOCHEMISTRY AND STATISTICAL ANALYSIS OF SELECTED SOIL PROFILES, SEDIMENTS, AND BANDELIER TUFF*"

Dear Dr. Dinwiddie:

Attached is the Los Alamos National Laboratory Environmental Restoration Project response to your request for supplemental information on our document *"Natural Background Geochemistry and Statistical Analysis of Selected Soil Profiles, Sediments, and Bandelier Tuff."* Your request for supplemental information, dated July 29, 1997, requested a response within 30 days. However, personnel from your office and our staff have been in communication regarding this response and agreed to a meeting prior to submitting the response. The meeting was held on October 15 and 16, 1997, and agreements were made on each comment response. The attached response reflects those agreements. In addition, it was agreed that a revised document will be submitted to your office no later than December 19, 1997. We appreciate the time commitment by your staff to review, comment, and meet with us regarding this document.

If you have any questions, please call Tracy Glatzmaier at (505) 665-2613 or Joe Mose at (505) 667-5808.

Sincerely,

Julie A. Canepa, Program Manager
LANL/ER Project

Sincerely,

for Theodore J. Taylor, Program Manager
DOE/LAAO

JJ/TT/rfr

Enclosure: Response to RSI on *"Natural Background Geochemistry and Statistical Analysis of Selected Soil Profiles, Sediments, and Bandelier Tuff"* Document

9751

Cy (w/ enc.):
T. Glatzmaier, DDEES/ER, MS M992
D. Griswold, AL-ERD, MS A906
J. Harry, EM/ER, MS M992
J. Mose, LAAO, MS A316
D. Neleigh, EPA, R.6, 6PD-N
J. Plum, LAAO, MS A316
C. Rodriguez, CIO/ER, MS M769
T. Taylor, LAAO, MS A316
J. White, ESH-19, MS K490
B. Garcia, NMED-HRMB
M. Leavitt, NMED-GWQB
G. Saums, NMED-SWQB
J. Parker, NMED-HRMB
S. Yanicak, NMED-AIP, MS J993
EM/ER File (CT #C339), MS M992
RPF, MS M707

Cy (w/o enc.):
T. Baca, EM, MS J591
J. Vozella, LAAO, MS A316
D. McInroy, EM/ER, MS M992
G. Rael, AL-ERD, MS A906
T. Longo, DOE-HQ, EM-453
EM/ER File, MS M992

INTRODUCTION

The document, "Natural Background Geochemistry and Statistical Analysis of Selected Soil Profiles, Sediments, and Bandelier Tuff, Los Alamos, New Mexico" (Longmire et al. 1995) as submitted, was a draft. This document will be revised based on these comments and other discussions between New Mexico Environment Department (NMED) and Los Alamos National Laboratory (LANL) Environmental Restoration (ER) Project personnel, as well as the collection and analysis of additional data, and resubmitted to the NMED by December 19, 1997. The document explains how the LANL background data for soils, tuff and sediment were collected and assembled into a data set for making background comparisons. This document does not describe LANL's procedures for making background comparisons.

LANL's approach for making background comparisons is presented in a policy document "Application of LANL Background Data to ER Project Decision-Making Part 1: Inorganics" (Ryti et al. 1996). NMED may find this policy document useful in putting the background data into the proper decision-making context. Of particular interest is the use of statistical distribution shifts test to detect differences of potential release site (PRS) data from background data. In addition, several other papers have been written to describe background data collected in support of site characterization for the ER Project. These papers are listed below and are readily available.

LANL appreciates NMED's interest in the background data set. In order to facilitate review of this response, the revised background document, and LANL's approach for making background comparison, NMED is encouraged to request field trips and one-on-one discussions with technical representatives of LANL's staff.

LANL's responses to NMED's comments are presented in Attachment A. To facilitate review of this response, NMED's comments are included verbatim.

BACKGROUND POLICY PAPERS

Environmental Restoration Project Decision Support Council and Earth Science Council. 1997. Application of LANL Background Data to ER Project Decision-Making Part II: Radionuclides in Soils, Sediments, and Tuff. Los Alamos National Laboratory, Environmental Restoration Records Processing Facility ID No. 56186, June 30, 1997

Ryti, R., P. Longmire, and E. McDonald, March 1996. "Application of LANL Background Data to ER Project Decision-Making Part I: Inorganics," Los Alamos National Laboratory Report LA-UR-96-1534, Los Alamos, New Mexico. (Ryti et al. 1996, 1298)

LANL BACKGROUND DATA REFERENCES

Broxton, D.E., R.T. Ryti, D. Carlson, R.G. Warren, E. Kluk, and S. Chipera. March 20, 1996. "Natural Background Geochemistry of the Bandelier Tuff at MDA P, Los Alamos National Laboratory," Los Alamos National Laboratory Report LA-UR-96-1151, Los Alamos, New Mexico. (Broxton et al. 1996, 1305)

Campbell, K. 1997. "Baseline Data for Fallout Radionuclides at LANL," Los Alamos National Laboratory Report LA-UR-97-____, Los Alamos, New Mexico. (Campbell 1997, draft)

Fresquez, P. R., M. A. Mullen, J. K. Ferenbaugh, and R. A. Perona, April 1996. "Radionuclides and Radioactivity in Soils Within and Around Los Alamos National Laboratory,1974 through 1994: Concentrations, Trends, and Dose Comparisons," Los Alamos National Laboratory Report LA-13149-MS, Los Alamos, New Mexico. (Fresquez et al. 1996, 1360)

Longmire, P., S. Reneau, P. Watt, L. McFadden, J. Gardner, C. Duffy, and R. Ryti, January 1995. "Natural Background Geochemistry, Geomorphology, and Pedogenesis of Selected Soil Profiles and Bandelier Tuff, Los Alamos, New Mexico," Los Alamos National Laboratory Report LA -12913-MS, Los Alamos, New Mexico. (Longmire et al. 1995, 1142)

Longmire, P. A., D. E. Broxton, and S. L Reneau (Eds.), October 1995. "Natural Background Geochemistry and Statistical Analysis of Selected Soil Profiles, Sediments, and Bandelier Tuff, Los Alamos, New Mexico, Los Alamos National Laboratory Report LA-UR-95-3486, Los Alamos, New Mexico. (Longmire et al. 1995, 1266)

McDonald, E., R. Ryti, S.L. Reneau, and D. Carlson, June 1997. "Natural Background Geochemistry of Sediments, Los Alamos National Laboratory," Los Alamos National Laboratory Report LA-UR-97-____, Los Alamos, New Mexico. (McDonald et al. 1997, draft)

"LOCAL" BACKGROUND REFERENCES

Environmental Restoration Project, October 1995. "RFI Report for Potential Release Sites 18-002(a-c), 18-003(a-h), 18-004(a,b), 18-005(a), 18-008, 18-010(b-f), 18-011, 18-012(a-c), 18-013, 27-002 (located in former Operable Unit 1093), Field Unit 2," Volumes I and II, Los Alamos National Laboratory Report LA-UR-95-3833, ER ID Nos. 52183 and 51854, Los Alamos, New Mexico. (Environmental Restoration Project 1995, 1283)

Environmental Restoration Project, September 1995. "RFI Report for Potential Release Sites 50-006(a), 50-006(c), 50-007 (formerly Operable Unit 1147), Field Unit 5," Los Alamos National Laboratory Report LA-UR-95-2738, ER ID No. 49925, Los Alamos, New Mexico. (Environmental Restoration Project, 1993, 1284)

LANL, January 1995. "RFI Report for TA-33", Los Alamos National Laboratory Report LA-UR-95-882, Los Alamos, New Mexico. (LANL 1995, 1212)

McDonald, E. V., R. Ryti, P. A. Longmire, and S. L. Reneau, March 1996. "Background Geochemistry of Soils and Colluvium at MDA-P, Los Alamos National Laboratory," Los Alamos National Laboratory Report LA-UR-96-1092, Los Alamos, New Mexico. (McDonald et al. 1996, 1354)

Ryti, R. 1997. Technical Position Paper on Use of TA-21 Baseline Data for RFI Reports Los Alamos National Laboratory Report LA-UR-97-, Los Alamos, New Mexico. (Ryti 1997)

ATTACHMENT A
Request for Supplemental Information
Natural Background Geochemistry and Statistical Analysis of Selected Soil Profiles, Sediments and Bandelier Tuff, Los Alamos, New Mexico
Los Alamos National Laboratory

This report was not reviewed with regards to background concentrations established for radionuclides.

General Comments:

1. **This document recommends that additional characterization (sampling) be performed on the A and C horizons. HRMB concurs with this recommendation based on the following:**

   The sample size for most analytes in the A and C horizons is small (generally <25).

   The A and C horizon Upper tolerance Limits (UTLs) and the corresponding proposed LANL background soil screening values repeatedly exceed the maximum analyte concentration. These exceedances are found in all three soil horizons, but primarily in soil horizons, A and C.

   RESPONSE: Per discussions during the LANL-NMED meeting of October 15, 1997, UTLs will be calculated for "all horizons" and not for individual soil master horizons. The reason for utilizing one background screening value or UTL value is to simplify the process for making background comparisons. Given that UTL values will be calculated for all horizons, the UTLs do not exceed the maximum values for any inorganic chemicals, and therefore additional data are not needed. LANL will include all additional relevant data collected to date in the revised document.

2. **The maximum soil concentrations of numerous analytes listed by horizons A, B and C do not coincide with those listed in Table 21. See Specific Comment 2.**

   RESPONSE: As stated on page 24, the values in Table 8 reflect <u>all</u> results for each analyte, including laboratory duplicate results. The data summarized in Table 21 has had laboratory duplicates averaged, non-detected values replaced by one-half of the detection limit and outliers removed. Thus, the values in Table 21 could differ from Table 8 for these reasons. However, LANL appreciates your careful review and comparison of these tables. LANL will verify that the information presented in these tables is accurate, and explain reasons for any discrepancies in the revised text of this draft document.

3. **A prerequisite of the statistical equation used to calculate LANL UTLs ($UTL_{0.95,0.95}$ = mean + standard deviation $*k_{0.95,0.95}$) is that the analyte's**

data set be normally distributed. The draft reports states that the majority of the analytes for which background soil screening values were determined had data that were "approximately" normally distributed either prior to or after transformation. If a data set is not normally distributed (prior to or after transformation), statistical measures based on the mean and standard deviation of that data set cannot be appropriately derived. LANL shall propose a method for "approximately" normally distributed data. See specific Comment 6.

RESPONSE: LANL used three, (normal, square-root normal and lognormal), out of a wealth of possible statistical distributions to model the inorganic concentration data. Out of these three distributions, the distribution that best fit the data was selected for calculation of the UTL. The term "approximately" was used to reflect the fact that data rarely "exactly" fit a statistical distribution. LANL will clarify the language used to describe the fit of the data to the suite of three statistical distributions. LANL will also include probability plots in the final document, so that the reviewer can independently assess the adequacy of the selected statistical distribution in estimating the UTL value.

4. **According to the Region III algorithms, to calculate the screening action levels (SALs), proposed LANL background soils screening values exceed the SALs for arsenic, beryllium and manganese. All three of these analytes show a significant difference in soil sample concentrations within subhorizons. This suggests that the data for these three analytes are variable and that soil concentrations may be laboratory derived (as opposed to natural background). LANL preferably shall either collect more data to address this variability or use the lowest concentration in deriving background soil constituent concentrations.**

RESPONSE: Longmire et al. (1996; 1995) discuss in detail the geochemical association of iron, beryllium, and arsenic, which are naturally-occurring elements found at LANL and elsewhere. Manganese is geochemically similar to iron and can occur as a trace element associated with magnetite (Fe_3O_4) and also can be absorbed onto ferric hydroxide present within soils and sediments. Bivariate plots of background concentrations of iron versus arsenic and iron versus beryllium are attached. Additional discussion of this topic is provided by Ryti et al. (1996). Iron, in the forms of amorphous $Fe(OH)_3$ and ferric oxyhydroxide, is naturally concentrated in soils through geochemical processes including precipitation and coprecipitation. These solids have large surface areas, which enhance their ability to adsorb many trace elements, including arsenic and beryllium. The adsorptive capacity of these solids has been experimentally investigated for several decades by numerous geochemists, chemists, and soil scientists. In addition, several of the background soil sites are located upwind from LANL and trenches and pits were excavated to depths of six meters to characterize the soil horizons and collect background soil samples for chemical analyses. Concentrations of arsenic, beryllium, and manganese within the Bandelier Tuff are above their respective SALs, as well. This supports the fact that certain trace elements are concentrated within geologic strata relative to calculated risk levels.

LANL has identified these three inorganics as requiring special attention when making background comparisons. This point is made in the introduction of the

background policy paper (Ryti et al. 1996). The additional data analyses that LANL recommends for these chemicals, include statistical distribution shift tests and evaluation of bivariate plots that show geochemical ratios (e.g., beryllium to iron) for PRS and background data. Please read the background policy paper for more information on this data assessment approach.

Specific Comments:

1. **Page 6. Table 2 does not contain a description or a legend defining the various soil horizons listed in the last column. LANL shall provide a table or a legend clarifying the various soil horizons as indicated in the last column of Table 2.**

   RESPONSE: A text discussion on this topic is provided on pages 11 and 12 of the draft document (Longmire et al., 1995). This discussion makes reference to Table 2 and additional discussion of soil horizon nomenclature is provide on page 13 (Soil Stratigraphy) of the draft document. LANL will revise Table 2 to include a description of the nomenclature for the different soil horizons and subhorizons.

2. **Page 28. The reported maximum soil sample concentrations listed in the "All Data" page of Table 8 do not coincide with the reported maximum soil sample concentrations in Table 21 (page 55) for the following analytes**

Aluminum	**Arsenic**	**Barium**
Beryllium	**Cadmium**	**Calcium**
Chromium	**Nickel**	**Potassium-TOTAL**
Thorium-TOTAL	**Uranium**	**Uranium-TOTAL**

   While the maximum reported concentration for calcium (730 mg/kg) was excluded as an outlier (according to discussions on page 46) many of the other analytes listed above had no outliers which might account for the maximum soil concentration discrepancies observed between Tables 8 and 21. LANL shall provide clarification indicating outliers and explaining the differences between Tables 8 and 21.

   RESPONSE: See response to General comment 2.

3. **Page 30. This section discusses an analysis of key inorganic elements, major elements and minor elements. LANL shall define the terms "key", "key major" and "key minor".**

   RESPONSE: "Key" references important elements from a soil chemistry perspective. These elements include aluminum (Al), arsenic (As), beryllium (Be), iron (Fe), manganese (Mn), thorium (Th), and uranium (U). "Total" references total- element concentration determined by either complete digestion of a soil

sample or by nondestructive analysis of a soil sample. A "major element" is a naturally occurring element (Al, Ca, Fe, Si, etc.) found in soils, sediments, and rocks at concentrations $\geq$ 10,000 ppm or 1 weight percent (wt. %). A "minor element" is a naturally occurring element (As, Be, Mn, Th, U, etc.) found in soils, sediments, and rocks at concentrations $\leq$ 10,000 ppm or 1 wt. %. The text in the final document will be revised to include this information.

4. **Page 41. LANL shall clarify "significant" correlation as defined with regards to the correlation reported between major elements and other trace elements. Although the document summarizes the correlations in Table 11, LANL fails to report the significance and define the correlations.**

RESPONSE: LANL had provided the number of samples used in developing the correlation coefficients as a way to determine the significance of these results. However, LANL recognizes that this does not clearly present the statistical significance of these results. LANL will add a column that shows the p-value (or statistical significance) associated with each correlation coefficient.

5. **Page 51, Item "d" of Step 3 states that UTLs calculated for normal, lognormal, or square root-transformed distributions were based on a 99th percentile and 95% confidence. Page 23 states that the UTL is determined as the 95% upper confidence limit of the 95th percentile. LANL shall clarify which percentile was used to calculate the UTL. LANL shall calculate UTLs at the 95% upper confidence level of the 95th percentile.**

RESPONSE: LANL used the 95% upper confidence level of the 95th percentile to calculate the UTLs. LANL apologizes for this typographical error in the document. The error will be corrected in the revised document.

6. **Page 52, Table 20 summarizes statistical analyses of each analyte's soil sample results. Of the 30 listed analytes in Table 20, 18 analytes are reported as having data which is "approximately" normally distributed or "more" normally distributed than without data transformations. Only four analytes (chromium, iron, manganese and sulfate) were normally distributed after data transformation. LANL shall define "approximately normally" distributed data and indicate if it has evaluated the exception to the required assumption for statistical determination of UTLs and how it will compromise the UTL results.**

RESPONSE: See response to General Comment 3.

7. **Pages 53 through 58, Table 21: Summary of Calculated UTLs and Maximum Concentrations by Soil Horizons. In determining the concentrations of natural background, LANL proposes to use the maximum detected concentration values for the following constituents with a low frequency of detection: antimony, cadmium, mercury, selenium, and thallium. LANL has proposed the least conservative approach to address the uncertainties associated with its data base. The maximum detected concentration values**

are not acceptable as natural background concentration values. Therefore, LANL shall propose an alternative and more credible approach to address these data gaps. Additional sampling and analyses using more sensitive analytical methodology and lower detection limits is warranted.

RESPONSE:

1. Issue: maximum detect is least conservative approach

The purpose of calculating UTL values is to provide a simple screening tool to detect possible releases from LANL potential release sites. First, consider that the UTL is an estimate of the upper percentiles of background. The maximum of a data set also represents an upper quantile, which can be calculated as (n-1)/n. Thus for 10 samples, the maximum is an estimate of the 90th percentile of the distribution. Thus, a maximum detected concentration is also a useful background screening value.

Second, consider the following summary of soil analytical results (based on Table 8):

Chemical	Number of values	Detection Frequency
Antimony	182	10%
Cadmium	40	10%
Mercury	39	5%
Selenium	41	56%
Thallium	182	61%

LANL suggests that the situation for each of these inorganic chemicals is somewhat unique and warrants individual attention. For example, antimony has a low detection frequency, but the actual number of detects is 19. Thus, these 19 detects are viewed as a fairly representative data set of the upper end of natural occurring antimony concentrations. In this sense, the maximum detected value should not be viewed as an unreasonable value. Likewise, the thallium data has both a large number of values and a detection frequency greater than 50%. Thus, the maximum value in these data should also represent a reasonable background value. Selenium was also detected in about 50% of the samples. Cadmium and mercury background data represent a small number of samples, and a low detection frequency.

As per discussions in the joint LANL/NMED meeting of October 15, 1997, LANL proposes to supplement the Laboratory-wide background data with site-specific background data collected for MDA P (McDonald et al. 1996, "Background Geochemistry of Soils and Colluvium at MDA-P, Los Alamos National Laboratory"). Specifically, LANL will add MDA-P soil background data to the "all horizons" soil data for antimony, cadmium, mercury, selenium, silver and thallium. This will provide an additional 55 samples for these chemicals. With this additional data, LANL expects that UTLs can be calculated for most of these chemicals. If a UTL cannot be calculated, then either a maximum detected concentration or the detection limit will be recommended as a background screening value. As in all of our data evaluations, we will emphasize the ultimate objective of the background comparisons (i.e., risk and regulatory compliance) as well as specific technical details (i.e., formal statistical tests and calculations).

2. Issue: carry forward all "detected" values

LANL would like to note that for that the reported mercury detect value of 0.1 mg/kg is equal to the detection limit value in this background data set (also 0.1 mg/kg). Thus, as far as mercury is concerned, LANL has in essence been carrying forward all "detected" mercury results relative to the soil background data. In addition, as mentioned above, additional data will be incorporated into the data sets for the remaining chemicals in order to address those data gaps.

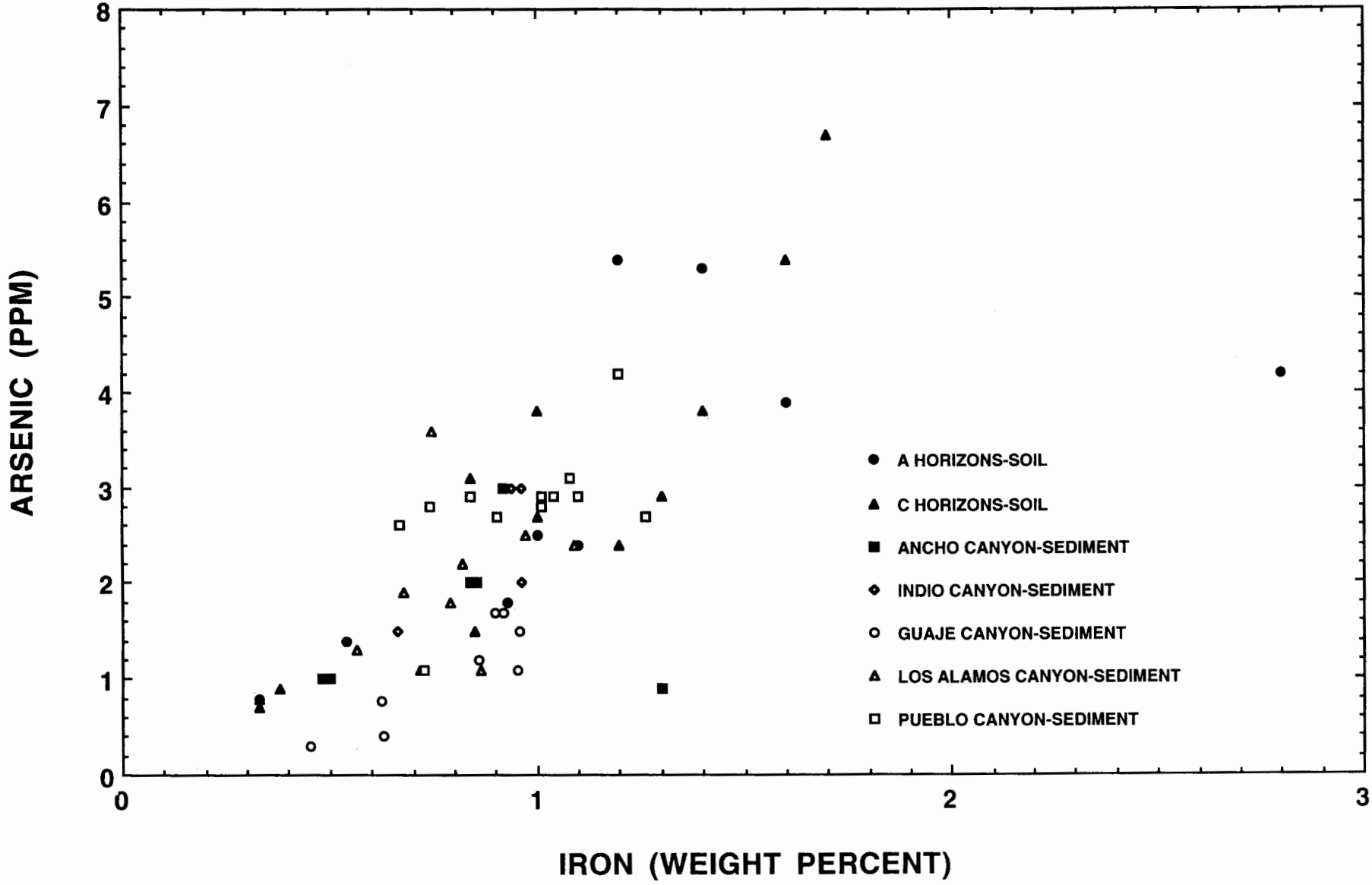
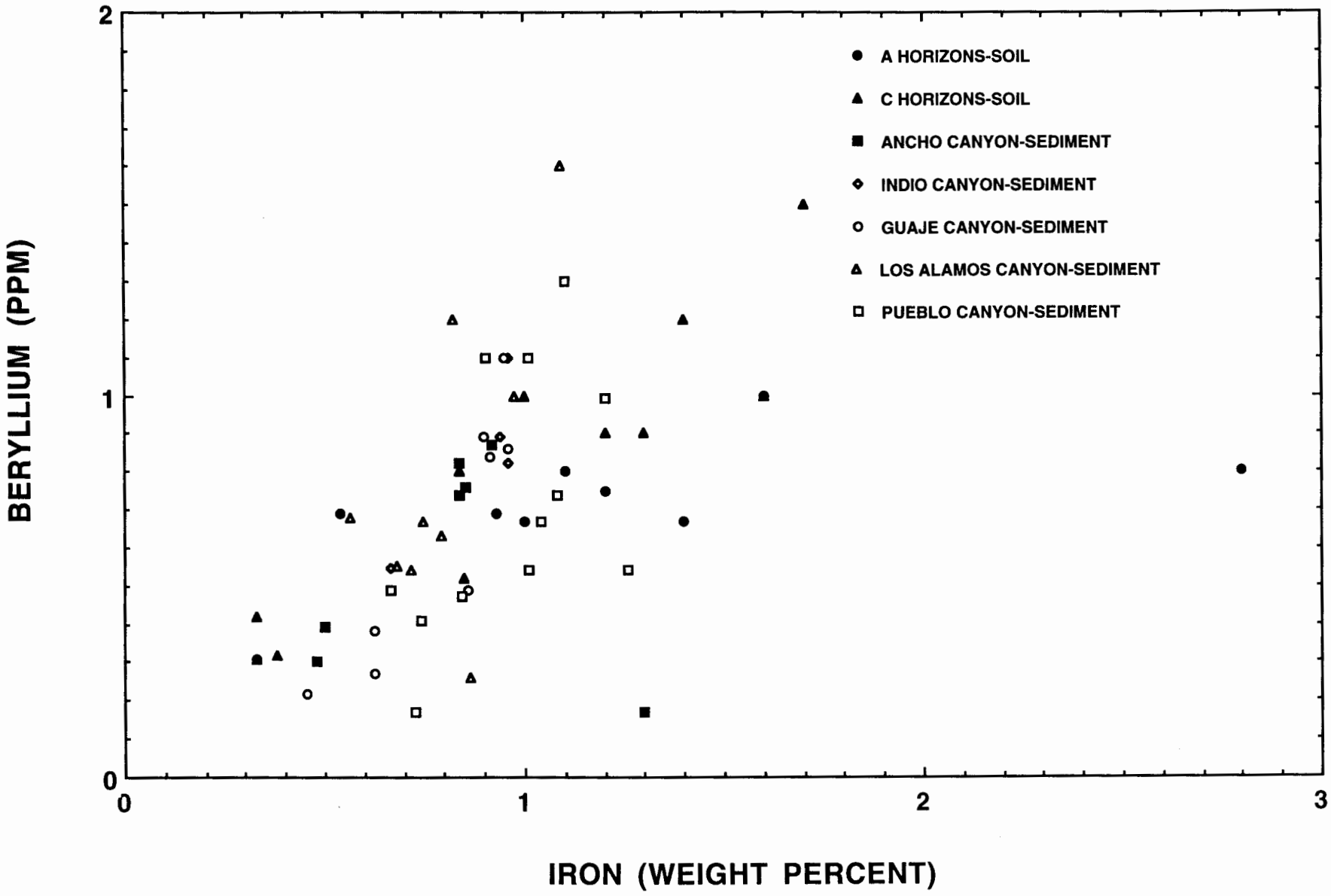
3. Issue: what method is acceptable

Per the LANL-NMED meeting of October 16, 1997, it was decided that the method detection limit issue related to PRS data and not to the background data. Thus, no change in analytical methods for the background data is needed. Thus LANL will emphasize, as is already discussed in the ER Project Policy Paper on background for inorganics, that analytical methods of the PRS data be evaluated for comparability to the background data before making background comparisons.

8. Page 55. A summary of the lead soil concentrations and the calculated UTLs are omitted from Table 21.

RESPONSE: LANL apologizes for this omission of the lead results from this draft, and will correct this problem in the revised document.

ARSENIC AND IRON CONCENTRATIONS IN BACKGROUND SOILS AND SEDIMENTS, LOS ALAMOS, NEW MEXICO.



BERYLLIUM AND IRON CONCENTRATIONS IN BACKGROUND SOILS AND SEDIMENTS, LOS ALAMOS, NEW MEXICO.