

# **NMED / LANL 1996 Sediment Results: Data Evaluation and Statistical Comparison**

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## **FOREWORD**

The mission of the New Mexico Environment Department DOE Oversight Bureau is to assure that activities at DOE facilities are protective of the public health and safety and the environment. The Bureau's activities are funded through a grant from the U.S. Department of Energy in accordance with the provisions set forth in the *Agreement-in-Principle between the State of New Mexico and the U.S. Department of Energy*. One of the primary objectives of the agreement is the development and implementation of a program of independent monitoring and oversight.





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## **ABSTRACT**

In 1996, the DOE Oversight Bureau of the New Mexico Environment Department collected 10 sediment samples paired with samples collected by Los Alamos National Laboratory. Samples were analyzed for beryllium, lead, isotopic plutonium and isotopic uranium. Analytical results were compared with the Laboratory's results to determine if there was a difference at the 95% confidence level. Plutonium -239, -240, lead, and beryllium results agreed with the Laboratory's. Plutonium-238 results were slightly lower than the Laboratory's. The Department's results for total uranium were significantly greater than those reported by the Laboratory. The investigation indicated that the methods used by the Laboratory to measure uranium in sediments should be re-evaluated. A summary comparison of all results showed no significant difference. All constituents measured were at levels below health-based standards and guidelines

## **INTRODUCTION**

Sediment transport associated with surface water runoff is a significant mechanism for contaminant movement. Accordingly, sediments are sampled by Los Alamos National Laboratory (LANL or the Laboratory) Environmental Safety and Health-18 Division (ESH-18) in all canyons that cross the facility, including those with either perennial or ephemeral flows (Johnston, Lujan-Pacheco, 1997). Sediment sampling at LANL began in 1949 with studies in Acid/Pueblo and DP/Los Alamos Canyons, where radioactive wastes were discharged in the early days of Laboratory operations. By 1996, LANL's environmental surveillance program for sediments had grown to include a network of 93 standard sampling locations, called "stations." These stations were located on Laboratory property, around the lab perimeter and at off-lab, regional locations.

In order to determine if LANL's environmental programs are protective of human health and the environment, the New Mexico Environment Department (NMED) must have confidence in the accuracy of the Laboratory's environmental data. To obtain this confidence, the DOE Oversight Bureau (DOE OB) duplicated part of LANL's surveillance program. NMED and LANL sediment data were compared for five contaminants at ten stations. If the data proved to be statistically comparable at a 95% confidence level, the results would support the validity of LANL's environmental data. If NMED and LANL data were not found to be statistically equivalent, either LANL or NMED's collection or analytical methods would be suspect.

In order to permit a statistical comparison between NMED and LANL data, a sufficient number of the samples collected had to contain the five target contaminants at levels in excess of their analytical detection limits. For this reason, eight of ten sampling stations were selected because of their proximity to contaminated areas. Two stations were selected to test the historical absence of these contaminants above background levels, downstream of LANL's current and past operations.

The five contaminants studied were plutonium-238, plutonium-239, -240, total uranium, lead and

beryllium. Plutonium was selected because historical data identify it as the most commonly found, anthropogenic (man-made) radionuclide measured above background on and around the Laboratory. The sources of radionuclides measured above background may be related to multiple sources, including atmospheric fallout, surface deposition from stack emissions, or surface transport from various Laboratory sources (Johnston, Lujan-Pacheco, 1997). Uranium was chosen because of its extensive role in Laboratory operations. Lead and beryllium were added to the list because their common, historical use by the Laboratory suggested that they might also be found entrained in sediments on and downstream of LANL property.

Except for the analytical method chosen for uranium, NMED duplicated LANL's sampling and analytical methods. LANL samples were submitted to their Analytical Services Group (CST-9) and analyzed for radionuclides, radioactivity, metals and/or organic suites. NMED samples were submitted to a commercial laboratory, Paragon Analytics, Inc., and analyzed for isotopic plutonium, isotopic uranium, lead and beryllium.

NMED data which met quality-assurance tests were compared to background values. Standard laboratory quality-assurance measures include: laboratory blanks to assure the absence of cross contamination, analytical duplicates to establish precision, and blank spike samples to establish accuracy. For radionuclides, background levels are attributable to worldwide fallout and/or naturally occurring elements. Results of radionuclide analyses of sediments from regional stations collected annually from 1974 through 1986 were used to establish statistical limits for worldwide fallout. In addition, natural background levels have been established for total uranium in northern New Mexico (Purtyman et al., 1987). The average activity level for each analyte, plus twice the standard deviation, was used as an indicator of the upper limit for worldwide fallout or natural background activity. For metals, NMED established the upper limit background concentration by calculating the mean plus two times the standard deviation from 1995 regional sample values reported in the Environmental Surveillance Report (ESR).

The data were then compared to the Screening Action Levels (SALs), threshold limits which are based on Environmental Protection Agency (EPA) guidance for human health-risk or DOE dose limits (Johnston, Lujan-Pacheco, 1997).

Finally, NMED and LANL data were statistically compared to determine if they were significantly different.

### **LANL's Surveillance Program**

ESH-18, LANL's Water Quality and Hydrology Group, annually collects sediment samples at 93 regional, perimeter and onsite sampling stations. Of 24 regional stations thought to be beyond the influence of known laboratory impacts, 15 are located at reservoirs.

LANL sediment sampling stations are located in the channels of ephemeral and perennial watercourses and in reservoirs both upstream and downstream of LANL. These stations are categorized according to proximity to the Laboratory. Regional stations are established at distances beyond the known influence of the Laboratory, perimeter stations are established within

distances beyond the known influence of the Laboratory, perimeter stations are established within about 4 km of the Laboratory boundaries, and onsite stations are located within the Laboratory boundaries. Data from perimeter stations provide information regarding potential migration of contaminants from Laboratory property. Data collected onsite are used to assess impacted areas within the laboratory boundaries. Data from regional stations are used to determine background levels of normally occurring elements and anthropogenic contaminants. Regional locations are shown on Figure 1. Since regulatory standards do not exist for sediments (Johnston, Lujan-Pacheco, 1997), the existence and degree of contamination in samples is based on comparisons to regional background levels for each constituent.

Sampling station data are interpreted in the context of the watersheds from which they are taken. For onsite and lab-perimeter stations, these watersheds consist of specific canyons or canyon systems. The canyons are distinguished by their drainage characteristics and by Laboratory operations which currently take place or have historically taken place in them. Some onsite stations were originally located because of industrial radioactive wastewater discharges into canyon systems, such as, Los Alamos/DP, Pueblo/Acid and Mortandad Canyons. Since these canyons also extend beyond Laboratory boundaries into populated areas, stations have been located in the canyons associated with White Rock, the Los Alamos Townsite, San Ildefonso Pueblo, Bandalier Monument, and on U.S. Forest Service land. To monitor fugitive emissions from ongoing waste-disposal operations at TA-54 or historical lab operations such as the hydronuclear test area at TA-49, some onsite stations are located above the canyons in mesa-top drainages.

### **Analyte-Selection Rationale**

In order to select 10 sampling stations for this study, NMED evaluated concentrations of contaminants on or near the Laboratory reported in LANL's 1995 ESR. LANL characterized the 1995 data as consistent with historical findings (Johnston, Lujan-Pacheco, 1996). Radiological constituents measured by LANL include tritium, strontium-90, total uranium, cesium-137, plutonium-238, plutonium-239, -240, americium-241 and gross alpha, beta and gamma radioactivity. Results for many samples taken within known radionuclide release areas exceeded background levels for one or more isotopes or radioactivity measurements, including tritium, strontium-90, cesium-137, plutonium isotopes, americium-241, and alpha, beta and gamma activities. LANL measured cesium-137 above the SAL, and plutonium-238, plutonium-239, -240 and americium-241 at elevated levels in Mortandad Canyon within the Laboratory boundaries. The Laboratory also reported various combinations of plutonium isotopes, cesium-137, americium-241 and gross gamma measurements above background at TA-54 and TA-49. LANL observed that cesium-137, plutonium-239, plutonium-240, total uranium and strontium-90 were above background at a number of locations on the Pajarito Plateau outside known contamination areas. Two regional locations exhibited strontium-90 levels above background. Cochiti, Abiquiu, and Heron Reservoirs also showed elevated measurements of plutonium-238.

Trace metals and heavy metals measured by the Laboratory include silver, aluminum, arsenic, boron, barium, beryllium, cadmium, cobalt, chromium, copper, iron, manganese, mercury,

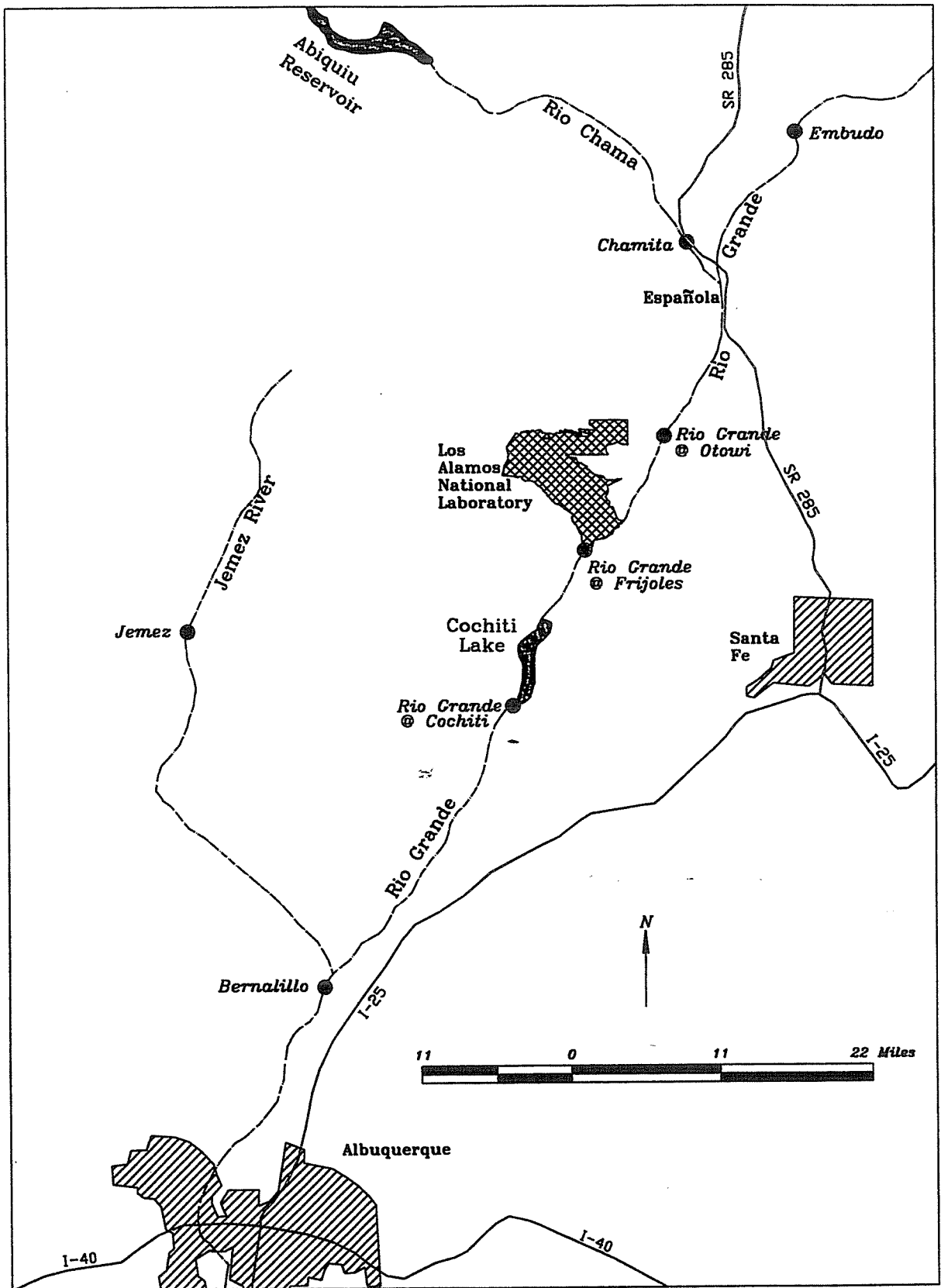


Figure 1. Regional sampling locations in relation to Los Alamos National Laboratory.

molybdenum, nickel, lead, antimony, selenium, strontium, thallium, vanadium, and zinc. In 1995, the ESR concluded that "None of the results show any significant accumulations of metals above background concentrations." (Johnston, Lujan-Pacheco, 1996). However, LANL did not present background levels for metals in the ESR. In order to facilitate an evaluation of the 1995 ESR metal results, NMED calculated an upper-limit background concentration for each metal. To determine these concentrations, means from eight regional stations plus two standard deviations were calculated for each metal. NMED then compared LANL measurements for each station and the means calculated for each parameter to background. Based on this methodology, a number of individual stations had metals higher in concentration than background.

According to this evaluation, the isotopes most commonly measured above background were the plutonium isotopes. Uranium, although commonly used both currently and historically by the Laboratory, was not measured above background at any location. However, LANL's analytical techniques for uranium changed in 1995. Lead tended to be found at higher levels than the other metallic contaminants. The beryllium background concentration is greater than the SAL and, based on public concern, NMED investigated levels of this contaminant. Therefore, this investigation focused on plutonium-238, combined plutonium-239 and -240, total uranium, lead and beryllium.

### **Site-Selection Rationale**

At least eight samples with measurable levels of constituents selected for this study were required to make an acceptable statistical comparison. Therefore, eight of the ten stations in this study were selected for their historically high levels of a variety of contaminants. Stations that have had one or more constituents repeatedly measured above background were considered as potential sites. These included two stations sited to monitor relic contaminants near the hydronuclear test area at TA-49, three stations located near the waste disposal facilities at TA-54's Area G to monitor fugitive contaminants, two stations monitoring the impacts of current liquid-waste disposal in Mortandad Canyon and one in Los Alamos Canyon at State Road 4 (SR-4) to monitor historic radioactive wastewater releases. Two stations that have not demonstrated Laboratory impacts in the past were included, one in Potrillo Canyon at SR-4, and one in Water Canyon at SR-4. All LANL stations and NMED co-located sites are shown on Figure 2.

## **METHODS**

NMED and LANL collected 10 sediment samples at the same time and location (co-located samples). Collection methods were identical. LANL submitted their samples to its onsite analytical laboratory, CST-9. NMED used a commercial analytical laboratory, Paragon Analytics, Inc. NMED screened its laboratory results for basic data quality parameters. The data were then compared to background means, upper limits for background, and LANL SALs to evaluate whether LANL operations had contributed contaminants to the sediments. LANL and NMED

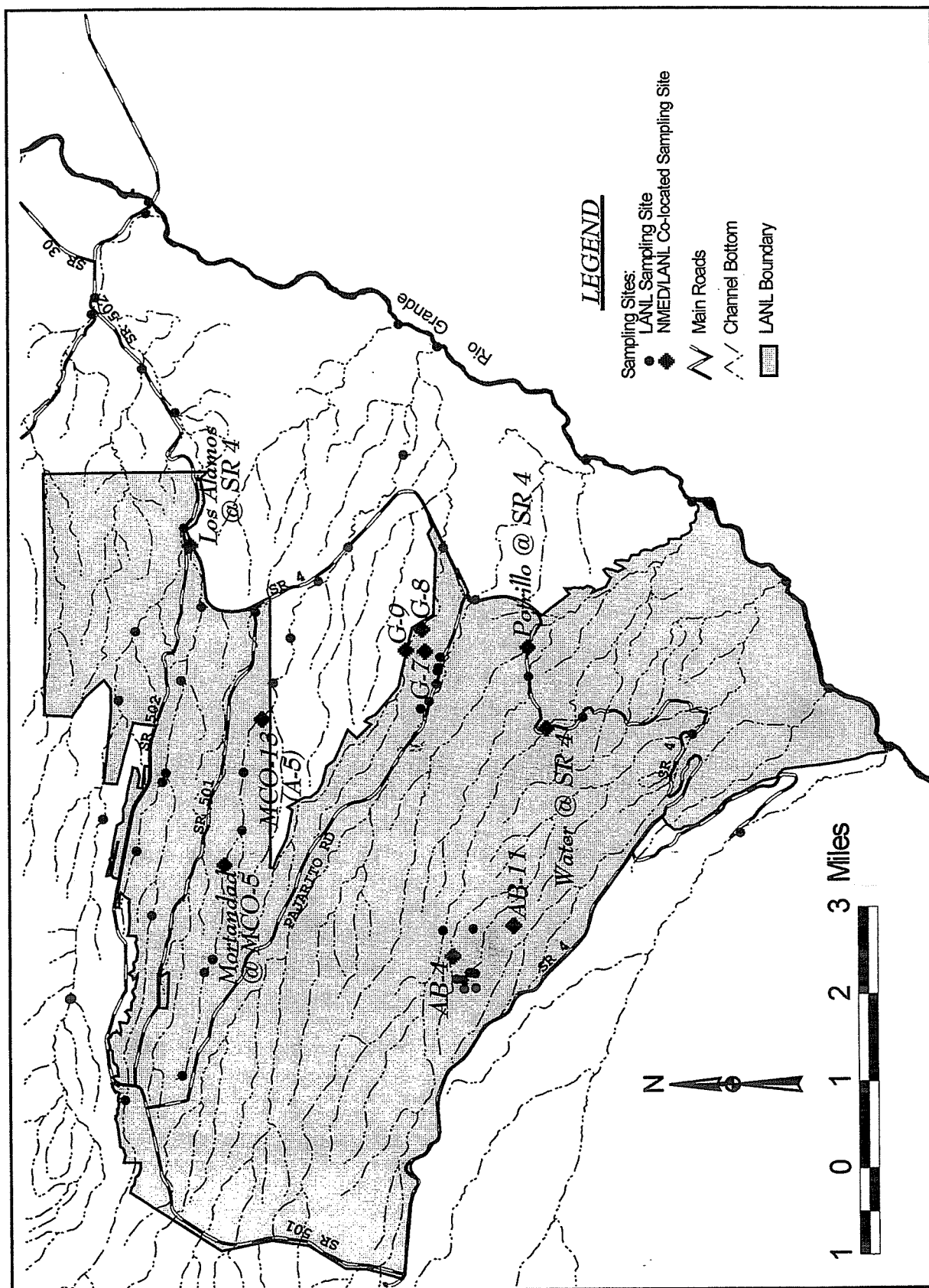


Figure 2. NMED and LANL Sediment Sampling Locations.



data sets were then statistically compared at a 95% confidence level.

## **Collection Methods**

NMED's sediment sample collection methods are described in the DOE OB Standard Operating Procedures For Sampling and Analytical Activities (Englert, 1997). These methods are based on guidelines established by federal and state government agencies, including DOE guidance. Both NMED and LANL used identical collection methods to obtain samples representative of most recently deposited sediments transported by surface water run-off.

NMED collected sufficient sediment to fill a 500 ml wide-mouth polypropylene bottle. Fine sediments were collected selectively after removing gravel and organic debris (twigs and leaves) from transects across dry stream beds. New disposable scoops were used at each location to collect the top layer of sediment and to transfer the material to a container. The filled containers were double bagged to reduce the potential for cross-contamination and placed into coolers at 4° C for submittal to an analytical laboratory. No chemical preservation was required and the samples were submitted within the recommended 6-mo holding time.

At each site, LANL's ESH-18 personnel filled their sample bottles from successive transects across the stream bed. At many sites several transects were required to obtain enough sample. When more than one transect was required, samples were collected from down-gradient to up-gradient to avoid including debris or other material not representative of the channel sediment. NMED personnel then repeated the collection procedure in as close to the same location as possible without collecting from an area disturbed by LANL sampling.

## **Analytical Methods**

Analytical procedures used by both laboratories were in keeping with the EPA's accepted methods (EPA, 1997) or other generally recognized and accepted methods. NMED's analytical laboratory used the same analytical methods as LANL's onsite lab, except for uranium.

NMED's laboratory evaluated isotopic uranium using alpha spectroscopy. The sample was totally dissolved using hydrofluoric acid. The uranium in solution was then micro-precipitated with lanthanum fluoride, and counted for alpha activity. LANL's laboratory evaluated uranium using Kinetic Phosphorescence Analysis (KPA). This method requires similar dissolution of the sample, but the analysis (measurement of photon emissions) is done on an aliquot of the hydrofluoric acid dissolved solution.

Isotopic plutonium was evaluated using alpha spectroscopy. For both LANL and NMED, the extraction for isotopic plutonium analysis employed a total dissolution using hydrofluoric acid. LANL electroplated the solution onto a planchette and the NMED laboratory micro-precipitated the solution by adding lanthanum fluoride and then filtering. The precipitate on the planchette or filter was then counted for alpha.

NMED and LANL's analytical labs analyzed beryllium and lead using EPA SW-846 method 6010.

This Inductively Coupled Plasma-Atomic Emission Spectrometry method measures the intensity of the lead and beryllium emission spectra. Extraction of metals from sediments was done using EPA SW-846 method 3051, a total recoverable metals dissolution using hot nitric acid.

Before the digestion and analysis, the sediment samples were dried by the analytical laboratories at 75° C for 24 hours, then ground and sieved. The values were then reported as dry weight of analyte per gram of dry sediment.

### **Data-Management Methods**

Upon sample collection and submittal to the analytical laboratory, a project number was given to the group of samples and a new project file was opened. This file included a tracking sheet, individual sample-identification numbers and field notes. Additional paperwork was added to the project file as it was received, for example, the chain of custody, the analytical laboratory submittal form, the analytical lab invoices, and finally, the analytical data.

### **Comparison Methods**

Upon receipt of the analytical results, the data were reviewed to assure data quality objectives and quality control criteria were met. The data were then evaluated for elevated measurements. Finally, NMED and LANL data sets were compared to determine whether there was a statistical difference. All environmental measurements include error; LANL and NMED data pairs were not expected to be identical. Statistical methods were used to determine whether the differences were significant (see Results section as well as the Appendix for presentations of data and statistics).

Descriptive statistics were calculated and histograms were prepared for each data set. The mean, median, standard deviation, kurtosis, skewness and range were calculated for each LANL and NMED data set. The distribution of each data set was also screened for normality using the Shapiro Wilks test. These statistics and histograms were inspected to qualitatively evaluate the data distributions for outliers, bimodal characteristics, homogeneity of the distributions and the overall similarities between the data sets. The data distributions also show the variability of the data between non-impacted areas and potentially contaminated areas.

Following the review of descriptive statistics, comparative statistical analyses were run on paired data sets within each data block using three statistical tests: (1) the paired t-test, (2) the Wilcoxon Matched Pairs Signed Rank Test, and (3) the Pearson Correlation. Each data block consisted of all DOE OB/LANL paired data measurements for an individual parameter. The distribution of the differences between the paired data sets were represented by the x-y distribution histogram.

Parametric statistical tests are used to evaluate normally distributed data, where non-parametric tests are used to compare non-normal data distributions. The paired t-test is a parametric method for evaluating difference in means between two data sets. Although this parametric test assumes each group of data is normally distributed, it is often reliable even when the data are not normally distributed.

The Wilcoxon Matched Pairs Signed Rank Test is a non-parametric alternative to the parametric paired t-test. This evaluation computes the number of times measurements from one data set are larger than matched data from the other data set and ranks the magnitude of the differences. For two sets of paired data that differ only randomly, corresponding data from the first set will be larger than the second approximately 50% of the time. If one set of data is systematically different from the other, that is if there is a bias, then data from the first set will be either larger or smaller than their pairs more than 50% of the time. The Wilcoxon test is also sensitive to the ranking of the magnitude of the differences between each data comparison, which make this test only slightly less powerful than the paired t-test. For both the paired t-test and the Wilcoxon test, differences were considered significant at the 95 % confidence level.

The Pearson Correlation Test is a method used to describe the relationship between two data sets. This test measures how closely two sets of data track, that is whether both paired measurements are similarly high or low in respect to other data pairs. If either or both the paired t-test and the Wilcoxon test show that NMED and LANL paired data are significantly different and the Pearson test finds that the data sets correlate, a system bias may be indicated. If the data sets are found to be significantly different and the Pearson test finds that the data sets do not correlate, it might be suspected that LANL and NMED are actually measuring completely different things. For example, it might be that NMED or LANL's analytical lab did not actually evaluate the set of samples for the target analyte, but for something else, or that one of the laboratories performed the measurement in so different a way that the resulting information is not comparable.

A summary test of all data acquired for 1996 was made (See Figure A-12). By using a larger number of comparisons during statistical tests, the more powerful or reliable these tests become. All five parameters from the ten locations selected in this study were grouped and compared to the corresponding data from LANL. This increased the number of data comparisons from ten to fifty matched pairs. The descriptive and comparative statistics described above were then used to determine whether a difference existed between LANL and NMED data.

In addition to the statistical methods used to compare the NMED/LANL data, each NMED measurement was compared to three screening levels. These levels were: 1) the background mean established from LANL data for eight regional locations, 2) the upper limit background level established by LANL for radionuclides or the background value established by NMED from LANL trace metal data, 3) and the SAL.

## RESULTS

Data from samples collected by NMED are presented in Table 1. Both sets of data, NMED and corresponding LANL results from the 1996 Environmental Surveillance Report are presented in Table 2. Tables of descriptive and comparative statistics and associated histograms are presented in the Appendix. Analytical laboratory Quality Assurance/Quality Control (QA/QC) results indicate that NMED data are all within control limits. Radiochemical QA/QC blanks, duplicates and blank spike samples were all within acceptance levels. Metal QA/QC reagent blanks, matrix

spike, and matrix spike duplicates were also all within acceptance criteria. The Shapiro-Wilks test indicate that none of the sampling data sets are normally distributed. A discussion of results and the data comparison is given in the following pages of this section.

Table 1. NMED radiochemical and trace metal analysis of sediments from the LANL area during 1996

	Date	Beryllium	Lead	Pu-238	Pu-239/240	U 234	U-235	U-238	Total U
LOCATION	Collected	(mg/kg)	(mg/kg)	(pCi/g)	(pCi/g)	(pCi/g)	(pCi/g)	(pCi/g)	(mg/kg)
									converted
LA Canyon @ SR-4	03/11/96	<0.5	16	0.01 +/- 0.0	0.10 +/- 0.0	1.52 +/- 0.2	0.08 +/- 0.0	1.44 +/- 0.2	4.32
Mortandad @ MCO-5	04/11/96	<0.5	2.7	2.06 +/- 0.2	5.59 +/- 0.6	0.25 +/- 0.0	0.02 +/- 0.0	0.29 +/- 0.0	0.87
Mortandad @ MCO-13 (A-5)	04/11/96	0.7	16	0.00 +/- 0.0	0.02 +/- 0.0	0.81 +/- 0.1	0.03 +/- 0.0	0.73 +/- 0.1	2.19
TA-54 G-7	03/22/96	<0.5	4.6	0.20 +/- 0.0	0.19 +/- 0.0	0.67 +/- 0.1	0.06 +/- 0.0	0.58 +/- 0.1	1.75
TA-54 G-8	03/22/96	<0.5	7.3	0.08 +/- 0.0	0.08 +/- 0.0	0.62 +/- 0.1	0.03 +/- 0.0	0.66 +/- 0.1	1.98
TA-54 G-9	03/22/96	<0.5	5.5	0.03 +/- 0.0	0.02 +/- 0.0	0.58 +/- 0.1	0.05 +/- 0.0	0.63 +/- 0.1	1.90
Potrillo @ SR4	03/11/96	0.6	8.4	0.00 +/- 0.0	0.00 +/- 0.0	0.52 +/- 0.0	0.04 +/- 0.0	0.52 +/- 0.0	1.57
Water Canyon @ SR4	03/11/96	1.2	26	0.00 +/- 0.0	0.01 +/- 0.0	0.90 +/- 0.1	0.05 +/- 0.0	1.09 +/- 0.1	3.27
TA-49 AB-4A	03/25/96	0.9	15	0.00 +/- 0.0	0.01 +/- 0.0	0.79 +/- 0.1	0.03 +/- 0.0	0.97 +/- 0.1	2.90
TA-49 AB-11	03/26/96	<0.5	5.1	0.00 +/- 0.0	0.01 +/- 0.0	0.38 +/- 0.0	0.02 +/- 0.0	0.41 +/- 0.0	1.23

Radiochemical and Trace Metal Analysis reported on a dry weight basis (pCi/g dry or mg/kg dry)

< indicates not detected at or above reporting limit

### Plutonium-238

NMED and LANL plutonium-238 data are tabulated and graphed in Figure A-1. Five NMED plutonium-238 measurements are above LANL's plutonium-238 upper limit for background (0.006 pCi/g): LA Canyon @ SR-4 (0.01 pCi/g), Mortandad Canyon at MCO-5 (2.06 pCi/g), TA-54 G-7

Table 2. NMED/LANL radiochemical and trace metal data comparisons

LOCATION	Date Collected	Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>	
		NMED Beryllium (mg/kg)	LANL Beryllium (mg/kg)	NMED Lead (mg/kg)	LANL Lead (mg/kg)	NMED Pu-238 (pCi/g)	LANL Pu-238 (pCi/g)	NMED Pu-238 (pCi/g)	LANL Pu-238 (pCi/g)	NMED Pu-239/240 (pCi/g)	LANL Pu-239/240 (pCi/g)	NMED Pu-239/240 (pCi/g)	LANL Pu-239/240 (pCi/g)
LA Canyon @ SR-4	03/11/96	<0.5 <sup>a</sup>	0.44	16	17.20	0.01	0.01	0.001	0.000	0.10	0.02	0.088	0.004
Mortandad @ MCO-5	04/11/96	<0.5	0.23	2.7	<5.70	2.06	0.26	2.220	0.110	5.59	0.68	8.250	0.330
Mortandad @ MCO-13	04/11/96	0.7	0.32	16	<5.70	0.00	0.01	0.002	0.001	0.02	0.01	0.026	0.002
TA-54 G-7	03/22/96	<0.5	<0.12	4.6	6.30	0.20	0.04	0.243	0.004	0.19	0.04	0.174	0.011
TA-54 G-8	03/22/96	<0.5	0.31	7.3	9.20	0.08	0.04	0.119	0.008	0.08	0.03	0.150	0.009
TA-54 G-9	03/22/96	<0.5	<0.12	5.5	3.40	0.03	0.02	0.091	0.005	0.02	0.01	0.040	0.003
Potrillo @ SR4	03/11/96	0.6	<1.18	8.4	<5.41	0.00	0.01	0.001	0.001	0.00	0.01	0.006	0.001
Water Canyon @ SR4	03/11/96	1.2	0.56	26	16.60	0.00	0.04	0.001	0.001	0.01	0.01	0.011	0.002
TA-49 AB-4A	03/25/96	0.9	<0.13	15	16.90	0.00	0.02	0.003	0.002	0.01	0.01	0.013	0.002
TA-49 AB-11	03/26/96	<0.5	<0.13	5.1	2.70	0.00	0.01	0.000	0.001	0.01	0.01	0.007	0.002
<sup>b</sup> Mean			0.82		10.0			0.006				0.008	
<sup>b</sup> Background (x+2s)			2.6		24.4			0.006				0.023	
<sup>b</sup> ISAL			BG		400			27				24	

LOCATION	Date Collected	Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>		Analysis Requested <sup>a,b</sup>	
		U-234 (pCi/g)	counting <sup>c</sup> uncertainties	U-235 (pCi/g)	counting <sup>c</sup> uncertainties	U-238 (pCi/g)	counting <sup>c</sup> uncertainties	NMED Total U* (mg/kg)	counting <sup>c</sup> uncertainties	LANL Total U† (mg/g)	counting <sup>d</sup> uncertainties
LA Canyon @ SR-4	03/11/96	1.52	0.21	0.08	0.03	1.44	0.21	4.32	0.64	1.09	0.11
Mortandad @ MCO-5	04/11/96	0.25	0.05	0.02	0.01	0.29	0.06	0.87	0.18	1.36	0.14
Mortandad @ MCO-13	04/11/96	0.81	0.12	0.03	0.02	0.73	0.12	2.19	0.37	1.24	0.12
TA-54 G-7	03/22/96	0.67	0.14	0.06	0.04	0.58	0.12	1.75	0.38	0.88	0.09
TA-54 G-8	03/22/96	0.62	0.10	0.03	0.02	0.66	0.10	1.98	0.31	1.36	0.14
TA-54 G-9	03/22/96	0.58	0.12	0.05	0.03	0.63	0.12	1.90	0.37	1.77	0.18
Potrillo @ SR4	03/11/96	0.52	0.09	0.04	0.02	0.52	0.09	1.57	0.28	1.22	0.12
Water Canyon @ SR4	03/11/96	0.90	0.14	0.05	0.02	1.09	0.16	3.27	0.49	1.84	0.18
TA-49 AB-4A	03/25/96	0.79	0.12	0.03	0.02	0.97	0.14	2.90	0.43	1.62	0.16
TA-49 AB-11	03/26/96	0.38	0.07	0.02	0.02	0.41	0.07	1.23	0.22	0.48	0.05
<sup>b</sup> Mean										2.72	
<sup>b</sup> Background (x+2s)										4.4	
<sup>b</sup> ISAL										67	

<sup>a</sup>Metals were digested following SW-846 Method 3050A and analyzed following Method 6010A. NMED radionuclides digested with hydrofluoric acid and analyzed by alpha spectroscopy.

<sup>c</sup>Counting uncertainties as reported by Paragon Analytics, Inc. (2 sigma, Total Propagated Uncertainty)

<sup>d</sup>Counting uncertainties as reported in the 96 ESR (1 sigma)

<sup>e</sup>NMED total uranium calculated from uranium isotopic measurements

<sup>f</sup>LANL total uranium by Kinetic Phosphorescence Analysis

<sup>g</sup>< indicates not detected at or above the reporting limit. To calculate means 1/2 reporting limit value used.

<sup>h</sup>Mean calculated by NMED from eight background stations

<sup>i</sup>Purtyman, 1987a; upper limit for background, (ESR 1995)

<sup>j</sup>ISALs; (LANL Screening Action Level), Environmental Restoration Program, March 1997 values; (ESR1997)

(0.20 pCi/g), TA-54 G-8 (0.08 pCi/g), and TA-54 G-9 (0.03 pCi/g). These NMED measurements are also greater than the 0.006 pCi/g mean calculated from eight regional stations. There are no measurements above the 27 pCi/g SAL.

Descriptive statistics, histograms and comparative statistics for plutonium 238 are presented in Figure A-2. The descriptive statistics and histograms show that NMED and LANL data are very similar. The mean of NMED data is 0.238 pCi/g and LANL's is 0.268 pCi/g. In addition to the similarity between the data distributions, the bimodal nature of both LANL and NMED distributions demonstrate that the samples were taken from two distinct sample populations: relatively clean locations and a contaminant-impacted area onsite. The sample in the higher range in both histograms was taken from Mortandad Canyon, where treated radiological waste waters are discharged.

The comparative statistics indicate some difference exists between LANL and NMED data. The Wilcoxon test indicates the data were significantly different, although the paired t-test indicates the data are not, and the Pearson Correlation test indicates the data sets track very well. LANL's data tended to be higher than NMED's although most values were close to zero. These results indicate the difference is non-random although small.

In summary, the statistical tests for plutonium-238 show these things:

1. The Wilcoxon test indicates that the data are different at the 95% confidence level ( $p=0.0390$ ). The paired t-test indicates that the means are not different at the 95% confidence level ( $p=0.0968$ ).
2. The Pearson Correlation indicates that the data sets track closely (correlation coefficient  $r=0.9995$ ).

### **Plutonium-239 and -240**

NMED and LANL plutonium-239, -240 data are tabulated and graphed in Figure A-3. Four NMED plutonium-239, -240 measurements are above LANL's upper background limit (0.023 pCi/g): Los Alamos Canyon at SR 4 (0.10 pCi/g), Mortandad Canyon at MCO-5 (5.59 pCi/g), TA-54 G-7 (0.19 pCi/g), and TA-54 G-8 (0.08 pCi/g). Potrillo Canyon at SR 4 is the only station that did not have a measurement above the mean calculated from LANL regional stations (0.008 pCi/g). There are no measurements above the 24 pCi/g SAL.

Descriptive statistics, histograms and comparative statistics for plutonium-239 and -240 are presented in Figure A-4. The descriptive statistics and histograms show the NMED and LANL data distributions are similar. The mean of NMED data is 0.603 pCi/g and LANL's is 0.876 pCi/g. In addition to the similarity between the data distributions, the bimodal nature of both LANL and NMED distributions demonstrate samples are from uncontaminated locations and an impacted area. The samples represented in the higher range on both histograms were from Mortandad Canyon, where treated radiological waste waters are discharged.

Neither the Wilcoxon nor the paired t-test show a significant difference between NMED and

LANL data. The Wilcoxon and paired t-test indicate the data are not from different populations at a 95% confidence level. The Pearson test indicates that the data sets track very well.

In summary, the statistical tests for plutonium-239 and -240 show these things:

1. The Wilcoxon test ( $p = 0.2754$ ) and the paired t-test ( $p = 0.3088$ ) indicate that the data are not different at the 95% confidence level.
2. The Pearson Correlation indicates that the data sets track well ( $r = 0.9999$ ).

### **Isotopic Uranium and Total Uranium**

NMED and LANL uranium data are tabulated and graphed in Figure A-5. No uranium measurements were above LANL's 4.40 mg/kg upper limit for background or close to the 67 mg/kg SAL. Three NMED measurements were above the 2.72 mg/kg background mean for total uranium: LA Canyon @ SR-4 (4.32 mg/kg), Water Canyon @ SR-4 (3.27 mg/kg), and TA-49 AB-4A (2.90 mg/kg).

NMED converted its species-specific, isotopic uranium data to total uranium for the purposes of comparing the data with LANL. The conversions of each uranium isotope (234, 235 and 238) activity measurement to a mass measure are presented in Figure A-6. The descriptive statistics, histograms and comparative statistical tests for total uranium are presented in Figure A-7. The descriptive statistics and the data distributions suggest that some differences exist between NMED and LANL data for total uranium. NMED's mean for uranium is 2.20 mg/kg and LANL's is 1.29 mg/kg. The data also differed with respect to the statistics that describe the variability of the data distributions (range, kurtosis and skewness).

Statistical comparisons of uranium results confirm the data sets are significantly different; neither the Wilcoxon test nor the paired t-test indicate that the data are the same. Additionally, LANL's data exhibit a negative bias – the reported concentrations are consistently lower than NMED's. Finally, the Pearson test indicates that the data sets track poorly.

In summary, the statistical tests for uranium show these things:

1. The Wilcoxon test ( $p = 0.0098$ ) and the paired t-test ( $p = 0.0260$ ) indicate the data are different at the 95% confidence level.
2. The Pearson Correlation indicates poor tracking ( $r = 0.3021$ ).

The NMED/LANL comparisons indicate a significant difference between NMED data and LANL data. To determine the possible source of the difference, the collection and analytical processes were reviewed. The adequacy of LANL's sample collection methods appeared to be verified by the comparisons of other parameters described above. NMED's analytical laboratory quality-assurance results appeared to be normal and both the data transcription and calculations appeared to be without error. The methods used by LANL's analytical lab were known to differ from those employed by NMED's laboratory. LANL obtained its total uranium measurements using Kinetic

Phosphorescence Analysis (KPA), while NMED's lab obtained uranium isotopic measurements by alpha spectroscopy. NMED believed alpha spectroscopy to be a more quantitatively sensitive method, the results of which could be converted to "total uranium" and compared to KPA data.

LANL began using the KPA method for uranium measurements in 1993. Before this, a fluorometric method had been used from 1974 to 1976, and a Delayed Neutron Activation (DNA) method from 1977 to 1992 (Fresquez et al., 1996). The DNA method requires the use of a nuclear reactor. When LANL's Omega Reactor was retired from service in 1994, the Laboratory adopted the KPA method, which provides data on total uranium, as opposed to various isotopes.

To test the KPA method, NMED chose alpha spectroscopy to measure the uranium content in sediments. In order to compare its uranium radioactivity results with LANL's total uranium results, NMED converted its isotopic measurements to mass data using the specific activities for each isotope. Total uranium was then determined by summing the mass calculations of uranium - 234, -235, and -238. These conversions were expected to yield results similar to the total measurements presented by LANL. NMED's uranium-mass calculations were also compared to the uranium-mass ratios representing natural, enriched or depleted uranium (Shleien, 1992). The mass ratios from NMED's uranium measurements very closely matched those for natural uranium. Natural uranium isotope percentages are expected to be 0.005 % U-234, 0.7 % U-235 and 99.3 % U-238. The mean isotope percentages calculated by NMED are 0.005% U-234, 0.92% U-235, and 99.08 % U-238. This comparison tends to support the accuracy of its isotopic measurements.

Review of NMED's analytical laboratory's QA/QC results indicate the uranium spectrometry measurements were accurate. Analytical QA/QC blank measurements were near zero, indicating no laboratory cross-contamination. Relative percent differences of laboratory duplicates ranged from zero to 13% and chemical recovery of the blank spike sample was 86%. These measurements were all within acceptance criteria.

NMED initiated discussions with LANL ESH-18 staff and chemists from both analytical laboratories. These discussions suggested the possibility that the digestion method used by LANL resulted in a physical or chemical interference that led the KPA method to yield consistently low total-uranium measurements. Other variables in the chemical and physical preparation of the samples could also cause differences in analytical results.

The digestion methods for KPA and isotopic uranium by alpha spectroscopy are similar in that the sample is totally dissolved in hydrofluoric acid. KPA is performed on an aliquot of the dissolved-sample solution while isotopic uranium is performed on a precipitate of the solution. In the alpha spectroscopy method, the solution is treated with lanthanum fluoride to micro-precipitate the uranium. The precipitate is captured on filter paper which is then counted for alpha radiation. These discussions implied that measurements of uranium by KPA may be lowered when other naturally occurring elements in the sample combine with fluoride in the hydrofluoric acid, quenching the optical emissions of uranium during the KPA. Since isotopic uranium analysis measures alpha emissions, this fluorine interference does not occur.

Discussions with the NMED commercial laboratory revealed that complications exist for analysis of uranium in sediments by KPA. There are strong indications that the hydrofluoric acid in the



sample-digesting step negatively affects total-uranium recoveries by the KPA technique (Fry, personal communication, 1998). During the 1994-1995 sampling season, the LANL ER program submitted solid samples to Analytical Technologies, Incorporated (ATI, now Paragon Analytics, Inc.), for total uranium analysis by KPA. Each batch of samples included: 1) a single blind, total-uranium laboratory control sample, prepared with hydrofluoric acid by LANL's analytical lab, 2) a pair of LANL soil-matrix samples, spiked with uranium in nitric acid solutions, and 3) one pair of ATI laboratory control samples, spiked with uranium in nitric acid solutions. When hydrofluoric acid was used, the uranium recoveries were approximately 50% lower than for samples prepared with nitric acid. Hydrofluoric acid appeared to depress the uranium recoveries in ATI's sediment KPA analysis.

KPA may be an appropriate uranium-measurement method for water, foodstuff, or urine; however based on the findings in this report, KPA does not appear to be an appropriate method for analyzing uranium in sediments. Besides isotopic uranium analysis by alpha spectroscopy, other analytical methods may be superior to KPA for uranium in sediments: for example, inductive-coupled plasma, inductive-coupled-plasma mass spectroscopy, and delayed-neutron analysis. If KPA is used, alternative digestion methods should be considered.

## **Lead**

NMED and LANL lead data are tabulated and graphed in Figure A-8. One NMED measurement, Water Canyon @ SR-4 (26 mg/kg), is above the upper limit for background calculated for lead (24.4 mg/kg). Four measurements are above the means calculated for LANL regional stations (10.0 mg/kg); Los Alamos Canyon at SR 4 (16 mg/kg), Mortandad Canyon at MCO-13 (16 mg/kg), Water Canyon at SR 4 (26 mg/kg), and TA-49 AB 4A (15 mg/kg).

The descriptive statistics, histograms and the comparative statistical tests for lead are presented in Figure A-9. The histograms indicate that the NMED and LANL data distributions are similar. The mean of NMED data is 10.660 mg/kg and LANL's is 7.230 mg/kg.

Neither the Wilcoxon test nor the paired t-test show a significant difference between NMED and LANL data. The Wilcoxon and paired t-test indicate the data are from the same populations, and the Pearson test indicates that the data sets track well.

In summary, the statistical tests for lead showed these things:

1. The Wilcoxon test ( $p = 0.5782$ ) and the paired t-test ( $p = 0.1041$ ) indicate the data are not different at the 95% confidence level.
2. The Pearson Correlation indicates the data sets track well ( $r = 0.8575$ ).

## **Beryllium**

NMED and LANL beryllium data are tabulated and graphed in Figure A-10. There are no NMED beryllium measurements above the upper limit for background calculated for beryllium (2.6

mg/kg). Two measurements are above the means (0.82 mg/g) calculated for LANL regional stations; Water Canyon at SR 4 (1.2 mg/kg) and TA-49 AB-4A (0.9 mg/kg).

The descriptive statistics and histograms for beryllium are presented in Figure A-11. Of the 10 co-located NMED/LANL sampling sites, only two locations (Mortandad @ MCO-13 (A-5) and Water Canyon @ SR-4) have measurements above their respective detection limits for both NMED and LANL. The remaining sites have measurements in which both or one analysis of the data pair are below their respective detection limit. Of the data pairs where only one measurement is above its detection limit, one is contradictory. At TA-49 AB-4A, LANL's reported measurement is <0.13 mg/kg and the NMED measurement is 0.9 mg/kg. The remaining data pairs are comparable. NMED's mean for beryllium is 0.34 mg/kg and LANL's is 0.186 mg/kg. Breakdown of both data sets and the histograms demonstrate that beryllium results are similar, where 40% of NMED data and 50% of LANL's were above detection levels.

Because there were only two data pairs in which both values were above method detection limits, comparative statistics could not be used to conclusively identify differences. Although quantitative comparisons are not presented, the evaluation of analytical data, and descriptive and breakdown statistics indicate that LANL and NMED data are similar.

### Summary Comparisons

A summary test of all data for 1996 is tabulated and the data differences are graphed in Figure A-12. The Wilcoxon, t-Test and Pearson tests were run on two data sets, one that included all parameters at all stations, and another that included all data except uranium. Both sets of tests indicate the data are not significantly different, although a greater degree of reliability is recognized without the uranium data.

The statistical tests for the summary data showed these things:

1. Using all of the data, the Wilcoxon test indicates that the data are not different at the 95% confidence level ( $p=0.1082$ ). The paired t-test also indicates the means are not different at a 95% confidence level ( $p=0.0637$ ).
2. Using all the data with the exception of uranium, the Wilcoxon test indicates that the data are not different at the 95% confidence level ( $p=0.8342$ ). The paired t-test indicates that the means are not different at the 95% confidence level ( $p=0.1029$ ).
3. The Pearson Correlation indicate that the data sets tracked well with uranium data ( $r = 0.8726$ ) and ( $r = 0.8754$ ) without.

## CONCLUSIONS

NMED co-located 10 sediment samples with LANL ESH-18 during 1996 and had them analyzed for plutonium-238, plutonium -239,-240, isotopic uranium, lead and beryllium. These stations and

parameters are only a subset of the LANL environmental surveillance program for sediments. Statistical comparisons were then made on the resulting data to determine whether there was a difference between LANL results presented in their 1996 Environmental Surveillance Report and NMED's. The data comparisons and evaluations of their collection and analytical procedures support these conclusions:

1. The NMED/LANL plutonium-238 data appear to be in agreement, although the NMED results are slightly lower than LANL's.
2. The NMED/LANL data for plutonium -239 and -240 in sediments are in agreement. Statistical comparisons of plutonium 239,-240 levels indicate that NMED and LANL data do not differ significantly.
3. The LANL data for total uranium in sediments are not in agreement. NMED data on total uranium in sediment is significantly higher than data from LANL co-located samples. The difference appears to stem from the analytical techniques used by the separate laboratories. The analytical techniques used to measure uranium in sediments and the conclusions based on those measurements should be re-evaluated.
4. The NMED/LANL data for lead in sediments are in agreement. Statistical comparisons of the lead levels in sediments reported by LANL and NMED laboratories do not differ significantly.
5. The LANL data for beryllium in sediments appear to be in agreement. Because there were only two data pairs in which both values were above the detection limits, comparative statistics could not be used to conclusively identify differences. However, descriptive and breakdown statistics demonstrate that beryllium measurements by NMED and LANL are similar.
6. According to a summary comparison of both data sets, the data are in agreement.

Statistical comparisons of plutonium-239,-240, lead and beryllium data show that the Department's results agree with the Laboratory's results and that Department's plutonium -238 results were slightly lower than the Laboratory's results. Based on our evaluation of collection methods, analytical procedures, and statistical comparisons of results, LANL's data for these constituents are accurate.

Statistical comparisons of uranium data show that the Department's isotopic total uranium results did not agree and were greater than the Laboratory's non-isotopic total uranium results. Based on this evaluation, the analytical techniques used by LANL to measure uranium in sediments and the conclusions based on those measurements should be re-evaluated.

All constituents were measured at levels below health-based standards and guidelines.

## ACKNOWLEDGMENTS

Figures 1 and 2, were digitized by Alice Mayer from U.S.G.S. 7.5' quadrangles and sample location coordinates from the 1995 ESR. Thanks to Dr. Bruce Swanton for his editing efforts and to Dr. William Stone, Dr. David Beach, David Bagget and Tim Michael for their review and comments. LANL ESH-18 personnel, particularly Max Maes, made this report possible by their coordination efforts and technical help during the 1996 sampling season.

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APPENDIX  
STATISTICAL AND ANALYTICAL DATA

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LOCATION	DOE OB Pu-238 pCi/g		LANL Pu-238 pCi/g	
	reported value	uncertainty <sup>1</sup> TPU ( 2sigma)	reported value	uncertainty <sup>2</sup> (1sigma)
LA Canyon @ SR-4	0.01	0.01	0.001	0.000
Mortandad @ MCO-5	2.06	0.26	2.220	0.110
Mortandad @ MCO-13 (A-5)	0.00	0.01	0.002	0.001
TA-54 G-7	0.20	0.04	0.243	0.004
TA-54 G-8	0.08	0.04	0.119	0.008
TA-54 G-9	0.03	0.02	0.091	0.005
Potrillo @ SR4	0.00	0.01	0.001	0.001
Water Canyon @ SR4	0.00	0.04	0.001	0.001
TA-49 AB-4A	0.00	0.02	0.003	0.002
TA-49 AB-11	0.00	0.01	0.000	0.001

<sup>1</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc.

<sup>2</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

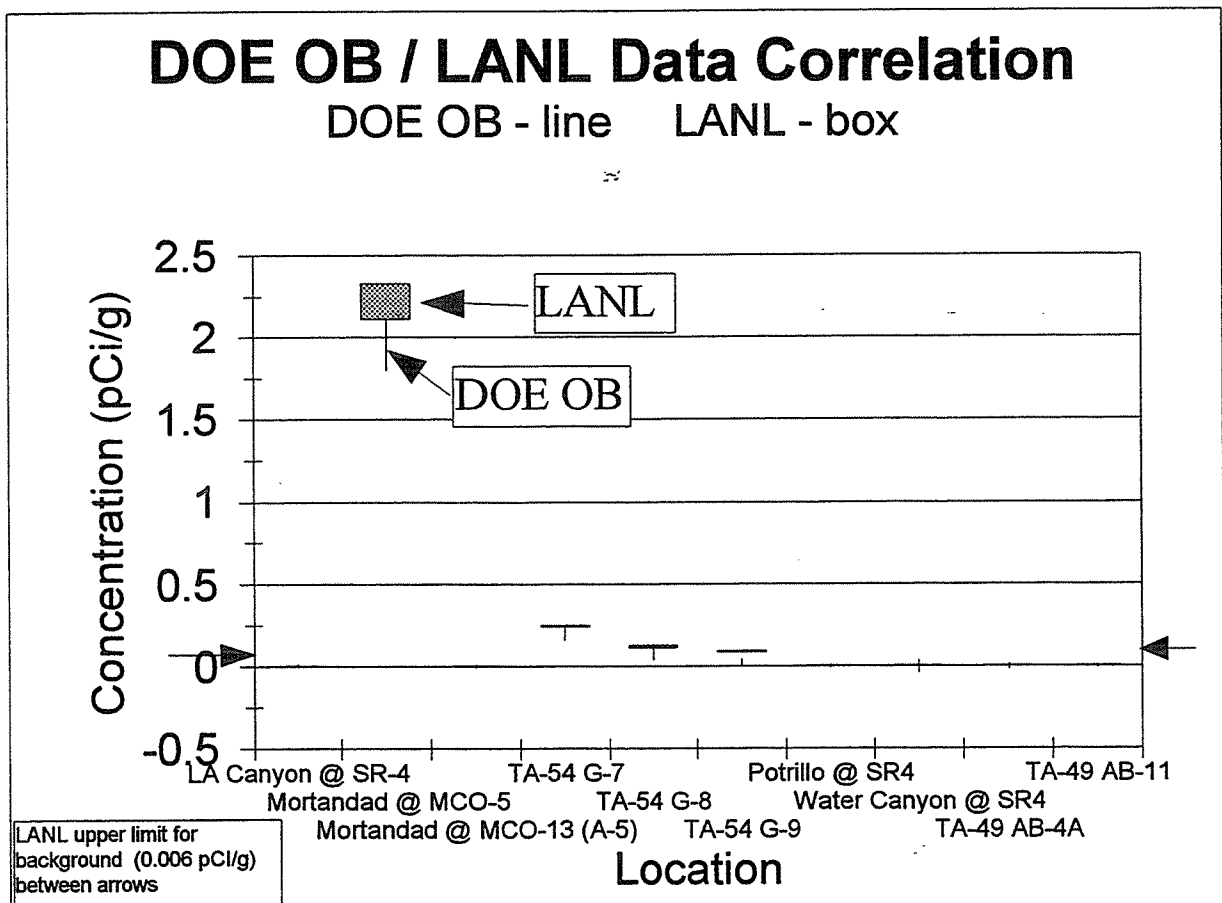


Figure A-1. NMED / LANL plutonium-238 1996 sediment surveillance data and correlation

LOCATION	DOE OB Pu238 pCi/g		LANL Pu238 pCi/g	
	reported value	uncertainty <sup>1</sup> TPU (2sigma)	reported value	uncertainty <sup>2</sup> (1sigma)
LA Canyon @ SR-4	0.01	0.01	0.001	0.000
Mortandad @ MCO-5	2.06	0.26	2.220	0.110
Mortandad @ MCO-13 (A-5)	0.00	0.01	0.002	0.001
TA-54 G-7	0.20	0.04	0.243	0.004
TA-54 G-8	0.08	0.04	0.119	0.008
TA-54 G-9	0.03	0.02	0.091	0.005
Potrillo @ SR4	0.00	0.01	0.001	0.001
Water Canyon @ SR4	0.00	0.04	0.001	0.001
TA-49 AB-4A	0.00	0.02	0.003	0.002
TA-49 AB-11	0.00	0.01	0.000	0.001

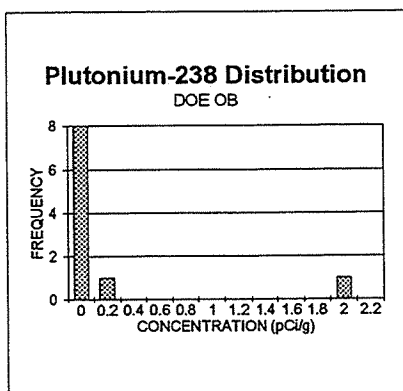
<sup>1</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc.

<sup>2</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

#### Descriptive Statistics

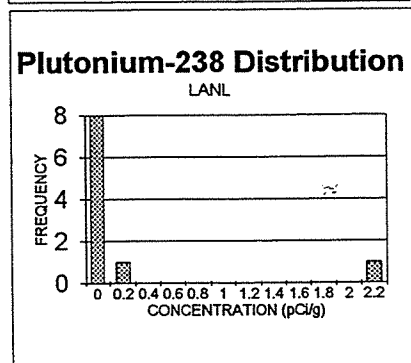
##### DOE OB

Mean	0.238
Median	0.005
Standard Deviation	0.643
Kurtosis	9.732
Skewness	3.107
Range	2.060
Minimum	0.000
Maximum	2.060



##### LANL

Mean	0.268
Median	0.003
Standard Deviation	0.691
Kurtosis	9.627
Skewness	3.085
Range	2.220
Minimum	0.000
Maximum	2.220



#### STATISTICAL COMPARISONS

##### Results:

Wilcoxon:	n=9	P=0.0390	(96.10% confident that data sets are from different populations)
t-Test:	n=10	P=0.0968	(90.32% confident that data sets are from different populations)
Pearson:	n=10	r=0.9995	(data sets track well)

X	Y	X-Y	X-Y	Rank	Bin	Frequency
0.01	0.001	0.009	0.009	5	-0.160	0
2.06	2.220	-0.16	0.16	9	-0.131	0
0.00	0.002	-0.002	0.002	3	-0.102	0
0.20	0.243	-0.043	0.043	7	-0.073	1
0.08	0.119	-0.039	0.039	6	-0.044	2
0.03	0.091	-0.061	0.061	8	-0.015	5
0.00	0.001	-0.001	0.001	1.5	0.015	0
0.00	0.001	-0.001	0.001	1.5	0.044	0
0.00	0.003	-0.003	0.003	4	0.073	0
					0.102	0
					0.131	0

0.0291  
X-Y groups are 0.029 units wide

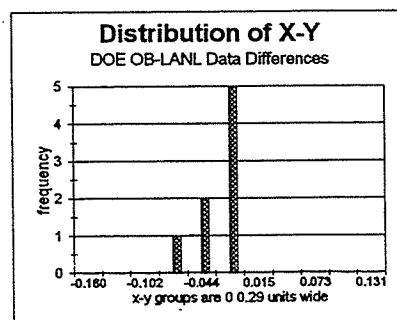


Figure A-2. NMED statistical comparisons of NMED/LANL1996 plutonium-238 data for sediments

LOCATION	DOE OB Pu-239/240 (pCi/g)		LANL Pu-239/240 (pCi/g)	
	reported value	uncertainty <sup>1</sup> TPU ( 2sigma)	reported value	uncertainty <sup>2</sup> (1sigma)
LA Canyon @ SR-4	0.10	0.02	0.088	0.004
Mortandad @ MCO-5	5.59	0.68	8.250	0.33
Mortandad @ MCO-13 (A-5)	0.02	0.01	0.026	0.002
TA-54 G-7	0.19	0.04	0.174	0.011
TA-54 G-8	0.08	0.03	0.150	0.009
TA-54 G-9	0.02	0.01	0.040	0.003
Potrillo @ SR4	0.00	0.01	0.006	0.001
Water Canyon @ SR4	0.01	0.01	0.011	0.002
TA-49 AB-4A	0.01	0.01	0.013	0.002
TA-49 AB-11	0.01	0.01	0.007	0.002

<sup>1</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc.

<sup>2</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

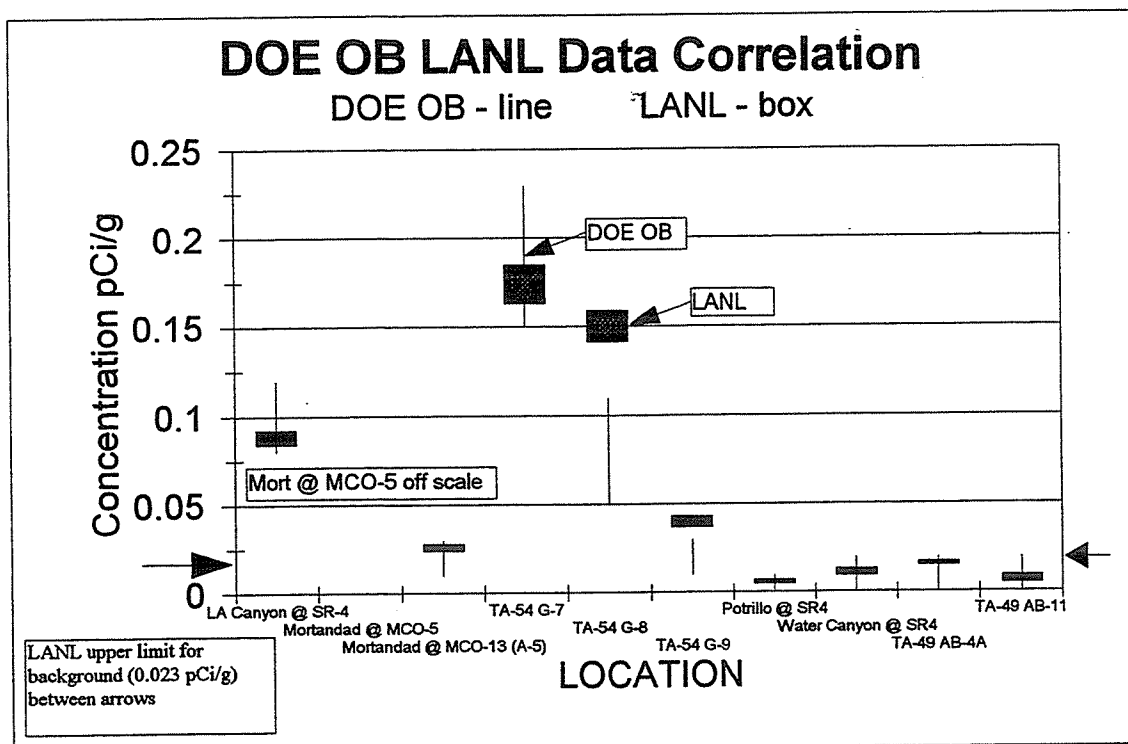


Figure A-3. NMED / LANL plutonium-239,-240 1996 sediment surveillance data and correlation



LOCATION	DOE OB Pu-239/240 (pCi/g)		LANL Pu-239/240 (pCi/g)	
	reported uncertainty <sup>1</sup>		reported uncertainty <sup>2</sup>	
	value	TPU (2sigma)	value	(1sigma)
LA Canyon @ SR-4	0.10	0.02	0.088	0.004
Mortandad @ MCO-5	5.59	0.68	8.250	0.33
Mortandad @ MCO-13 (A-5)	0.02	0.01	0.026	0.002
TA-54 G-7	0.19	0.04	0.174	0.011
TA-54 G-8	0.08	0.03	0.150	0.009
TA-54 G-9	0.02	0.01	0.040	0.003
Potrillo @ SR4	0.00	0.01	0.006	0.001
Water Canyon @ SR4	0.01	0.01	0.011	0.002
TA-49 AB-4A	0.01	0.01	0.013	0.002
TA-49 AB-11	0.01	0.01	0.007	0.002

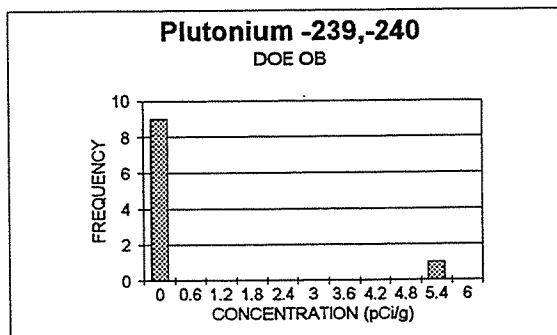
<sup>1</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc.

<sup>2</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

## DESCRIPTIVE STATISTICS

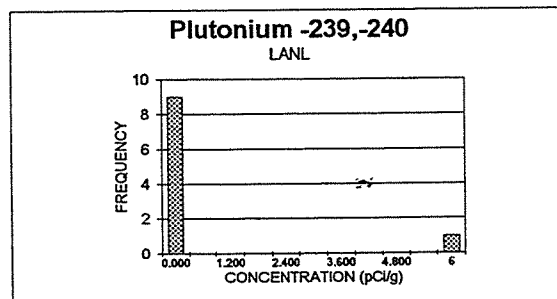
### DOE OB

Mean	0.603
Median	0.020
Standard Deviation	1.753
Kurtosis	9.968
Skewness	3.155
Range	5.590
Minimum	0.000
Maximum	5.590



### LANL

Mean	0.876
Median	0.033
Standard Deviation	2.592
Kurtosis	9.985
Skewness	3.159
Range	8.244
Minimum	0.006
Maximum	8.250



## STATISTICAL COMPARISON

### Results:

Wilcoxon:	n=10	P=0.2754	(72.46% confident that data sets are from different populations)
t-Test:	n=10	P=0.3088	(69.12% confident that data sets are from different populations)
Pearson:	n=10	r=0.9999	(data sets track well)

X	Y	X-Y	X-Y	Rank	Bin	Frequency
0.10	0.088	0.012	0.012	6	-2.660	1
5.59	8.250	-2.66	2.66	10	-2.176	0
0.02	0.026	-0.006	0.006	4	-1.693	0
0.19	0.174	0.016	0.016	7	-1.209	0
0.08	0.150	-0.07	0.07	9	-0.725	0
0.02	0.040	-0.02	0.02	8	-0.242	9
0.00	0.006	-0.006	0.006	5	0.242	0
0.01	0.011	-0.001	0.001	1	0.725	0
0.01	0.013	-0.003	0.003	2	1.209	0
0.01	0.007	0.003	0.003	3	1.693	0
					2.176	0

-2.660

0.484

X-Y groups are 0.484 units wide

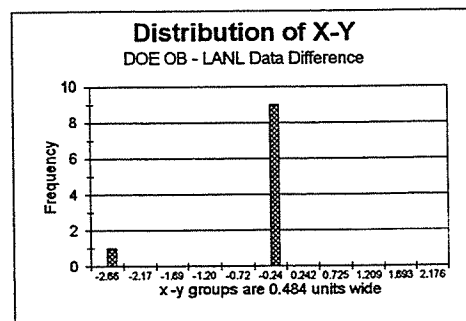


Figure A-4. NMED statistical comparisons of NMED/LANL 1996 plutonium-239, -240 data for sediments

LOCATION	DOE OB Total U by calculation <sup>1</sup> mg/kg		LANL Total U by KPA measurement mg/kg	
	calculated value	uncertainty <sup>2</sup> TPU ( 2sigma)	reported value	uncertainty <sup>3</sup> (1sigma)
LA Canyon @ SR-4	4.32	0.64	1.09	0.11
Mortandad @ MCO-5	0.87	0.18	1.36	0.14
Mortandad @ MCO-13 (A-5)	2.19	0.37	1.24	0.12
TA-54 G-7	1.75	0.38	0.88	0.09
TA-54 G-8	1.98	0.31	1.36	0.14
TA-54 G-9	1.90	0.37	1.77	0.18
Potrillo @ SR4	1.57	0.28	1.22	0.12
Water Canyon @ SR4	3.27	0.49	1.84	0.18
TA-49 AB-4A	2.90	0.43	1.62	0.16
TA-49 AB-11	1.23	0.22	0.48	0.05

<sup>1</sup> Total uranium concentration derived from Paragon Analytics, Inc. reported isotopic activity and activity to mass calculations.

<sup>2</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc. and converted to mass

<sup>3</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

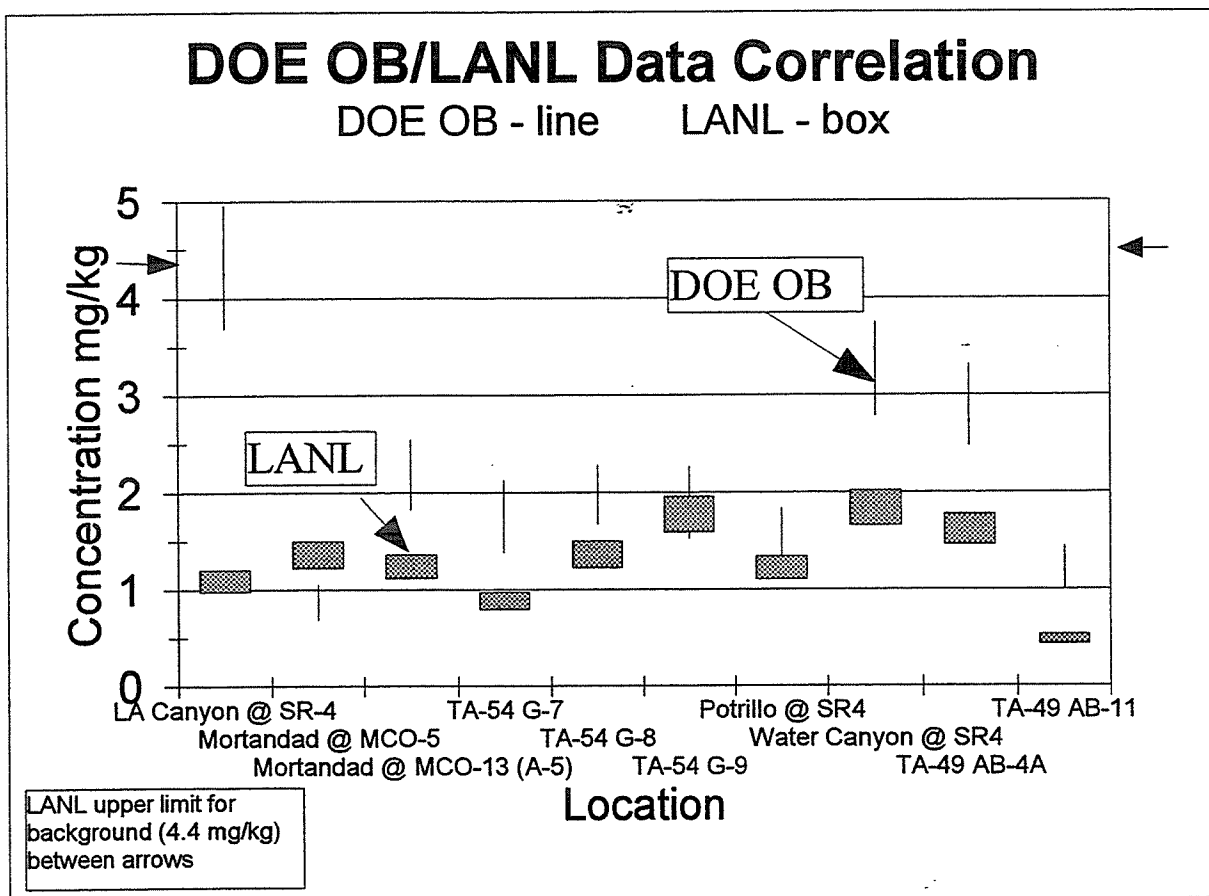


Figure A-5. NMED / LANL total uranium 1996 sediment surveillance data and correlation

### Isotopic Analysis

From "The Health Physics and Radiological Health Handbook,"  
By B. Shleien

LOCATION	U 234 (pCi/g)	U-235 (pCi/g)	U-238 (pCi/g)
LA Canyon @ SR-4	1.52 +/- 0.21	0.08 +/- 0.03	1.44 +/- 0.21
Mortandad @ MCO-5	0.25 +/- 0.05	0.02 +/- 0.01	0.29 +/- 0.06
Mortandad @ MCO-13 (A-5)	0.81 +/- 0.12	0.03 +/- 0.02	0.73 +/- 0.12
TA-54 G-7	0.67 +/- 0.14	0.06 +/- 0.04	0.58 +/- 0.12
TA-54 G-8	0.62 +/- 0.10	0.03 +/- 0.02	0.66 +/- 0.10
TA-54 G-9	0.58 +/- 0.12	0.05 +/- 0.03	0.63 +/- 0.12
Potrillo @ SR4	0.52 +/- 0.09	0.04 +/- 0.02	0.52 +/- 0.09
Water Canyon @ SR4	0.90 +/- 0.14	0.05 +/- 0.02	1.09 +/- 0.16
TA-49 AB-4A	0.79 +/- 0.12	0.03 +/- 0.02	0.97 +/- 0.14
TA-49 AB-11	0.38 +/- 0.07	0.02 +/- 0.02	0.41 +/- 0.07

	Half Life (yr)	Specific Activity (Ci/g)
U-234	244,500	6.25E-03
U-235	7.04E+08	2.16E-06
U-238	4.47E+09	3.36E-07

ABUNDANCE (%)		
U-234	U-235	U-238
U NATURAL	0.72	99.276
U ENRICHED	93.29	5.61
UDEPLETED	0.25	99.75

### Uranium Activity Converted to Mass Calculations

### Percentages of Isotope Mass

	U 234 (mg/kg)	U 235 (mg/kg)	U-238 (mg/kg)	Total U (mg/kg)
LA Canyon @ SR-4	2.43E-04	3.70E-02	4.29E+00	4.32E+00
Mortandad @ MCO-5	4.00E-05	9.26E-03	8.63E-01	8.72E-01
Mortandad @ MCO-13 (A-5)	1.30E-04	1.39E-02	2.17E+00	2.19E+00
TA-54 G-7	1.07E-04	2.78E-02	1.73E+00	1.75E+00
TA-54 G-8	9.92E-05	1.39E-02	1.96E+00	1.98E+00
TA-54 G-9	9.28E-05	2.31E-02	1.88E+00	1.90E+00
Potrillo @ SR4	8.32E-05	1.85E-02	1.55E+00	1.57E+00
Water Canyon @ SR4	1.44E-04	2.31E-02	3.24E+00	3.27E+00
TA-49 AB-4A	1.26E-04	1.39E-02	2.89E+00	2.90E+00
TA-49 AB-11	6.08E-05	9.26E-03	1.22E+00	1.23E+00

	% U 234 mass	% U 235 mass	% U 238 mass
LA Canyon @ SR-4	5.626E-03	0.857	99.138
Mortandad @ MCO-5	4.585E-03	1.061	98.934
Mortandad @ MCO-13 (A-5)	5.927E-03	0.635	99.359
TA-54 G-7	6.111E-03	1.584	98.410
TA-54 G-8	5.014E-03	0.702	99.293
TA-54 G-9	4.889E-03	1.219	98.776
Potrillo @ SR4	5.312E-03	1.182	98.812
Water Canyon @ SR4	4.407E-03	0.708	99.287
TA-49 AB-4A	4.357E-03	0.479	99.517
TA-49 AB-11	4.945E-03	0.753	99.242

Mean 0.00512 0.9181 99.0768

Figure A-6. Isotopic uranium conversions to total mass and uranium signature

LOCATION	DOE OB Total U by calculation <sup>1</sup> mg/kg		LANL Total U by KPA measurement mg/kg	
	calculated value	uncertainty <sup>2</sup> TPU (2sigma)	reported value	uncertainty <sup>3</sup> (1sigma)
LA Canyon @ SR-4	4.32	0.64	1.09	0.11
Mortandad @ MCO-5	0.87	0.18	1.36	0.14
Mortandad @ MCO-13 (A-5)	2.19	0.37	1.24	0.12
TA-54 G-7	1.75	0.38	0.88	0.09
TA-54 G-8	1.98	0.31	1.36	0.14
TA-54 G-9	1.90	0.37	1.77	0.18
Potrillo @ SR4	1.57	0.28	1.22	0.12
Water Canyon @ SR4	3.27	0.49	1.84	0.18
TA-49 AB-4A	2.90	0.43	1.62	0.16
TA-49 AB-11	1.23	0.22	0.48	0.05

<sup>1</sup> Total uranium concentration derived from Paragon Analytics, Inc. reported isotopic activity and activity to mass calculations.

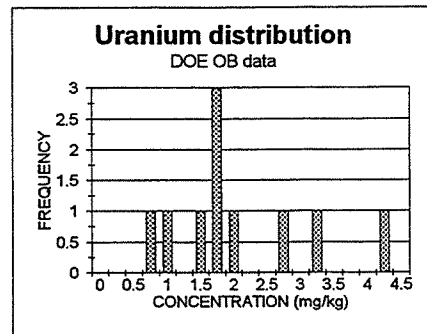
<sup>2</sup> Total Propagated Uncertainty as reported by Paragon Analytics, Inc. and converted to mass

<sup>3</sup> Uncertainty as reported by LANL's analytical laboratory (CST-9)

## Descriptive Statistics

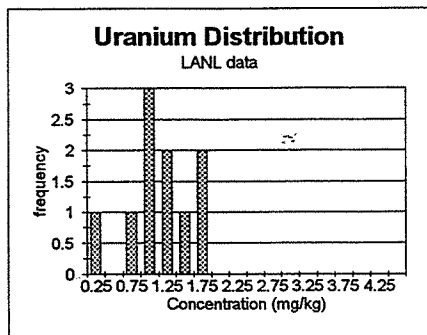
### DOE OB

Mean	2.20
Median	1.94
Standard Deviation	1.03
Kurtosis	0.69
Skewness	0.96
Range	3.45
Minimum	0.87
Maximum	4.32



### LANL

Mean	1.29
Median	1.30
Standard Deviation	0.41
Kurtosis	0.33
Skewness	-0.55
Range	1.36
Minimum	0.48
Maximum	1.84



## Comparative Statistics

### Results:

Wilcoxon:	n=10	P=0.0098	(99.02% confident that data sets are from different populations)
t-Test:	n=10	P=0.0260	(97.40% confident that data sets are from different populations)
Pearson:	n=10	r=0.3021	(data sets track poorly)

X	Y	X-Y	X-Y	Rank	Bin	Frequency
4.32	1.09	3.23	3.233	10	-3.233	0
0.87	1.36	-0.49	0.488	3	-2.645	0
2.19	1.24	0.95	0.947	7	-2.057	0
1.75	0.88	0.87	0.874	6	-1.469	0
1.98	1.36	0.62	0.618	4	-0.882	1
1.90	1.77	0.13	0.128	1	-0.294	1
1.57	1.22	0.35	0.346	2	0.294	4
3.27	1.84	1.43	1.427	9	0.882	3
2.90	1.62	1.28	1.281	8	1.469	0
1.23	0.48	0.75	0.749	5	2.057	0
					2.645	1

-3.233

0.588

X-Y groups are 0.5878 units wide

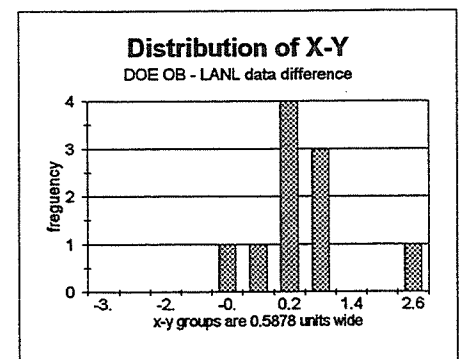


Figure A-7. NMED statistical comparisons of NMED/LANL1996 total uranium data for sediments

LOCATION	DOE OB Lead (mg/kg) reported value	LANL Lead (mg/kg) reported value
LA Canyon @ SR-4	16	17.20
Mortandad @ MCO-5	2.7	<5.70 <sup>1,2</sup>
Mortandad @ MCO-13 (A-5)	16	<5.70
TA-54 G-7	4.6	6.30
TA-54 G-8	7.3	9.20
TA-54 G-9	5.5	3.40
Potrillo @ SR4	8.4	<5.41
Water Canyon @ SR4	26	16.60
TA-49 AB-4A	15	16.90
TA-49 AB-11	5.1	2.70

<sup>1</sup> < indicates level below detection limit

<sup>2</sup> values were reported as below detection limit, 1/2 detection value plotted on graph below

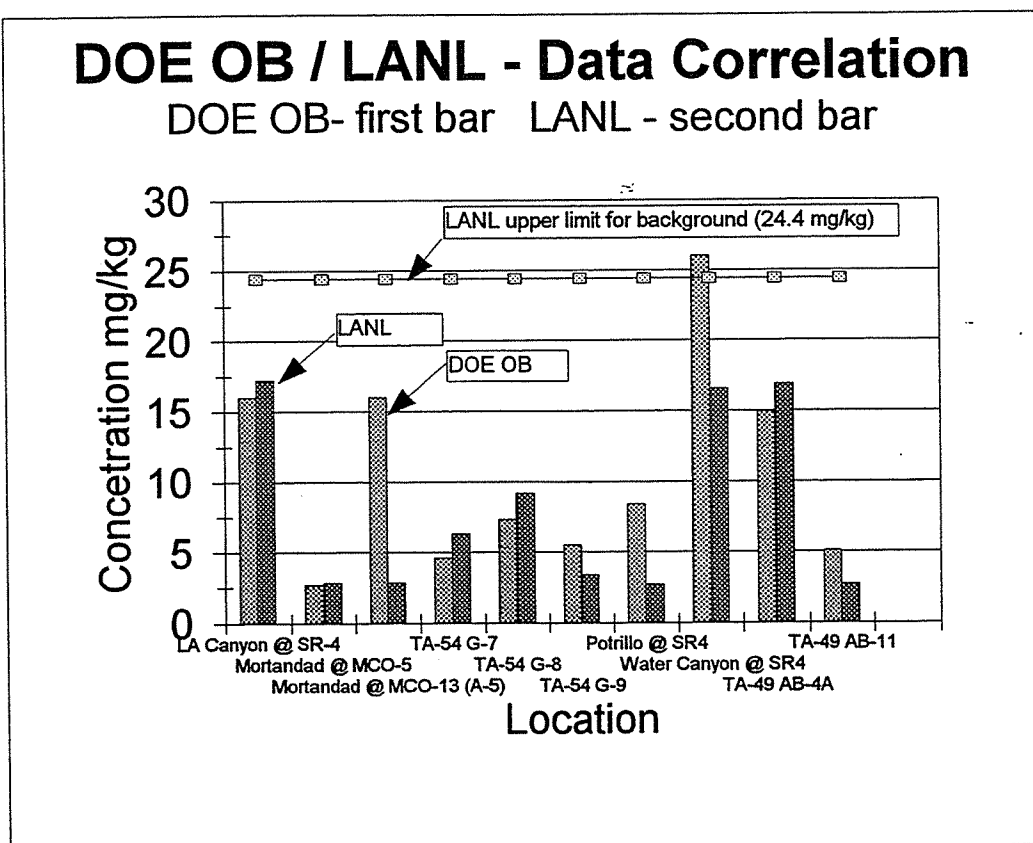


Figure A-8. NMED / LANL lead 1996 sediment surveillance data and correlation

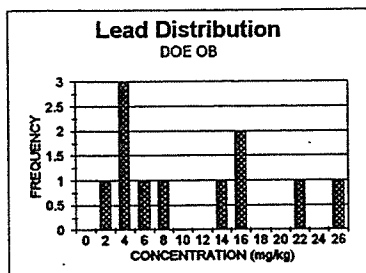
LOCATION	DOE OB Lead (mg/kg) reported value	LANL Lead (mg/kg) reported value
LA Canyon @ SR-4	16	17.20
Mortandad @ MCO-5	2.7	<5.70 <sup>1,2</sup>
Mortandad @ MCO-13 (A)	16	<5.70
TA-54 G-7	4.6	6.30
TA-54 G-8	7.3	9.20
TA-54 G-9	5.5	3.40
Potrillo @ SR4	8.4	<5.41
Water Canyon @ SR4	26	16.60
TA-49 AB-4A	15	16.90
TA-49 AB-11	5.1	2.70

<sup>1</sup> < indicates level below detection limit  
<sup>2</sup> value was reported as below detection limit

#### Descriptive Statistics

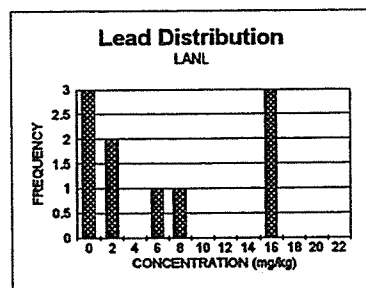
##### DOE OB

Mean	10.660
Median	7.850
Standard Deviation	7.342
Kurtosis	0.507
Skewness	1.021
Range	23.300
Minimum	2.700
Maximum	26.000



##### LANL

Mean	7.230
Median	9.200
Standard Deviation	7.284
Kurtosis	-2.367
Skewness	0.010
Range	14.500
Minimum	0.000
Maximum	17.200



#### Comparative Statistics

##### Results:

Wilcoxon:	n=7	P=0.5782	(42.18% confident that data sets are from different populations)
t-Test:	n=10	P=0.1041	(89.59% confident that data sets are from different populations)
Pearson:	n=10	r=0.8575	(data sets track well)

X	Y	X-Y	X-Y	Rank	Bin	Frequency
16	17.20	-1.2	1.2	1	-9.4	0
4.6	6.30	-1.7	1.7	2	-7.7	0
7.3	9.20	-1.9	1.9	4	-6.0	0
5.5	3.40	2.1	2.1	5	-4.3	0
26	16.60	9.4	9.4	7	-2.6	4
15	16.90	-1.9	1.9	3	-0.9	0
5.1	2.70	2.4	2.4	6	0.9	2
					2.6	0
					4.3	0
					6.0	0
					7.7	1
					-9.4	

1.71  
X-Y groups are 1.709 units wide

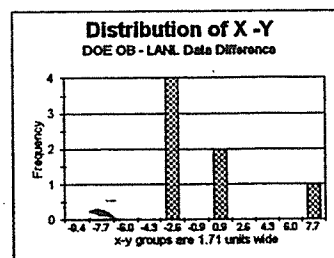


Figure A-9. NMED statistical comparisons of NMED/LANL1996 lead data for sediments

LOCATION	DOE OB Beryllium (mg/kg) reporting value	LANL Beryllium (mg/kg) reporting value
LA Canyon @ SR-4	<0.5 <sup>1,2</sup>	0.44
Mortandad @ MCO-5	<0.5	0.23
Mortandad @ MCO-13 (A-5)	0.7	0.32
TA-54 G-7	<0.5	<0.12
TA-54 G-8	<0.5	0.31
TA-54 G-9	<0.5	<0.12
Potrillo @ SR4	0.6	<1.18
Water Canyon @ SR4	1.2	0.56
TA-49 AB-4A	0.9	<0.13
TA-49 AB-11	<0.5	<0.13

<sup>1</sup> < indicates level below detection limit

<sup>2</sup> value was reported as below detection limit, 1/2 detection value plotted on graph below

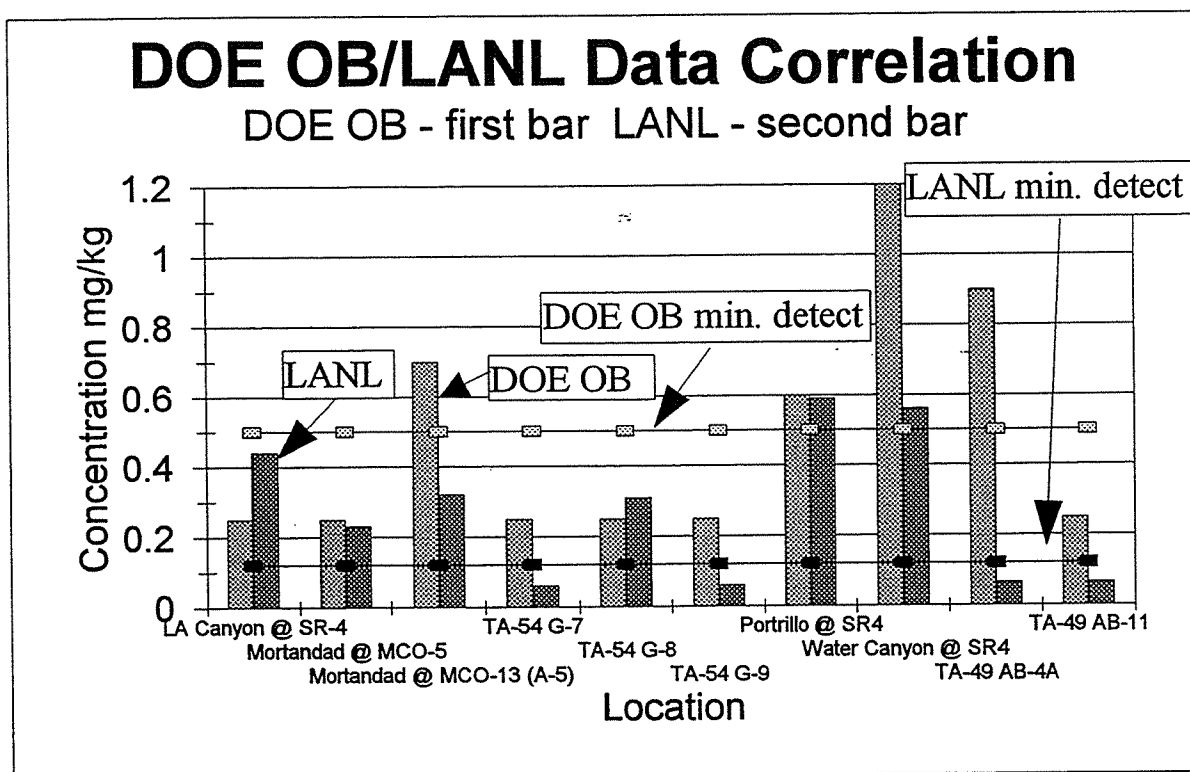


Figure A-10. NMED / LANL beryllium 1996 sediment surveillance data and correlation

LOCATION	DOE OB Beryllium (mg/kg) reporting value	LANL Beryllium (mg/kg) reporting value
LA Canyon @ SR-4	<0.5 <sup>1,2</sup>	0.44
Mortandad @ MCO-5	<0.5	0.23
Mortandad @ MCO-13	0.7	0.32
TA-54 G-7	<0.5	<0.12
TA-54 G-8	<0.5	0.31
TA-54 G-9	<0.5	<0.12
Potrillo @ SR4	0.6	<1.18
Water Canyon @ SR4	1.2	0.56
TA-49 AB-4A	0.9	<0.13
TA-49 AB-11	<0.5	<0.13

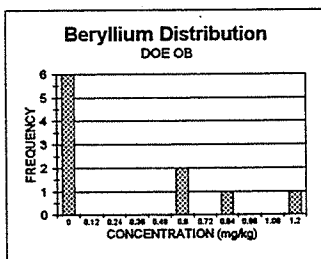
<sup>1</sup> < indicates level below detection limit

<sup>2</sup> value was reported as below detection limit

#### Descriptive Statistics

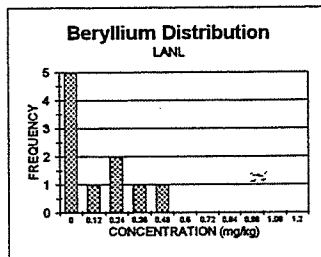
##### DOE OB

Mean	0.340
Median	0.800
Standard Deviation	0.465
Range	0.600
Minimum	0.000
Maximum	1.200



##### LANL

Mean	0.186
Median	0.320
Standard Deviation	0.214
Range	0.330
Minimum	0.000
Maximum	0.560



#### Statistical Comparison

##### Results:<sup>1</sup>

Wilcoxon: <sup>2</sup>	n=2	P=0.05935	(94.07% confident that data sets are from different populations)
t-Test:	n=10	P=0.2886	(71.14% confident that data sets are from different populations)
Pearson:	n=10	r=1.0000	(data sets track well)

<sup>1</sup>Only two comparisons are possible, results reported above are extremely unreliable

<sup>2</sup>Wilcoxon run with Statistica program, using 1/2 detection values for non-detects

X	Y	X-Y	X-Y	Rank	Bin	Frequency
0.7	0.32	0.38	0.38	1	-0.640	0
1.2	0.56	0.64	0.64	2	-0.524	0
					-0.407	0
					-0.291	0
					-0.175	0
					-0.058	0
					0.058	0
					0.175	0
					0.291	1
					0.407	0
					0.524	1
					-0.640	

0.11636

X-Y groups are 0.1163 units wide

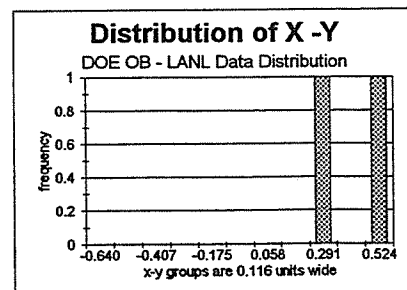


Figure A-11. NMED statistical comparisons of NMED/LANL1996 beryllium data for sediments



### Summary statistics including uranium

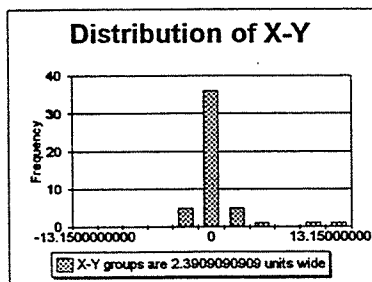
DOE OB LANL  
Rep Value Rep Value

Pu 239/240	0.10	0.088
	5.59	8.250
	0.02	0.026
	0.19	0.174
	0.08	0.150
	0.02	0.040
	0.00	0.006
	0.01	0.011
	0.01	0.013
	0.01	0.007
Pu 238	0.01	0.001
	2.06	2.220
	0.00	0.002
	0.20	0.243
	0.08	0.119
	0.03	0.091
	0.00	0.001
	0.00	0.001
	0.00	0.003
	0.00	0.000
Total U	4.32	1.09
	0.87	1.36
	2.19	1.24
	1.75	0.88
	1.98	1.36
	1.90	1.77
	1.57	1.22
	3.27	1.84
	2.90	1.62
	1.23	0.48
Pb	16.00	17.20
	2.70	2.85
	16.00	2.85
	4.60	6.30
	7.30	9.20
	5.50	3.40
	8.40	2.71
	26.00	16.60
	15.00	16.90
	5.10	2.70
Be	0.25	0.44
	0.25	0.23
	0.70	0.32
	0.25	0.06
	0.25	0.31
	0.25	0.06
	0.60	0.56
	1.20	0.56
	0.90	0.07
	0.03	0.07

values reported below detection limits were included as 1/2 value

#### Descriptive Statistics

Mean	2.83	2.15
Median	0.65	0.38
Standard Deviation	5.18	4.25
Kurtosis	8.72	7.20
Skewness	2.83	2.78
Range	26.00	17.20
Minimum	0.00	0.00
Maximum	26.00	17.20



#### Results:

Wilcoxon: n=49 P=0.1082 (89.2% confident that data sets are from different populations)  
t-Test: n=50 P=0.0637 (93.6% confident that data sets are from different populations)  
Pearson: n=50 r=0.8726 (data sets track well)

### Summary statistics without uranium

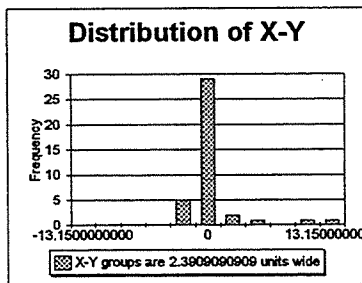
DOE OB LANL  
Rep Value Rep Value

Pu 239/240	0.10	0.088
	5.59	8.250
	0.02	0.026
	0.19	0.174
	0.08	0.150
	0.02	0.040
	0.00	0.006
	0.01	0.011
	0.01	0.013
	0.01	0.007
Pu 238	0.01	0.001
	2.06	2.220
	0.00	0.002
	0.20	0.243
	0.08	0.119
	0.03	0.091
	0.00	0.001
	0.00	0.001
	0.00	0.003
	0.00	0.000
Pb	16.00	17.20
	2.70	2.85
	16.00	2.85
	4.60	6.30
	7.30	9.20
	5.50	3.40
	8.40	2.71
	26.00	16.60
	15.00	16.90
	5.10	2.70
Be	0.25	0.44
	0.25	0.23
	0.70	0.32
	0.25	0.06
	0.25	0.31
	0.25	0.06
	0.60	0.56
	1.20	0.56
	0.90	0.07
	0.03	0.07

values reported below detection limits were included as 1/2 value

#### Descriptive Statistics

Mean	2.99	2.37
Median	0.25	0.16
Standard Deviation	5.78	4.73
Kurtosis	6.45	5.00
Skewness	2.51	2.41
Range	26.00	17.20
Minimum	0.00	0.00
Maximum	26.00	17.20



#### Results:

Wilcoxon: n=39 P=0.8342 (16.6% confident that data sets are from different populations)  
t-Test: n=40 P=0.1029 (89.7% confident that data sets are from different populations)  
Pearson: n=40 r=0.8754 (data sets track well)

Figure A-12. Summary statistics

