LANL

XI

CONFIDENTIAL

RESPONSE TO NMED COMPLIANCE ORDER 94-09, FINDING 12

NMED Finding:

"Respondents have failed to conduct an adequate hazardous waste determination on metal-containing wastes removed from a septic tank at the TA-0-030(g) former Catholic Church site, in violation of §30I of HMMR-7, which incorporates federal regulation 40 CFR §262.11."

XI

LANL Response:

The following discussion is divided into two parts. The first part reviews EPA guidance contained in SW-846 [Test Methods for Evaluating Solid Waste. Volume II: Field Manual. Third Edition. Office of Solid Waste and Emergency Response, SW-846, November 1986] on what constitutes "adequate" hazardous waste determination for solid wastes. The second part applies this guidance to demonstrate that the existing data from the SWMU 0-030(g) septic tank are adequate for TCLP characterization of the waste from that site.

Regulatory guidance on characterization of solid waste

The only published regulatory guidance on what constitutes "adequate" characterization of non-listed chemicals in a solid waste is found in SW-846, Chapter 9. In particular, Page NINE-6 of this document states:

> "The two sample values, $\bar{x}$ and $s_{\bar{x}}$, are used to estimate the interval within which the true mean (μ) of the chemical concentration probably occurs, under the assumption that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which μ occurs *if the sample is representative*, which is expected of about 80 out of 100 samples. *The upper limit of the 80% CI is then compared with the appropriate regulatory threshold.* If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable) there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, *the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.*" (our italics)

(Please notice that this quote, as well as the following discussion, uses the word "sample" in its statistical sense, as the set of observations, not a single physical sample on which one or more observations are made. A physical sample will be called a "specimen" below, to avoid confusion. "Sample values", like the sample mean $\bar{x}$ and the standard error of the mean $s_{\bar{x}}$, are calculated from such a set of observations using, for example, formulas given in Table 9-1 of SW-846. The "sample maximum" is the largest observation in the set. "Sample size" refers to the number of independent observations in the sample. The sample size, denoted by n or N, is usually equal to the number of specimens measured, but adjustments need to be made if the

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sample includes splits or duplicate pairs of specimens on which the observations can not be considered to be statistically independent.)

Guidance provided by the above excerpt from SW-846 is summarized by the following statement:

> **Whether or not a chemical is present at unacceptable levels in a solid waste is to be judged by comparing a 90% upper confidence bound (UCB) on the mean concentration of the chemical in the waste with the regulatory threshold. This upper confidence bound should be calculated using sample statistics based on a representative sample of the solid waste.**

This statement applies whether the waste is relatively homogeneous or very heterogenous. If possible, however, a heterogeneous solid waste should be stratified to increase homogeneity within strata, and the formulas for $\bar{x}$ and $s_{\bar{x}}$ based on a stratified sample should be used, as given in Table 9-1 of SW-846. (Whether or not stratification is feasible depends in general on the availability of rapid and inexpensive ways to sort the waste at the site, such as field screening or knowledge of process.)

A key phrase in the SW-846 guidance is that the sample should be "representative". "Representative" is defined on page NINE-5 of SW-846 as "exhibiting average properties of the whole waste". For example, selecting for TCLP analysis only those specimens for which total metal concentrations exceeds the 10- or 20-fold limit, or even all of those samples plus some subset of the remaining ones, does <u>not</u> produce a representative sample. The most generally accepted way of generating a representative samples involves the use of randomization.

The other key point of the SW-846 guidance is, of course, that a solid waste shall not be considered to exceed the regulatory limit on the basis of a single observation above the regulatory threshold. The statistic to be compared with the regulatory threshold is not the sample maximum, but an upper confidence bound on the sample mean.

A waste is thus considered to be adequately characterized when the following conditions are met:

1) **At least four measurements have been made.** The minimum number four appears in several EPA documents and is reiterated on page NINE-5 of SW-846.

2) **The sample size is large enough so that the two-sided 80% confidence interval for the mean does not include the regulatory limit.** In this case, we can say with 90% confidence, either that the waste is acceptable, or that it exceeds the regulatory limit. This is the basis for the formula for the "appropriate number of samples" given in Table 9-1 of SW-846.

3) **The sample on which the calculations are based is representative of the solid waste.**

Application to 0-030(g) wastes and analyses

This section discusses the size and representativeness of the SWMU 0-030(g) samples submitted for lead and mercury TCLP analyses and the resulting confidence intervals. It concludes, in contrast to the finding by NMED, that by the above criteria the wastes have been adequately characterized with respect to TCLP.

Shipping manifests show that approximately 725 tons of waste were shipped to LANL's Area G from the Catholic Church septic tank (SWMU 0-030(g)). About 15% of this was drummed soil from the western half of the tank. The remaining 85% was bulk waste consisting of the contents of the eastern half of the tank, soil from beneath the tank and around and beneath the clay outfall pipe and the remains of the concrete tank itself, and also miscellaneous drums of discarded personal protective equipment, etc. In general, higher and more variable levels of both radionuclides and inorganics were found in the western half of the tank than elsewhere, so this division represents a natural stratification of the wastes. The most contaminated materials were found near the bottom of the tank. The material in the top half of the tank was broken up concrete and soil fill.

For the characterization of the metal-containing wastes being removed from the septic tank 0-030(g) at the Catholic Church as addressed by the NMED finding, the regulatory limits in question are TCLP limits, specifically, the limits for TCLP lead (5 mg/L) and TCLP mercury (0.2 mg/L).

Sample sizes: A total of twelve specimens collected from the waste material were submitted for mercury TCLP, and ten for lead TCLP. In addition, 43 specimens were submitted for total mercury analysis and 34 for total lead analysis. Both types of analyses (total metals and TCLP) were done on ten specimens for mercury and eight specimens for lead. These analyses are summarized in Table 1.

Table 1. Metals analyses for 0-030(g) waste

	Total Pb	TCLP Pb	Total Hg	TCLP Hg
Drummed waste	16	3	18	2
Bulk waste	18	7	25	10
Total	34	10	43	12

Representativeness: The lower proportion of TCLP samples submitted for TCLP analysis that come from the drummed wastes (17% of the mercury TCLP samples, 30% of the lead TCLP samples) reflects the fact that only about 15% of the total waste was drummed. However, that portion of the waste, coming from the west half of the tank, also had higher levels of total metals, so it is also important to evaluate the representativeness of the TCLP samples when considered as a subsample of the total metals analyses. This is summarized in Table 2.

Table 2. Comparison of total metals results for TCLP specimens with complete set of total metals results

	Lead			Mercury		
	<DL	>DL		<DL	>DL	
	%	Average (mg/kg)	S.D. (mg/kg)	%	Average (mg/kg)	S.D. (mg/kg)
All specimens	6%	105	161	35%	12.3(6.1*)	34.1(9.9*)
TCLP specimens	0%	272	235	18%	14.9	13.3

* Computed omitting results for AAA4349.

From Table 2 we see that the specimens submitted for lead TCLP analysis were above average with respect to both the sample mean and sample standard deviation of the total lead measurements, and also excluded the couple of samples for which the total lead measurement was below the detection level. (The averages and standard deviations shown in Table 2 are computed for the results above detection level only.) In the case of mercury, while more than 1/3 of the total mercury measurements were below the detection level, these specimens composed only 18% of the sample submitted for TCLP. The sample mean of the TCLP specimens with total mercury above detect was higher than the mean of all specimens above detect, but the sample standard deviation was smaller. This was because the specimen with the highest total mercury (AAA4349, a sample from a drum, measured in triplicate at 30, 77 and 430 mg/kg) was not submitted for TCLP analysis. The calculation of the sample mean and especially of the sample standard deviation is very strongly influenced by an outlier like this, five times the next largest observation. This is seen by repeating the calculations omitting this one observation; those results are shown in parentheses in Table 2. Overall, it appears the that TCLP specimens represent the total population with, if anything, an upward bias. However, the potential effects of excluding the outlier AAA4349 from the TCLP sample are further considered in the section on upper confidence bounds, below.

The specimens submitted for total metals analysis, in turn, are approximately representative of the depths and strata from which the 0-030(g) wastes came, being somewhat biased towards the lower depths within the two tanks where the more contaminated material was found. This is shown in Table 3.

Table 3. Distribution of samples submitted for total lead and total mercury analyses

	Lead		Mercury	
	West*	East*	West*	East*
Depth = 0'-3'	5	3	7	8
Depth = 4'-7'	9	9	9	11
Below tank	2	3	2	3
Clay pipe*	3		3	

* ***"West" includes specimens from within and below the west tank and also specimens from drums. "East" includes specimens from within and below the east tank. The remaining specimens were collected along the clay pipe to the outfall, including some from the valve box excavation on the north side of the tank.***

Analytical results: Tables 4 and 5 show the results of the TCLP measurements (specifically, the maximum in the case of replicated TCLP measurements) together with the results of the total metals measurements for those samples for which those are available (the mean in the case of replicated total measurements). The TCLP/total metals ratio is also given when both the TCLP and total metals measurements are above detection levels.

It is theoretically possible for the TCLP measurement, reported in mg/L, to reach 0.05 of the total metals measurement, reported in mg/kg. However, as the ratio columns in Tables 4 and 5 show, this ratio was not approached for any specimen for which both types of measurements are above detection level. In particular, in order for a sample with 430 mg/kg total mercury to exceed the TCLP criterion of 0.2 mg/L, this ratio would have to be at least 0.000046, which is

five times as large as the largest ratio reported in Table 5. (If we use the average of the three replicates for AAA4349, 179 mg/kg, the required ratio goes up to 0.00112).

Table 4. Total and TCLP measurements for lead

Sample/Location*	Total (mg/kg)	TCLP (mg/L)	ratio
AAA1907/W	520	0.13	0.00025
AAA4328/W		<0.03	
AAA4329/W		0.04	
AAA4364/E	135	<1.00	
AAA4365/E	190	<1.00	
AAA4366/E	490	<1.00	
AAA4401/E	200	0.11	0.00055
AAA4402/E	610	0.07	0.00011
AAA1909/P	15	<0.03	
AAA4372/P	17	<0.03	

* Location: W=west tank, E=east tank, P=along clay pipe

Table 5. Total and TCLP measurements for mercury

Sample/Location*	Total (mg/kg)	TCLP (mg/L)	ratio
AAA1907/W	35.333	<0.0002	
AAA4346/W	4.533	0.0004	0.000088
AAA1904/E	2.5	<0.0002	
AAA4364/E	18	0.0002	0.000011
AAA4365/E		<0.0002	
AAA4366/E	25.333	0.0004	0.000016
AAA4386/E	<0.1	<0.0002	
AAA4401/E	17.917	<0.0002	
AAA4402/E	29.033	0.0002	0.000007
AAA4403/E	1.433	<0.0002	
AAA1909/P	0.1	<0.0002	
AAA4372/B	<0.1	<0.0002	

* Location: W=west tank, E=east tank, P=along clay pipe, B=below tank

<u>Upper confidence bounds</u>: In order to estimate the mean TCLP measurement, some convention must be adopted for including the below-detection level measurements. Possibilities mentioned in the regulatory literature are to replace them with (a) the reported detection level, which inflates $\bar{x}$ but decreases $s_{\bar{x}}$, or (b) one-half the reported detection level, which decreases $\bar{x}$ but increases $s_{\bar{x}}$. The upper confidence bound is a linear combination of both $\bar{x}$ and $s_{\bar{x}}$, but for both lead and mercury option (a) produces the higher value, so option (a) was used in generating Table 6.

With small samples including many below-detection level observations, it is not possible to evaluate the condition of normality, but the data in Tables 4 and 5 do not suggest any reason for rejecting the hypothesis of normality. Therefore the usual normal formulas for computing upper confidence bounds are used:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

$$s^2 = \frac{1}{n-1}\sum (x_i - \bar{x})^2$$

$$UCB_{0.90} = \bar{x} + t_{n-1,0.90}\frac{s}{\sqrt{n}}.$$

Here n is the sample size (10 for lead TCLP, 12 for mercury TCLP), the x_i are the values given in the TCLP columns of Tables 4 and 5 (where "less-than" symbols are ignored, i.e., the reported detection limit is substituted for below-detection-level observations), and $t_{n-1,.90}$ is the upper 90% point of the Student's t distribution with n-1 degrees of freedom (which is tabled in SW-846, Table 9-2.)

As seen in Table 6, the 90% upper confidence bound for the mean lead value in the 0-030(g) waste is one order of magnitude below the TCLP regulatory limit of 5.0 mg/L. For mercury it is three orders of magnitude below the regulatory limit of 0.2 mg/L.

Table 6. 90% upper confidence bounds for mean lead and mercury TCLP values from SWMU 0-030(g) (mg/L)

	n	$\bar{x}$	$s_{\bar{x}}$	90% UCB
Lead	10	0.344	0.145	0.543
Mercury	12	0.000233	0.0000225	0.000264

A hypothetical thirteenth mercury TCLP measurement from AAA4349 would have to be greater than 1 mg/L to drive the 90% UCB above 0.2 mg/L. 1 mg/L would correspond to a TCLP/total ratio of .002 to .006 (depending on the choice of a total value for AAA4349, between the mean and maximum of the replicates). This is more than 25 times greater than the ratios actually observed for any specimen from this site.

Conclusion: In view of these results, Los Alamos does not believe that the fact that TCLP for Hg was not performed on AAA4349 (and on some other samples for which the 10- or 20-fold TCLP limit was exceeded by the corresponding total metals measurement) compromises the following conclusion, which is based directly on the EPA guidance document SW-846:

> **Lead and mercury TCLP analyses were carried out on a representative sample of adequate size, and the results show that with 90% confidence the mean TCLP values for the wastes are well below their respective regulatory limits of 5 mg/L for lead and 0.2 mg/L for mercury. The hazardous metals in SWMU 0-030(g)**

wastes have been adequately characterized to demonstrate that the soil did not constitute a hazardous waste.

ID NO.	COMPLIANCE ORDER REQUIREMENT	DATE DUE	DATE RE-QUESTED	EXTENDED TO	FILED/ COM-PLETED ON	NOTES
22	within fifteen days ship container of restricted waste at TA 54 Area L permitted container storage area that has exceeded one year storage limit or provide proof such storage is solely for purposes of accumulation	9/30/94				
23	within ninety calendar days ship containers at TA 54 Area L gas cylinder storage area that have exceeded one year storage limit or provide proof such storage is solely for purpose of accumulation	12/12/94				
24	within ten days submit to Complainant waste analysis plan for treatment of restricted hazardous waste in containers at lead decontamination trailer at TA 50	9/23/94	10/13/94			
28	within five days update waste analysis plan in Attachment A of facility permit to specify procedures used to sample and analyze wastes	9/16/94	9/28/94			

PRINTED -- October 3, 1994

Re: **In the Matter of U.S. Department of Energy and Regents of the University of California, Los Alamos, New Mexico; Compliance Order No. 94-12**

ORDER FILED 8/12/94; ANSWER DUE 9/15/94

ORD NO.	COMPLIANCE ORDER REQUIREMENT	DATE DUE	DATE RE-QUESTED	EXTENDED TO	FILED/ COM-PLETED ON	NOTES
	answer to compliance order	9/15/94			10/14/94	
1	within sixty days from receipt submit complete site characterization plan for Pit 37, Area G, TA-54, in order to determine the vertical and horizontal extent of contamination	~~11/11/94~~ 10/14/94				
1	within one hundred sixty days after NMED approval of plan complete site characterization of Pit 37 and submit report to Complainant					
2	within thirty working days from receipt submit a corrective action plan addressing deficiencies of current knowledge of process method	9/27/94	9/23/94 (motion)	10/14/94		

PRINTED -- October 3, 1994

Re: **In the Matter of U.S. Department of Energy and Regents of the University of California, Los Alamos, New Mexico; Compliance Order No. 94-09**

ORDER FILED 9/2/94; ANSWER DUE 10/11/94

ORD NO.	COMPLIANCE ORDER REQUIREMENT	DATE DUE	DATE RE-QUESTED	EXTENDED TO	FILED/ COM-PLETED ON	NOTES
	answer to compliance order	10/11/94	9/23/94 (motion)	10/28/94		
3	within fifteen working days report in writing as to status of measures taken to conduct adequate hazardous waste determination in paragraphs 68-73	9/30/94				
5	within ten working days equip TA-3-132-C1, 3-2056, 41-1 and 21-427 less than 90 day hazardous waste accumulation areas with shower/eye wash devices	9/23/94				
7	within ten working days TA 21-427 less than 90 day accumulation area with device for providing emergency instruction to personnel	9/23/94				
8	within ten working days equip TA 21-427 less than 90 day accumulation area with telephone or radio for summoning emergency assistance	9/23/94				
9	within five working days include TA 21-427 less than 90 day accumulation area in facility contingency plan	9/16/94	9/14/94	10 working days after requested meeting		
14	within five working days initiate measures to ensure hazardous waste is managed under control of operator of processing generating waste stored at each of the satellite accumulation points in paragraph 88	9/16/94				
15	within five working days provide Houlton and Larson with required hazardous waste annual review training and institute measures to ensure all employees are trained by required renewal dates	9/16/94				
16	within ten working days provide Complainant with record documenting adequate hazardous waste determination for sludges generated from explosives processing at TA 9-21-AE191	9/23/94				
21	within fifteen working days ship containers of restricted waste at TA 54 area L building 5469 that have exceeded one year storage limit, or provide proof such storage is solely for purposes off accumulation	9/30/94				