

ATTACHMENT ~~B~~ C2

STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

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1 **ATTACHMENT ~~B~~ C2**

2 **STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS**

3 Introduction

4 The ~~Permittees~~ Department of Energy Carlsbad Field Office (~~DOE~~) shall require
5 generator/storage sites (**sites**) to use the following statistical methods for sampling and analysis
6 of TRU mixed waste which is managed, stored, or disposed at WIPP, unless determined
7 unnecessary by ~~the Permittees~~ ~~DOE~~ as a result of an Acceptable Knowledge (AK) Sufficiency
8 Determination. These statistical methods include methods for selecting waste containers for
9 totals analysis, selecting waste containers for headspace gas sampling and analysis, and
10 setting the upper confidence limit.

11 BC2-1 Approach for Selecting Waste Containers for Statistical Sampling

12 BC2-1a Statistical Selection of Containers for Totals Analysis

13 The statistical approach for characterizing retrievably stored and newly generated
14 homogeneous solids (S3000) and soil/gravel (S4000) waste and repackaged or treated S3000
15 waste relies on using acceptable knowledge to segregate waste containers into relatively
16 homogeneous waste streams. Using acceptable knowledge, generator/storage sites will classify
17 the entire waste stream as hazardous or nonhazardous rather than individual waste containers.
18 Individual waste containers serve as convenient units for characterizing the combined mass of
19 waste from the waste stream of interest. Once segregated by waste stream, random selection
20 and sampling of the waste containers followed by analysis of the waste samples shall be
21 performed to ensure that the resulting mean contaminant concentration provides an unbiased
22 representation of the true mean contaminant concentration for each waste stream. ~~The~~
23 ~~Permittees~~ ~~DOE~~ shall require each site project manager to verify that the samples collected
24 from within a waste stream were selected randomly.

25 An end use of analytical results for retrievably stored homogeneous solids and soil/gravel is for
26 assigning the Environmental Protection Agency (**EPA**) hazardous waste numbers associated
27 with toxicity characteristic waste (D-numbers) that apply to each mixed waste stream. The
28 toxicity characteristic D-numbers are indicators that the waste exhibits the toxicity characteristic
29 for specific contaminants under the Resource Conservation and Recovery Act (**RCRA**). The
30 RCRA-toxicity determination is made on the basis of sampling and analysis of waste streams
31 and on whether or not the waste stream includes F-number wastes. If a waste stream includes
32 one or more RCRA F-numbers identified via acceptable knowledge, toxicity characteristic
33 contaminants associated with the F-number waste(s) are not included in the RCRA-toxicity
34 characteristic determination. That is, the F-numbers take precedence over RCRA-toxicity D-
35 number, and the waste stream is assumed hazardous regardless of the concentration.
36 Therefore, toxicity characteristics contaminants associated with F-numbers for a waste stream
37 shall be omitted from all calculations for determining the number of containers to sample
38 because these wastes streams are assumed to be hazardous. In addition, each toxicity
39 characteristic contaminant associated with the F-number(s) shall be excluded from evaluation of
40 analytical results to determine D-numbers. Contaminants of interest for the sampling, analysis,
41 and RCRA-toxicity determination of a waste stream, then, excludes contaminants associated
42 with F-numbers that have been assigned to the waste stream.

1 | The sampling and analysis strategy is illustrated in Figure-B_C2-1. Preliminary estimates of the
2 | mean concentration and variance of each RCRA regulated contaminant in the waste will be
3 | used to determine the number of waste containers to select for sampling and analysis.
4 | Preliminary estimates will be based on a minimum of five samples selected randomly from the
5 | waste stream. If the entire waste stream is not accessible for sampling then a minimum of five
6 | preliminary samples will be selected randomly from the accessible population. As the rest of the
7 | waste stream is retrieved or generated, additional selected containers will be sampled as
8 | provided below and the analytical results will be reported to ~~the Permittees DOE~~. Samples
9 | collected to establish preliminary estimates that are selected, sampled, and analyzed using a
10 | ~~Permittee DOE~~ approved laboratory in accordance with applicable provisions of the WAP may
11 | be used as part of the required number of samples to be collected. The applicability of the
12 | preliminary estimates to the waste stream to be sampled shall be justified and documented. The
13 | preliminary estimates will be determined in accordance with the following equations:

14 |
$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (\text{BC2-1})$$

15 |
$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \quad (\text{BC2-2})$$

16 | Where:

17 | \bar{x} = the calculated mean.

18 | s^2 = the calculated concentration variance.

19 | n = the number of samples analyzed.

20 | x_i = the concentration determined in the *i*th sample.

21 | i = an index from 1 to n .

22 | Based upon the preliminary estimates of \bar{x} and s^2 for each chemical contaminant of concern,
23 | estimate the appropriate minimum number of samples (n) to be collected for each contaminant
24 | using the following formula from SW-846 (EPA 1996):

25 |
$$n = \frac{t_{\alpha, n_0-1}^2 s^2}{(RT - \bar{x})^2} \quad (\text{BC2-3})$$

26 | Where:

27 | n_0 = the initial number of samples used to calculate the preliminary estimates.

28 | n = the calculated minimum number of samples to be collected.

29 | $t_{\alpha, n-1}$ = the 90th percentile for the t distribution with n_0-1 degrees of freedom.

30 | RT = the Regulatory Threshold of the contaminant (TC limit for toxicity characteristic wastes,
31 | PRQL for listed wastes)

1 The number of samples to be collected will be based upon the largest n calculated for each of
2 the contaminants of concern. The actual number of samples collected shall be adjusted as
3 necessary to ensure that an adequate number of samples are collected to allow for acceptable
4 levels of completeness.

5 Non-integer results of calculations for the required sample size should be rounded up to the
6 next integer. A minimum of five containers shall be sampled and analyzed in each waste
7 stream. If there are fewer containers than the minimum or required number of samples in a
8 waste stream, one or more randomly selected containers shall be sampled more than once to
9 obtain the number of needed samples of the waste. Otherwise any one container may be
10 selected for sampling only once.

11 The calculated total number of required waste containers will then be randomly sampled and
12 analyzed using a ~~Permittee-DOE~~ approved laboratory. Waste container samples from the
13 preliminary mean and variance estimates may be counted as part of the total number of
14 calculated required samples if and only if:

- 15 • There is documented evidence that the waste containers for the preliminary estimate
16 samples were selected in the same random manner as is chosen for the required
17 samples.
- 18 • There is documented evidence that the method of sample collection in the preliminary
19 estimate samples were identical to the methodology to be employed for the required
20 samples.
- 21 • There is documented evidence that the method of sample analysis in the preliminary
22 estimate samples were identical to the analytical methodology employed for the
23 required samples.
- 24 • There is documented evidence that the validation of the sample analyses in the
25 preliminary estimate samples were comparable to the validation employed for the
26 required samples. In addition, the validated samples results shall indicate that all
27 sample results were valid according to the analytical methodology.

28 If only a portion of a waste stream is accessible for sampling (e.g., the remainder of the waste
29 stream will be recovered from storage at the generator/storage site, or only a portion of the
30 waste stream has been repackaged, treated, or generated), the calculated number of samples
31 will be randomly selected from the accessible portion of the waste stream. A minimum of five
32 randomly selected samples will be obtained and analyzed from the accessible portion of the
33 waste stream. ~~The Permittees-DOE~~ may approve the WSPF and authorize the
34 generator/storage site to begin shipping the waste stream to WIPP once the analytical data for
35 the randomly selected samples from the accessible portion of the waste stream have been
36 obtained.

37 The generator/storage site will also randomly select the calculated number of sample locations
38 from the waste stream as a whole. A minimum of five randomly selected sample locations will
39 be selected from the waste stream as a whole. As those randomly selected locations (e.g.,
40 buried or newly generated waste containers) become accessible for sampling, samples will be
41 obtained and analyzed.

1 For those waste streams where the population of the waste stream as a whole is indeterminate
2 (e.g., continually generated waste streams from ongoing processes) or to facilitate waste
3 processing, the generator/storage site may divide the waste stream into lots. In this case, a
4 minimum of five randomly selected sample locations will be selected from within each
5 subsequent lot. As those randomly selected locations (e.g., buried or newly generated waste
6 containers) become accessible, samples will be obtained and analyzed. As with sampling from
7 the waste stream as a whole, the generator/storage site may ship waste from the lot being
8 generated or retrieved prior to completing sampling and analysis of the lot.

9 The generator/storage site will use the data to update the UCL₉₀ values for the waste stream as
10 described in Section B C2-2a and assign EPA hazardous waste numbers as appropriate. The
11 generator/storage sites will submit the analytical data from subsequent sampling to ~~the~~
12 Permittees-DOE for inclusion in the WIPP facility operating record upon completion of project
13 level data validation in Permit Attachment B C3, Section B C3-10b. If changes to EPA
14 hazardous waste numbers are required as a result of subsequent sampling, the
15 generator/storage site will notify the Permittees-DOE and shipments of the affected waste
16 stream shall be suspended until the Permittees-DOE approves a revised WSPF for the affected
17 waste stream.

18 Upon collection and analysis of the preliminary samples, or at any time after the preliminary
19 samples have been analyzed, the generator/storage site may presumptively assign hazardous
20 waste numbers to a waste stream even if the calculated number of required samples is greater
21 than the preliminary number of samples collected. For waste streams with calculated upper
22 confidence limits below the regulatory threshold, the site shall collect the required number of
23 samples if the site intends to establish that the constituent is below the regulatory threshold.

24 BC2-1b Statistical Selection of Containers for Headspace Gas Analysis

25 Headspace gas sampling of a waste stream may be done on a randomly selected portion of
26 containers in the waste stream. The minimum number of containers, n , that must be sampled is
27 determined by taking an initial VOC sample from ten randomly selected containers. These
28 samples are analyzed for all the target analytes using a Permittee-DOE approved
29 laboratory. The standard deviation, s , is calculated for each of the nine VOCs in Module IV Part
30 4, Table IV-D.1 4.4.1. The value of n is determined as the largest number of samples (not to
31 exceed the number of containers in the waste stream or waste stream lot) calculated using the
32 following equation:

$$33 \quad n_{voc_i} = \frac{t_{\alpha, n-1}^2 s^2 e_{voc_i}}{E^2_{voc_i}} \quad (\text{BC2-4})$$

34 Where:

35 n_{voc_i} = the number of samples needed to representatively sample the waste stream for the VOC _{i}
36 from Table IV-D.1 4.4.1

37 $t_{\alpha, n-1}$ = the 90th percentile of the t distribution with $n-1$ degrees of freedom

1 s_{evoci} = the estimated standard deviation, based on the initial n samples, for VOC_{*i*} from
2 Table ~~IV.D.1~~ 4.4.1

3 E_{voci} = the allowable error determined as 1 percent of the limiting concentration for VOC_{*i*} from
4 Table ~~IV.D.1~~ 4.4.1

5 Non-integer results of calculations for the required sample size should be rounded up to the
6 next integer. A minimum of ten containers shall be sampled and analyzed in each waste stream.
7 If there are fewer containers than the minimum or required number of samples in a waste
8 stream, then each container should be sampled once.

9 The calculated total number of required waste containers will then be randomly sampled and
10 analyzed. Waste container samples from the preliminary mean and variance estimates may be
11 counted as part of the total number of calculated required samples if and only if:

- 12 • There is documented evidence that the waste containers for the preliminary estimate
13 samples were selected in the same random manner as is chosen for the required
14 samples.
- 15 • There is documented evidence that the method of sample collection in the preliminary
16 estimate samples were identical to the methodology to be employed for the required
17 samples.
- 18 • There is documented evidence that the method of sample analysis in the preliminary
19 estimate samples were identical to the analytical methodology employed for the
20 required samples.
- 21 • There is documented evidence that the validation of the sample analyses in the
22 preliminary estimate samples were comparable to the validation employed for the
23 required samples. In addition, the validated samples results shall indicate that all
24 sample results were valid according to the analytical methodology.

25 The mean and standard deviation calculated after sampling n containers can be used to
26 calculate a UCL_{90} for each of the headspace gas VOCs using the methodology presented in
27 Section ~~B.C2~~-2b.

28 If only a portion of a waste stream is accessible for sampling (e.g., the remainder of the waste
29 stream will be recovered from storage at the generator/storage site or only a portion of the
30 waste stream has been repackaged or treated), the calculated number of samples will be
31 randomly selected from the accessible portion of the waste stream. A minimum of ten randomly
32 selected samples will be obtained and analyzed from the accessible portion of the waste
33 stream. ~~The Permittees DOE~~ may approve the WSPF and authorize the generator/storage site
34 to begin shipping the waste stream to WIPP once the analytical data for the randomly selected
35 samples from the accessible portion of the waste stream has been obtained.

36 The generator/storage site will also randomly select the calculated number of sample locations
37 from the waste stream as a whole. A minimum of ten randomly selected sample locations will be
38 selected from the waste stream as a whole. As those randomly selected locations (e.g., buried
39 or newly generated waste containers) become accessible for sampling, samples will be
40 obtained and analyzed.

1 For those waste streams where the population of the waste stream as a whole is indeterminate
2 (e.g., continually generated waste streams from ongoing processes) or to facilitate waste
3 processing, the generator/storage site may divide the waste stream into lots. In this case, a
4 minimum of ten randomly selected containers will be selected from within each subsequent lot.
5 As those randomly selected containers (e.g., buried or newly generated waste containers)
6 become accessible, samples will be obtained and analyzed. As with sampling from the waste
7 stream as a whole, the generator/storage site may ship waste from the lot being generated or
8 retrieved prior to completing sampling and analysis of the lot.

9 The generator/storage site will use the data to update the UCL₉₀ values for the waste stream as
10 described in Section B C2-2b and assign EPA hazardous waste numbers as appropriate. The
11 generator/storage sites will submit the analytical data from subsequent sampling to ~~the~~
12 Permittees-DOE for inclusion in the WIPP facility operating record upon completion of project
13 level data validation in Permit Attachment B C3, Section B C3-10b. If changes to EPA
14 hazardous waste numbers are required as a result of subsequent sampling, the
15 generator/storage site will notify ~~the Permittees-DOE~~, and shipments of the affected waste
16 stream shall be suspended until ~~the Permittees-DOE~~ approves a revised WSPF for the affected
17 waste stream.

18 Upon collection and analysis of the preliminary samples, or at any time after the preliminary
19 samples have been analyzed, the generator/storage site may presumptively assign hazardous
20 waste numbers to a waste stream even if the calculated number of required samples is greater
21 than the preliminary number of samples collected. For waste streams with calculated upper
22 confidence limits below the regulatory threshold, the site shall collect the required number of
23 samples if the site intends to establish that the constituent is below the regulatory threshold.

24 BC2-2 Upper Confidence Limits for Statistical Sampling

25 BC2-2a Upper Confidence Limit for Statistical Solid Sampling

26 Upon completion of the required sampling, final mean and variance estimates and the UCL₉₀ for
27 the mean concentration for each contaminant shall be determined. The observed sample n^*
28 shall be checked against the preliminary estimate for the number of samples (n) to be collected
29 before proceeding, where n^* is:

$$30 \quad n^* = \frac{t^2_{\alpha, n-1} s^2}{(RT - \bar{x})^2} \quad (\text{BC2-5})$$

31 and the right-side terms in the equation are as defined in Section B C2-1a.

32 If the observed sample n^* estimate results in greater than 20 percent or more required samples
33 than were originally calculated, then the additional samples required to fulfill the revised sample
34 estimate shall be collected and analyzed. The determination of n^* is an iterative process that
35 follows the collection and analysis of any additional samples and continues until the difference
36 between n^* and the previous sample size determination is less than 20 percent.

1 Once sufficient sampling and analysis has occurred, the waste characterization will proceed.
2 The assessment will be made at the 90 percent confidence level. The UCL_{90} for the mean
3 concentration of each contaminant will be calculated using the following equation from OSWER
4 9285.6-10 (EPA 2002):

5
$$UCL_{90} = \bar{x} + \frac{t_{\alpha, n-1} s}{\sqrt{n}} \quad (\text{BC2-6})$$

6 If the UCL_{90} for the mean concentration is less than the regulatory threshold limit, the waste
7 stream is not required to be assigned the hazardous waste number for the associated
8 contaminant. If the UCL_{90} is greater than or equal to the regulatory threshold limit, the waste
9 stream will be assigned the hazardous waste number for the associated contaminant.

10 **BC2-2b Upper Confidence Limit for Statistical Headspace Gas Sampling**

11 A UCL_{90} concentration for each of the headspace gas VOCs must be calculated from the
12 sample data collected. The observed sample n^* shall be checked against the estimate for the
13 number of samples (n) to be collected before proceeding, where n^* is:

14
$$n^* = \frac{t_{\alpha, n-1}^2 s^2}{E^2} \quad (\text{BC2-7})$$

15 where E is as defined in Section **BC2-1b** and the remaining right-side terms in the equation are
16 defined in Section **BC2-1a**. When composite headspace gas sample results are used, the
17 mean, standard deviation, and t-statistic are based on the number of composite samples
18 analyzed, rather than the number of containers sampled.

19 If the observed sample n^* estimate results in greater than 20 percent or more required samples
20 than were originally calculated, then the additional samples required to fulfill the revised sample
21 estimate shall be collected and analyzed. The determination of n^* is an iterative process that
22 follows the collection and analysis of any additional samples and continues until the difference
23 between n^* and the previous sample size determination is less than 20 percent. The UCL_{90} is
24 then calculated using equation **BC2-6**. In this case, UCL_{90} is the 90 percent upper confidence
25 limit for the mean VOC concentration, \bar{x} is the calculated sample mean VOC concentration and
26 s is the calculated sample standard deviation. The value of $t_{(\alpha, n-1)}$ is found in Table 9-2 of
27 Chapter 9 of SW-846 (EPA, 1996).

1 References

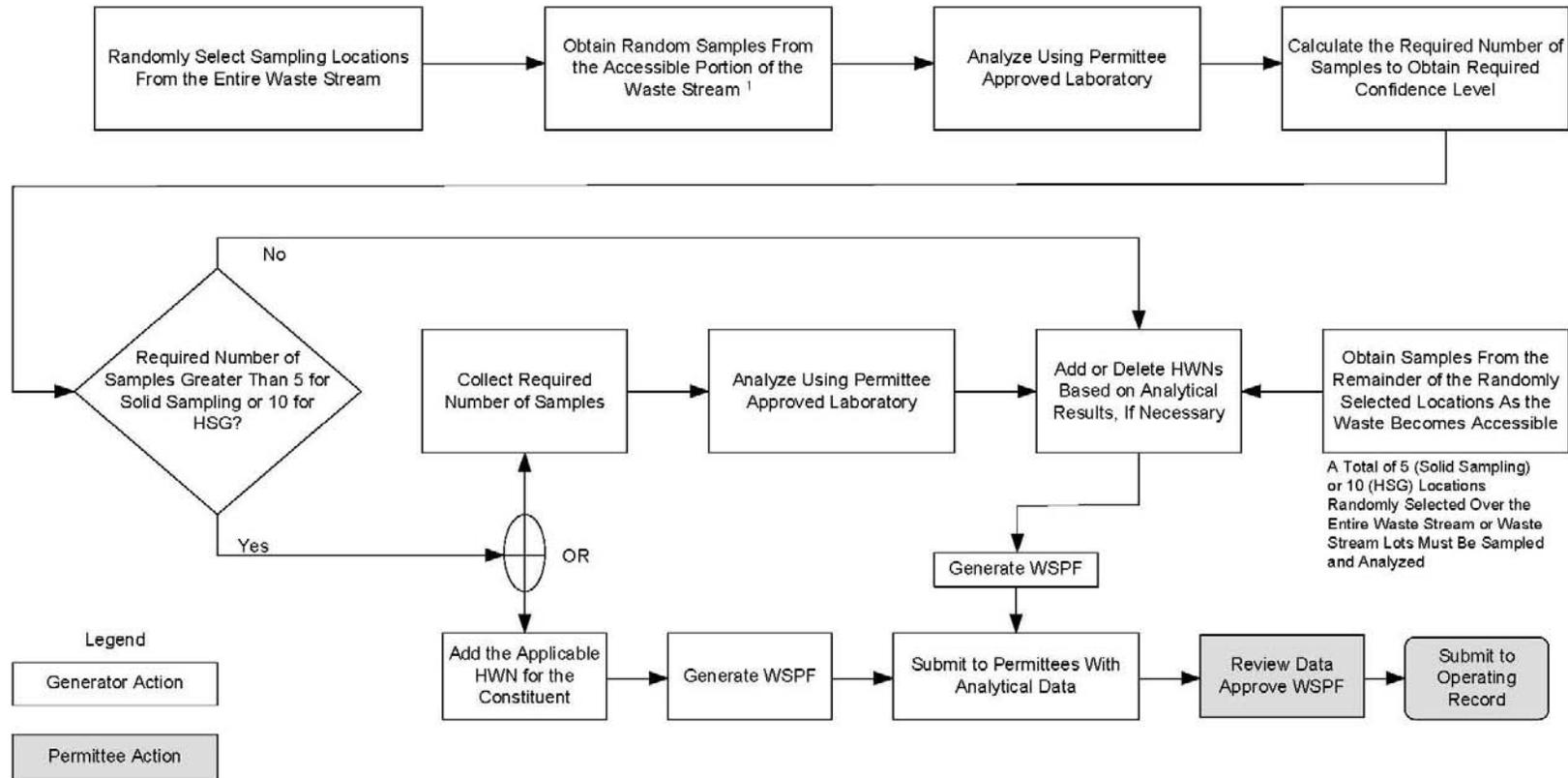
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1

FIGURES

1

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¹ Samples Are Obtained From the First Five Accessible Random Locations for Solid Sampling and the First Ten Accessible Random Locations for Headspace Gas Sampling

Figure B_C2-1
Approach for Solid and Headspace Gas Sampling and Analysis to Obtain Additional Waste Characterization Information