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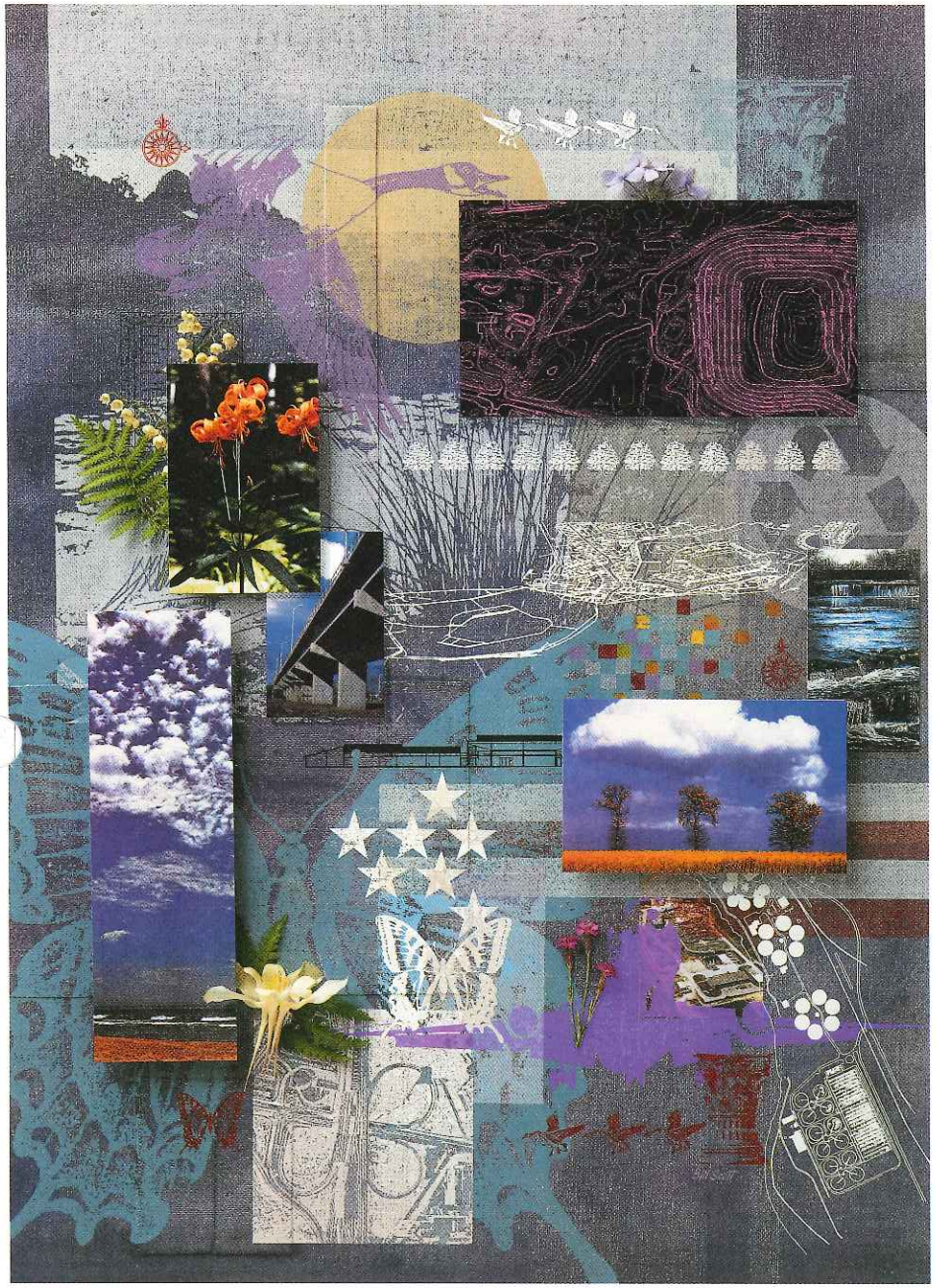

Quality through teamwork

RCRA Facility Investigation (RFI) Phase I Work Plan

Quality Assurance Project Plan (QAPP)

Chemical Waste Management
Vickery, Ohio

U.S. EPA ID No.
OHD 020 273 819

Prepared for:

CWM - Vickery, Inc.

November 1997

RUST

Rust Environment & Infrastructure

RESPONSE TO U.S. EPA TECHNICAL REVIEW COMMENTS PHASE I RFI QUALITY ASSURANCE PROJECT PLAN (QAPjP) CWM VICKERY FACILITY

SPECIFIC COMMENTS

1. **Response to General Comment 1.** This comment has been only partially addressed. Section 1.4.2 of the QAPP defines potential contamination as any detection above the project reporting limits (PRL) or any nondetect for which the PRL is above the EPA Region 5 data quality level (DQL).

   a. The procedure for data comparison shall be presented as follows:

      i. On-site soil sample metal data will be compared to background concentrations. All other on-site soil sample data will be compared to U.S. EPA Region 9 industrial PRLs.

      ii. Groundwater sample metal data will be compared to background concentrations. All other groundwater sample data will be compared to U.S. EPA Region 5 DQLs.

      iii. Surface water and sediment sample data will be compared to surface water quality levels, if available. If surface water quality levels are not available, the data will be compared to Ecotox thresholds. If Ecotox thresholds are not available, the data will be compared to DQLs.

REI Response

The procedure for data comparison to determine the need for additional investigation in the Phase II RFI was changed to conform to that specified in the comment (except for the references to surface water, because no surface water samples will be collected during the Phase I RFI). The appropriate changes were made in Section 1.4.2 of the QAPjP.

   b. The QAPP should be revised to state that Phase II samples will be collected at every Phase I location where analytical results exceed any of the following, as outlined in the previous condition, (DQLs, PRLs, background concentrations, surface water quality levels, and Ecotox thresholds). The text in the QAPP should also indicate whether nondetected analyte data will be reported as the PRLs for use in the risk assessment. Finally, the QAPP's use of the term "potential contamination" must be clarified to underscore that all Phase I and Phase II data shall be used in the risk assessment. The appropriate sections of the QAPP should be revised accordingly.

REI Response

Section 1.4.2 of the QAPjP was changed as directed in the comment. As discussed at the meeting on October 15, 1997, CWM-Vickery's position is that non-detected analyte data should be reported at the laboratory's Method Detection Limit (MDL; the concentration at which presence/absence can be determined), rather than the Project Reporting Limit (PRL; a concentration higher than the MDL at which the concentration can be reliably quantified). Similarly, CWM-Vickery intends to use non-detect results at ½ the MDL in the Quantitative Risk Assessment. The changes to Section 1.4.2 of the QAPjP reflect CWM-Vickery's position and intent as stated here. It is understood that resolution of this issue depends on USEPA's evaluation of the laboratory's MDL study which will be submitted separately as part of the Performance Evaluation Sample Demonstration Audit.

2. **Response to General Comment 7.** The QAPP still contains several deficiencies, inconsistencies, and discrepancies regarding some of the analytical methods used to determine target parameters. These deficiencies, inconsistencies, and discrepancies are discussed below and shall be addressed accordingly. Specific Comment 56 also applies here and shall be addressed.

a. The QAPP includes references to Method 8240B, which is not being performed during this project. The reference to Method 8240B shall be deleted throughout the QAPP, and appropriate sections of the QAPP shall be revised accordingly.

REI Response

The QAPjP has been changed to reflect the use of Method 8260B for volatile organics analysis.

b. Two versions (July 1995 and April 1996) of the standard operation procedures (SOP) for Methods 8270B, 8080A, and 6010A are included in the QAPP. The QAPP shall be revised to include only the most recent version of these methods.

REI Response

The QAPjP has been changed to include only one copy (the most recent) of each SOP.

c. Table 3-4 is titled "Precision and Accuracy Criteria, Appendix IX Volatile Organic Compound by Method 8260A" but presents precision and accuracy criteria for organophosphate pesticides by Method 8141. This discrepancy shall be addressed.

REI Response

The title of Table 3-4 was changed as directed in the comment.

d. Table 6-1 does not include calibration procedures for Methods 300 (chloride) and 376.1 (sulfide). Table 6-1 shall be revised to include this information. In addition, Table 6-1 presents calibration procedures for Method 8240B, which is not being performed during the RFI. This discrepancy shall be addressed.

REI Response

Calibration requirements for Method 300.0 have been added to Table 6-1, and the reference to Method 8240B has been deleted from the table. Method 376.1 is a manual titrametric procedure and as such there is no analytical instrument (other than standard volumetric glassware) and no instrument calibration procedure.

e. SOP No. 13.1 for Method 8240B has been included in the QAPP. However, this method is not being used during this project. Therefore, SOP No. 13.1 shall be deleted from the QAPP.

REI Response

The laboratory's SOP for Method 8240B has been deleted from the QAPjP.

f. No SOP for Method 300 (chloride) has been included in the QAPP. However, a SOP for Method 325.3 (chloride), which is not being used during the RFI, is included. Therefore, the SOP for Method 325.3 shall be deleted from the QAPP, and the SOP for Method 300 shall be added to the QAPP. In addition, no SOP for EPA Method 9080, cation exchange capacity analyses, which is identified on Table 7-2 of the QAPP, is included in the QAPP. This discrepancy shall be addressed.

REI Response

The correct SOP for chloride analysis and the SOP for cation exchange capacity (CEC) analysis have been included in the QAPjP.

RESPONSES TO SPECIFIC COMMENTS

3. **Response to Specific Comment 2.** Several inconsistencies still exist between the table of contents and the materials included in the appendices to the QAPP. The items listed below are incorrectly identified in the table of contents as being included in Appendix A of the QAPP. These materials shall be included in Appendix A.

- GP Environmental Services SOP for Chloride (SOP No. 11.55)
- Rust Environment and Infrastructure, Inc., geotechnical laboratory SOPs
- SOP No. QA000-0000 for data validation
- Guidelines for the preparation of SOPs of field and laboratory measurements
- SOP for the field measurement of volatile organics by HNu
- SOP for the measurement of pH in the field using the Fisher Accumet Model 955 portable pH/mV temperature meter
- SOP for the measurement of specific conductance in the field using the Cole Parmer Model 4070 conductivity meter

REI Response

All SOPs referenced in the QAPjP and its Table of Contents have been included in the QAPjP.

4. **Response to Specific Comment 3.** The response to this comment states that data will be validated using the SOP entitled "Data Validation Procedures for EPA Level III Data." Level II data is not sufficient for use in an RFI. Data packages comparable to a CLP-like content should be generated and submitted to the U.S. EPA. The QAPP shall be revised to include provisions for submittal of a CLP-like data package with independent data validation of these packages comparable and analogous to the CLP Functional guidelines.

REI Response

This comment is moot. The QAPjP text indicated validation at EPA Level III, and the SOP referenced in the text is for validation at EPA Level III.

5. **Response to Specific Comment 6.** The response to this comment states that a field duplicate will be collected at the capillary drain sump to provide additional information on the reproducibility or statistical significance of the results. However, collection of a field duplicate does not ensure statistical significance. In order to ensure statistical significance, more investigative samples (at least three) shall be collected from the capillary drain sump. Therefore, the QAPP shall revise the first sentence of the second bullet on Page 3 of Section 1 to include the phrase, ". . . Closure Cell by collecting three groundwater samples from the capillary drainage layer."

REI Response

Section 1.4.1 and Table 1-1 of the QAPjP were changed to show that sampling of the capillary drain is now part of the Phase I RFI groundwater sampling activity. As discussed at the meeting on October 15, 1997, only one investigative sample will be collected from the capillary drain. However, two (2) field duplicates will be collected as part of groundwater sampling activity -- one from the capillary drain and one from a monitoring well.

6. **Response to Specific Comment 7.** Section 1.1.2 shall be revised to state:

   a. An undisturbed soil sample from an area that is unaffected by land-use activities will be collected to verify the true extent of the surficial soil layer and,

   b. This sample may be collected at a depth of greater than 24 inches below ground surface (bgs), depending on land-use activities.

   Therefore, the following sentences shall be added after the third bullet on Page 4 in Section 1.1.2: "An undisturbed soil sample will be collected from an area that is unaffected by land-use activities to verify the true extent of the surficial soil layer. The undisturbed soil sample may be collected more than 24 inches below ground surface."

REI Response

Section 1.1.2 and Table 1-1 of the QAPjP was changed to indicate that soil samples collected to develop background data for metals will be collected in areas of the site property that have not been used for waste management purposes. Both surface and subsurface samples will be collected for this purpose. Section 5.12 was added to the Work Plan to describe this activity.

7. **Response to Specific Comment 9.** This comment has been partially addressed. During groundwater sampling, several field parameters need to be monitored to verify that a representative groundwater sample is collected. In addition to pH, these parameters include turbidity, dissolved oxygen, specific conductivity, and temperature. Presently, the QAPP does not identify turbidity, dissolved oxygen, specific conductivity, and temperature as field parameters that will be measured. These parameters shall be identified in Table 1-1 and in all other relevant parts of the QAPP. For example, the following sentence shall be added at the end of the first paragraph on Page 5 in Section 1.1.2: "The field parameters to be monitored during groundwater sampling activities will include pH, turbidity, dissolved oxygen, specific conductivity, and temperature to verify that a representative groundwater sample is collected."

Also, turbidity and temperature shall be added to the test parameter column of Table 1-1 for the solid waste management unit (SWMU) Group A in the MW-15R location row, Group B row, Group C MW-20R row, and Meyer's Ditch row. In addition, an SOP for turbidity measurement shall be added to Appendix A.

REI Response

Section 1.1.2 and Table 1-1 of the QAPjP were modified to describe 1) the collection of pH, specific conductivity, and temperature field data during monitoring well purging to ensure the representativeness of groundwater samples, and 2) the measurement of turbidity in the actual sample collected. An SOP for turbidity measurement was added to Appendix A of the QAPjP as directed in the comment. The on-going measurement of pH, specific conductivity, and temperature has been part of the Facility's groundwater sampling protocol for many years; and evaluation of the resulting analytical data indicates that it has been sufficient to ensure the collection of representative samples -- the historical data show good reproducibility. Furthermore, while the use of turbidity and dissolved oxygen measurements during purging may be required for representative micro-purge sampling (which seeks to minimize the amount of water purged), this technique is not needed for this project because micro-purge sampling will not be used in the Phase I RFI. The bedrock wells have dedicated purge/sampling pumps that are designed for high-flow/volume purging (not micro-purge sampling), and the lacustrine wells yield water too slowly for micro-purge sampling (about 1000 mL/day) and will have to be bailed dry and sampled upon recovery.

8. **Response to Specific Comment 12.** This comment has been partially addressed. The response states that data collected during Phase I will be compared to PRLs. However, the text in Section 1.1.2 needs to be further revised to reflect how data collected during Phase I will be compared to PRLs and how Phase II will be initiated, based on the results of the Phase I data. The following sentences shall be added to Section 1.1.2: "Data collected during the Phase I investigation will be used to determine whether a release to the environment has occurred. Data collected during the Phase I investigation will also be used to determine Phase II sampling locations and frequencies in order to assess the vertical and horizontal extent of soil and groundwater contamination."

REI Response

Section 1.1.2 of the QAPjP was changed as directed in the comment.

9. **Response to Specific Comment 15.** This comment has not been addressed. The text in Section 1.3.3, Page 13, Bullet No. 1, states that all releases to Little Raccoon Creek and Meyers Ditch were remediated immediately after the release. However, Table 3-1 of the 1993 report referenced in Section 1.3.3 lists high metals concentrations in sediment samples collected from Little Raccoon Creek. Therefore,

an additional sediment sample from Meyer's Ditch and three sediment samples from Little Raccoon Creek shall be collected for metals, semivolatile organic compound (SVOC), and polychlorinated biphenyl (PCB) analyses to evaluate the contamination in Little Raccoon Creek and Meyer's Ditch. Table 1-1 and appropriate sections of the QAPP and RFI work plan shall be revised accordingly.

REI Response

Section 5.10.8 of the Work Plan has been changed to indicate that eight (8) sediment samples will be collected in Meyers Ditch (on-site) and that three (3) sediment samples will be collected in Little Raccoon Creek (off-site). The text of this section and Table 1-1 of the QAPjP have been changed to show that sediment samples will be analyzed for metals, SVOCs and PCB, in addition to the parameters previously specified.

10. **Response to Specific Comment 18.** This comment has been partially addressed. The QAPP shall be revised to state that Phase II activities will be undertaken at all locations where any Phase I analytical result exceed a DQL, PRL, Surface Water Quality Level, Ecotox level, or background for a specific compound, according to the criteria in **1. Response to General Comment 1**, identified during the Phase I investigation. Risk will be evaluated after all data from both phases of the RFI are collected, and the need for corrective measures will be determined during the risk assessment. The QAPP shall be revised accordingly.

REI Response

See response to Item 1 b) above.

11. **Response to Specific Comment 19.** This comment has not been addressed. The text on page 15, paragraph 4 of Section 1.4.1 states that samples of residual materials will be collected at SWMUs where clean closure has not been certified. However, the text shall be revised to state: ". . . where clean closure has not been performed, samples of the residual materials and soil samples from an appropriate depth below the residual materials will be collected and analyzed for Appendix IX parameters." Specific sampling depths for SWMUS and AOCs are provided in Section 5.0 of the RFI work plan.

REI Response

Section 1.4.1 of the QAPjP was changed to clarify that soils adjacent to and underlying the SWMUs will be sampled and analyzed.

12. **Response to Specific Comment 20.** This comment has been partially addressed. The text in Section 1.4.2 states that Phase I data will be compared to PRLs in order to define potential contamination for use in the QRA. However, several issues

regarding the comparison of data to PRLs need to be discussed in text. The text in section 1.4.2 of the QAPP shall be revised to state that Phase II samples will be collected at every Phase I location where an analytical result exceeds the PRL or, if the result is a nondetect, the PRL exceeds the DQL, possibly using more sensitive instrumentation. The text shall also discuss whether nondetects will be reported as the PRLs for use in the QRA. Finally, the text shall be revised to specify the process that will be used to assess and interpret the analytical results.

REI Response

See response to Item 1 b) above.

13. **Response to Specific Comment 21.** This comment has been partially addressed. Section 1.5, Page 18, Paragraph 2, states that additional soil samples will be collected at locations where field observations indicate that the uppermost native soil is contaminated. However, the text shall be revised to state: "If additional soil samples are collected at locations where field observations indicate that the uppermost native soil is contaminated, a sampling plan addendum will be submitted to the U.S. EPA. Implementation of this activity should be suspended until written approval is obtained from the U.S. EPA Project Officer."

REI Response

At the meeting on October 15, 1997, it was agreed that procedures for collecting additional soil samples when the uppermost native soil shows evidence of contamination would be written into Section 5.7.1 of the Work Plan. This approach would prevent delays and allow the field project to continue smoothly.

14. **Response to Specific Comment 23.** This comment has been partially addressed. However, several inconsistencies are still present in Table 1-2. These inconsistencies are discussed below.

    a. Table 1-2 presents the DQLs for 2-chloro-1,3 butadiene; chloromethane; and 1,1-dichloroethene. However, the December 1995 EPA Region 5 DQL document does not list DQLs for these compounds. Therefore, a footnote shall be added to Table 1-2 to identify the source of these DQLs.

REI Response

The DQL listed for 2-chloro-1,3-butadiene has been removed. DQLs for the remaining two compounds are correct, but are found in EPA Region 5's December 1995 DQL document under the synonyms methyl chloride and 1,1-dichloroethylene. For clarification, synonyms have been included in Table 1-2 (in parentheses) where applicable.

b. The water PRLs listed in Table 1-2 for 1,2-dibromo-3-chloropropane; 1,2-dibromomethane; 1,2-dichloroethane; 1,1,1,2-tetrachloroethane; 1,1,2,2-tetrachloroethane; and 1,1,2-trichloroethane are greater than the EPA Region 5 DQLs. The December 1995 EPA Region 5 DQL document states that if Method 8260B is used instead of Method 8260, reporting limits (RL) for water analysis can either satisfy or be close to EPA DQLs for the above compounds. The QAPP proposes use of Method 8260A for the analysis of these compounds; however, lower RLs, that are less than the DQLs, can be achieved by Method 8260B. Therefore, the QAPP should be revised to propose use of Method 8260B with a 25 mL purge volume instead of Method 8260A, so that lower PRLs can be achieved for these compounds. (Demonstration of appropriate detection limits shall take place during the U.S. EPA's evaluation of the proposed laboratory.)

REI Response

Table 1-2 of the QAPjP was changed to reflect the use of Method 8260B with a 25 mL purge. The SOP for Method 8260B included with the QAPjP contains a 25 mL purge option. We assume that the portion of the comment concerning the PRL for 1,2-dibromomethane actually refers to 1,2-dibromoethane.

15. **Response to Specific Comment 24.** Several deficiencies are still present in Table 1-3. According to the December 1995 EPA Region 5 DQL document, lower RLs for water analysis could be achieved if alternative methods other than Method 8270 are used for some compounds. These compounds, RLs, and methods are listed in the table below.

Parameter	Lower RL (μg/L)	Method
Benzo(a)anthracene	0.13	8310
Benzo(b)fluoranthene	0.18	8310
Benzo(k)fluoranthene	0.17	8310
Benzo(g,h,i)perylene	0.76	8310
Benzo(a)pyrene	0.23	8310
Bis(2-ethylhexyl)phthalate	2.7	8061A
Dibenzo(a,h)anthracene	0.3	8310
1,4-Dichlorobenzene	0.07/1.0	8021B/8260B

Parameter	Lower RL (μg/L)	Method
3,3'-Dimethylbenzidine	10	8210C
Hexachlorobenzene	0.056	8121
Hexachlorobutadiene	0.014	8121
Hexachloroethane	0.016	8121
Indeno(1,2,3-cd)pyrene	0.43	8310
2-Nitroanaline	10	8131
n-Nitrosodimethylamine	1.5	8070A
n-Nitrosodi-n-propylamine	4.6	8070A

The QAPP shall be revised to use the methods listed above so that lower RLs can be achieved. SOPs for these methods shall also be provided.

REI Response

Tables 1-2 and 1-3 of the QAPjP were changed to indicate that analysis for 1,4-dichlorobenzene will be done by Method 8260B rather than 8270B. Table 1-3 of the QAPjP was changed to reflect lower PRLs for Method 8270B for 10 compounds (i.e., benzo(ghi)perylene, benzo(a)pyrene, bis(2-ethylhexyl)phthalate, dibenz(a,h)anthracene, 3,3'-dimethylbenzidine, hexachlorobenzene, hexachlorobutadiene, 2-nitroanaline, n-nitrosodimethylamine, and n-nitrosodi-n-propylamine) which are now possible due to technical improvements in the laboratory's analytical and computer equipment. The PRL for bis(2-ethylhexyl)phthalate is now below the DQL. PRLs for three of the four carcinogenic PAHs and the three hexachloro compounds are closer to the DQLs by a factor of 3. PRLs for 2-nitroanaline, n-nitrosodimethylamine, and n-nitrosodi-n-propylamine are still above the PRLs; however, this will not affect achievement of the project objectives because waste streams containing significant amounts of these compounds were not received at the site. Additional discussion of this issue is expected to occur during the Performance Evaluation Sample Demonstration Audit.

16. **Response to Specific Comment 25.** Several deficiencies still exist in Table 1-4. The December 1995 EPA Region 5 DQL document does not list DQLs for arochlor compounds. However, Table 1-4 lists DQLs for arochlor compounds. The table shall be revised to indicate the source of these DQLs. In addition, lower RLs for water analysis can be achieved for heptachlor epoxide and toxaphene by using Method 8081A. Table 1-4 shall be revised to list RLs of 0.32 and 0.86 μg/L for heptachlor expoxide and toxaphene, respectively.

REI Response

Table 1-4 of the QAPjP was changed to eliminate DQLs not derived from EPA Region 5's December 1995 DQL document. In addition, Table 1-4 and other text and tables in the QAPjP were changed to indicate that Method 8081 will be used instead of Method 8080. The water PRLs for heptachlor epoxide and toxaphene have been revised as directed in the comment.

17. **Response to Specific Comment 26.** No PRLs for soil and water analyses are listed in Table 1-5 for parathion. Although no DQLs for parathion are listed in the December 1995 EPA Region 5 DQL document, Table 1-5 should be revised to indicate that the PRL for parathion will be consistent with the detection limits in Method 8141A. If there was no recommended Region 5 DQL expressed in the Region 5 guidance document, the source of the values indicated in Table 1-5 shall be cited.

REI Response

Table 1-5 of the QAPjP was changed to show a single line of information for parathion (a.k.a ethyl parathion).

18. **Response to Specific Comment 34.** This comment has been partially addressed. Figure 2-1 still contains names of personnel whose responsibilities are not discussed in text. Figure 2-1 must contain the names of all personnel whose responsibilities are discussed in the text. The text in section 2 of the QAPP shall be revised to discuss responsibilities of all individuals indicated in figure 2-1. Figure 2-1 shall be revised to show the names of all personnel and their corresponding responsibilities. For example, Bryan Kline is listed in Figure 2-1, but his responsibilities are not discussed in text. Also, the names of the drilling and ground penetrating radar subcontractors are shown in Figure 2-1, but their responsibilities are not discussed in text.

REI Response

Section 2 and Figure 2-1 of the QAPjP were changed to reflect the new members of the REI/CWM-Vickery project team. The text and figure were made internally consistent as directed in the comment.

19. **Response to Specific Comment 41.** This comment has not been addressed. A footnote to Table 3-3 states that a minimum 10 percent recovery of the surrogate compound is used as an action limit. However, Table 3-3 also indicates that the acceptable range for surrogate recovery is 24 to 150 percent. The following sentence shall be added to the footnote in Table 3-3: "A recovery of less than 10 percent will

require rejection of the associated analytical results. A recovery of 10 to 23 percent will require that the associated analytical results be qualified as estimated."

REI Response

A footnote was added to Table 3-3 of the QAPjP as directed in the comment.

20. **Response to Specific Comment 42.** This comment has not been addressed. Table 3-6 shows that arsenic will be analyzed for using SW-846 Method 7060. This table and other relevant portions of the QAPP shall be revised to indicate that arsenic will be analyzed for using SW-846 Method 7060A, which is the most recently promulgated method.

REI Response

At the meeting on October 15, 1997, it was agreed that arsenic, lead, selenium, and thallium would be analyzed by Method 6010A using the "trace ICP" option, eliminating the need for GFAA methods for these parameters. The text, tables and SOP appendices of the QAPjP have been changed to reflect this agreement.

21. **Response to Specific Comment 44.** This comment has been partially addressed. Inconsistencies and deficiencies still exist in Section 4.0 of the QAPP and sections of the work plan, which are referenced in the QAPP.

a. Section 4.0 of the QAPP should be revised to correctly cite sections of the RFI work plan. Correspondingly, the following phrases should be revised:

i. Bullet 4 shall be revised to "Field Blank Collection-Section 5.2.5.1.3."

ii. Bullet 5 shall be revised to "Field Duplicate Collection-Section 5.2.5.1.1."

iii. Bullet 6 shall be revised to "MS/MSD Duplicate Collection-Section 5.2.5.1.2."

iv. Bullet 7 shall be revised to "Trip Blank Preparation-Section 5.2.5.1.4."

REI Response

Section 4 of the QAPjP was changed as directed in the comment.

b. Section 5.2.5.1.4 of the work plan shall be revised to state that trip blanks will be included in every cooler or shipping container with aqueous samples for volatile organic compound (VOC) analysis.

REI Response

Section 5.2.5.1.4 of the Work Plan was changed as directed in the comment.

c. Footnote 2 from Table 4-2 shall define the holding time as beginning from the time of sample collection and not as beginning from the time of sample receipt. Footnote 2 of Table 4-2 shall be revised to read "...following the Validated Time of Sample Collection." In addition, the reference to Footnote 6 in Row 4, Column 1 of Table 4-2 should be deleted because Footnote 6 does not apply to metals.

REI Response

Table 4-2 of the QAPjP was changed as directed in the comment.

d. The order in which sample parameters will be collected is not specified in Section 4.0 of the QAPP or Section 5.0 of the work plan. Therefore, Section 4.0 of the QAPP and Section 5.0 of the RFI work plan shall be revised to specify the order of sample collection. The following text shall be added to these sections:

"Samples will be collected in the following order:

1. Samples for VOC analysis
2. Samples for SVOC analysis
3. Samples for inorganic analysis"

REI Response

Section 5.2.3.7 of the Work Plan was changed to specify the order of sample/parameter collection as directed in the comment.

22. **Response to Specific Comment 46.** This comment has been partially addressed. The text in Section 6.1.3 of the work plan states that field and trip blanks will have unique identification numbers. Examples of the unique identification numbers shall be provided, in Section 6.1.3. In addition, Section 6.1.3 shall be revised to explain how the sample identification scheme will indicate the SWMU number, sample type, matrix type, sampling location, and sampling depth (if appropriate). Further, sample tags and labels will be used.

REI Response

Section 6.1.3 of the Work Plan was changed to more clearly define the sample numbering system.

23. **Response to Specific Comment 47.** This comment has been partially addressed. Section 5.2, Page 4, Paragraph 1, of the QAPP states that laboratory custody procedures for Rust Environment and Infrastructure, Inc., are included in Appendix A (SOP No. GT-001). However, this information is not included in Appendix A. The QAPP shall be revised to include this SOP.

REI Response

See response to Item 3 above.

24. **Response to Specific Comment 49.** This comment has been partially addressed. Table 6-1 shall be revised to provide the number of standards for Method 8280. In addition, Table 6-1 describes the frequency of initial calibration verification for Methods 8080a and 8270B as "as needed." Table 6-1 shall be revised to explicitly state what is meant by "as needed" by providing a quantitative frequency and shall specify the conditions under which verification would be performed. The following sentence shall be added to Table 6-1: "The minimum frequency for initial calibration verification is whenever the continuing calibration verification for any analyte exceeds the quality control limit."

REI Response

The number of calibration standards for Method 8280 has been added to Table 6-1 as directed in the comment. The requested footnote has been added to explain the meaning of "as needed". In addition, the line for Method 8080A has been updated to reflect the change to Method 8081, and references to GFAA and non-trace ICP instruments have been deleted, because these instruments will not be used for analysis of samples (as discussed during the October 15, 1997 meeting).

25. **Response to Specific Comment 52.** This comment has been partially addressed. Table 7-1 of the QAPP indicates that sulfide will be analyzed for by Method 376.1. However, Table 8-1 shows that sulfide will be analyzed for by SW-846 Method 9030. To be consistent with the rest of the QAPP, Method 9030 shall be deleted from this table and replaced with Method 376.1.

REI Response

Table 8-1 of the QAPjP was changed to show the correct method for sulfide analysis.

26. **Response to Specific Comment 56.** This comment has been partially addressed.

a. Table 8-1 identifies storage blanks, method blanks, laboratory control samples, and blank spike/blank spike duplicate samples as internal quality control checks. However, these samples are not discussed in Section 8.2. Thus, Section 8.2 shall be revised to explain the purpose of these samples and how they will be prepared. In the case of blank spike samples, specific information concerning the preparation procedure, collection frequency and associated purpose must be inserted into the appropriate QAPP section. Therefore, the following definitions should be added to Section 8.2 of the QAPP:

i. Storage blanks: a blank prepared and stored in a refrigerated area to determine whether additional contaminants are present.

ii. Method blank: a matrix blank carried through the complete sample preparation and analytical procedure to document contamination resulting from the analytical process.

iii. Laboratory control sample: a known matrix spiked with one or more chemicals representative of the target analytes that is used to document laboratory performance.

REI Response

Section 8.2 of the QAPjP was changed as directed in the comment with respect to storage blanks, method blanks, and laboratory control samples. The term "blank spike" is exactly equivalent to the term "LCS" (Laboratory Control Sample). Therefore, in order to avoid confusion, all occurrences of the words "blank spike" in Table 8-1 were replaced with "LCS".

b. Table 8-1 of the QAPP references Method 9030, which is not identified elsewhere in the QAPP. This discrepancy shall be resolved. In addition, Table 8-1 does not specify internal QC checks for Method 8141 (organophosphorus pesticides), Method 325.3 (chloride), and Method 376.1 (sulfide). Table 8-1 shall be revised accordingly to include this information.

REI Response

The reference to Method 9030 was corrected to read 376.1. QC requirements for sulfide analysis remain unchanged. QC requirements for Method 8141 have been added to Table 8-1. In addition, Table 3-4 has been corrected to indicate precision and accuracy criteria for Method 8141. References in the QAPjP to Method 325.4 have been corrected to read

300.0, and QC requirements for Method 300.0 have been added to Table 8-1. A new Table 3-8 has been added, which presents the precision and accuracy requirements for Method 300.0.

c. Method 9030 shall be deleted from the table and replaced with Method 376.1. The internal QC checks for Method 8141 shall consist of the same procedures as those outlined for Method 8080A in Table 8-2, with the surrogates and matrix spikes consisting of compounds listed in Table 3-4. The internal QC checks for Methods 376.1 and 325.3 shall consist of the same procedures as those outlined for Method 9030A in Table 8-2.

REI Response

The reference to Method 9030 has been corrected to read 376.1. QC requirements for sulfide analysis remain unchanged. The title of Table 3-4 has been corrected to reflect its actual contents (precision and accuracy criteria for organophosphorus pesticides by Method 8141). QA requirements for Method 8141 have been added to Table 8-1. In addition, we have corrected the surrogate compound presented in Table 3-4, and have deleted precision/accuracy criteria for Sulfotepp from this table, because Sulfotepp will not be analyzed by this method.

27. **Response to Specific Comment 60.** Table 11-1 still contains several inconsistencies and deficiencies that are discussed below.

a. Table 11-1 shows that the Perkin-Elmer 3030B and 460AA spectrophotometers will be used during the RFI. However, the analytical methods for which these instruments will be used is not identified. Therefore, Table 11-1 shall be revised to identify the analytical methods for which these instruments will be used.

REI Response

Table 11-1 was changed to eliminate instruments that will not be used for analysis of Phase I RFI samples.

b. Table 11-1 shows that Method 8240B will be used during the RFI. However, this method will not be used during this project and shall be deleted from Table 11-1.

REI Response

Table 11-1 was changed to eliminate references to Method 8240B.

c. Table 11-1 shows that the Spectronic 21 Spectrophotometer will be used during the RFI. However, the analytical methods for which this instrument will be used is not identified. Table 11-1 shall be revised to identify the analytical methods for which this instrument will be used.

REI Response

Table 11-1 was changed to eliminate instruments that will not be used for analysis of Phase I RFI samples.

d. Dioxins and furans will be analyzed for during the RFI using Method 8280. However, Table 11-1 does not specify the types of equipment that will be used to perform the analysis. Table 11-1 shall be revised to identify the equipment that will be used to analyze for dioxins and furans.

REI Response

Table 11-1 was changed to include the equipment that will be used for Method 8280.

28. Before the RFI can be implemented, the laboratory CWM-Vickery has selected must participate in and pass a laboratory performance evaluation sample demonstration audit. Samples of unknown nature and substance will be delivered to proposed laboratories for analysis. CWM-Vickery must agree to pay for the analysis and reporting of data for these performance evaluation demonstration samples. These samples must be analyzed in accordance with provisions of this conditionally approved QAPP. If the results and supporting data packages are not of an accurate and appropriate nature, then this evidence will be used as basis for rejecting the audited laboratory. This would necessitate withdrawing the conditional approval of the RFI work plan and QAPP. Only after the proposed laboratory has passed the audit demonstrations will the QAPP qualify for final approval, resulting in a document to be signed by the RCRA Permitting QA Coordinator prior to project implementation.

REI Response

CWM-Vickery and its selected laboratories will participate in the performance evaluation sample demonstration audit.

PHASE I RCRA FACILITY INVESTIGATION
QUALITY ASSURANCE PROJECT PLAN

CHEMICAL WASTE MANAGEMENT
VICKERY, OHIO

U.S. EPA ID NO. OHD 020 273 819

NOVEMBER 1997

Prepared By: Rust Environment & Infrastructure

Prepared For: CWM-Vickery

Project Management Signatures

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Thomas W. Matheson, RCRA Corrective Action Project Manager U.S. EPA	Date
Willie Harris, Regional QA Manager U.S. EPA	Date

PHASE I RCRA FACILITY INVESTIGATION
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- Extraction of PCDD/PCDF from Solid Samples - 8280 and DFL M01.1, SOP No. DSP224, Version 8
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- SOP No. QA000-0000 - Data Validation Procedures for EPA Level III Data.

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B GP Environmental Services Sample Custody Standard Operating Procedures and Triangle Laboratories Quality Assurance Plan

C Report Titled "Evaluation of Impacts on Acidic Material Spill on Aquatic Communities in Little Raccoon and Raccoon Creeks" Dated August 1993 by ENSR Consulting and Engineering.

LIST OF PERSONS WHO HAVE RECEIVED THIS QAPjP

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SECTION 1
PROJECT DESCRIPTION

This section describes the purpose and scope of the Phase I Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) at the Chemical Waste Management (CWM) Vickery Treatment, Storage and Disposal (TSD) Facility. It indicates how the findings of this investigation will be used to determine the appropriate course of further action, if any, required to address the overall objectives of the RCRA Corrective Action process. The Phase I RFI is being completed under the direction of the United States Environmental Protection Agency (U.S. EPA) as a condition to the issuance of a Part B Permit to CWM-Vickery dated October 24, 1994. As stated in the Part B Permit, CWM-Vickery must investigate potential releases of hazardous waste(s) or hazardous constituent(s) from all Solid Waste Management Units (SWMUs) at the facility, regardless of when the waste was placed in such units. If these investigations show the presence of hazardous waste constituents in the environment at concentrations that pose a risk to human health and the environment, Corrective Measures may be necessary.

This Quality Assurance Project Plan (QAPjP) presents the organization, objectives, planned activities, and specific Quality Assurance/Quality Control (QA/QC) procedures associated with the Phase I RFI for this facility. Specific protocols for sampling, sample handling and storage, chain-of-custody (COC), and laboratory and field analyses described herein. All QA/QC procedures will be structured in accordance with applicable technical standards, U.S. EPA's requirements, regulations, guidance, and technical standards. This QAPjP has been prepared in accordance with a guidance manual entitled, "Region 5 Model RCRA Quality Assurance Project Plan," May 1993.

1.1 Introduction

This Phase I QAPjP was prepared by Rust Environment & Infrastructure (Rust) for the CWM-Vickery TSD Facility at the request of CWM-Vickery. The QAPjP is appended to the Phase I RFI Work Plan, dated August 1995, revised May 1996 and November 1997. A Field Sampling Plan (FSP) which is included as Section 5 of the Phase I Work Plan (WP) is hereby explicitly incorporated into this QAPjP by reference. The Health and Safety Plan (HASP) is also appended to the WP.

1.1.1 Objectives of Phase I

The purpose of the Phase I RFI is to determine if releases have actually occurred from 53 SWMUs and 10 AOCs identified in (and/or subsequent to) the RCRA Facility Assessment (RFA). Specifically, are there hazardous waste constituents in the soils adjacent to and underlying the SWMUs and AOCs or in the sediments of surface streams draining the site. The Phase I RFI will also include preliminary characterization of the groundwater in the areas around the land-based SWMUs and AOCs. This will be done by using the soil sampling proposed in this Phase I WP and a combination of historical and newly acquired groundwater monitoring data. The Phase I RFI report will propose specific and focussed investigations to assess the extent and risk-impact of those releases, including further characterization of groundwater, if necessary, during the Phase II RFI. All data collected during Phase I and Phase II will be used to support a Quantitative Risk Assessment (QRA) to recommend an appropriate CMS, if necessary.

This approach is being taken because most of the SWMUs and AOCs at the facility were land-based units used for the storage of liquid hazardous waste prior to deep-well injection or for the treatment of residuals by land-farming. Some of these units have been clean closed and some have been only partially closed. They are underlain by clayey lacustrine and glacial till soils which, based on several years of semi-annual and quarterly groundwater monitoring, have substantially limited the migration of hazardous waste or hazardous waste constituents into the subsurface.

Objectives of the data collection will be as follows:

- Characterize the nature of residual materials at those SWMUs and AOCs not clean closed by drilling borings and collecting samples of these materials.

- Determine through borings and soil sampling if there are hazardous waste constituents in the soils adjacent to and underlying the SWMUs and AOCs i.e., have hazardous waste constituents been released beyond the boundaries of the SWMUs and into the environment. This will involve the collection of soil samples from beneath residual waste materials, or the collection of surficial soil samples. During this determination, it may be readily apparent from field observations that hazardous waste constituents are present in the soil, and if so, the borings would be extended to assess the vertical extent of migration.

- Characterize the effectiveness of the clean closure of former SWMUs now underneath the Toxic Substances Control Act (TSCA) Closure Cell by collecting a sample of water from the capillary drainage layer. This layer has continual inward flow, and the groundwater flowing into it has traveled through the clean closed soils of the former SWMUs.

- Characterize residual effects of releases to surface water drainage-ways at the site by collecting samples of sediment at exit points from the site, which have been impacted by previous spills.

- Preliminarily characterize groundwater in the uppermost flow system (lacustrine sediments) and the uppermost aquifer (bedrock) downgradient of land-based SWMUs and AOCs that still contain residual waste materials through validation of the three most-recent rounds of historical groundwater monitoring data and the collection and analysis of new groundwater samples from 10 existing monitoring wells.

1.1.2 Project Status/Phase I

Rust will utilize an integrated and phased approach for the RFI. The Phase I RFI will integrate existing data with information that will be gathered during the Phase I RFI.

The Phase I RFI will include:

- Residual waste material sampling to characterize SWMUs and AOCs not clean closed;

- Subsurface soil sampling at SWMUs and AOCs where residual materials are still present to determine if hazardous waste constituents have been released into the underlying native soils.

- Surface soil (0 to 24 inches) sampling at SWMUs and AOCs where liquids or sludges were or could have been released to the ground surface;

- Subsurface soil (>24 inches) sampling to assess the vertical extent of contamination where the uppermost native soil shows field evidence of contamination;

- Surface and subsurface soil sampling in areas not used for waste management purposes to establish background metals data;

- Sampling of water from the capillary drainage layer of the TSCA Closure Cell to characterize the effectiveness of clean closures at former SWMUs now located beneath the Closure Cell;

- The validation of the three most recent rounds of historical groundwater monitoring data and the collection and analysis of groundwater samples from ten groundwater monitoring wells;

- Sediment sampling of surface water drainageways at the exit points for streams draining the site to assess residual impacts of releases to surface water;

Soil, sediment and groundwater samples will be analyzed for Appendix IX volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides (organochlorine and organophosphate), polychlorinated biphenyls (PCBs), dioxins\furans, herbicides, metals, cyanide, sulfide, and chloride. Approximately 10 percent of the soil samples will also be analyzed for soil pH, cation exchange capacity (CEC), Atterberg limits, percent moisture, grain size distribution, and total organic carbon (TOC) to determine soil physical parameters and their effect on possible contamination migration. Field parameters, to be monitored during monitoring well purging to verify that a representative groundwater sample is collected, will include pH, temperature, and specific conductivity. A turbidity measurement will be made at the time of actual sample collection.

Data collected during the Phase I investigation will be used to determine whether a release to the environment has occurred. Data collected during the Phase I investigation will also be used to determine Phase II sampling locations and frequencies in order to assess the vertical and horizontal extent of soil and groundwater contamination.

A QRA will be performed using all data collected from the Phase I and Phase II investigations. If unexpected risks are derived from the QRA, a corrective measures study will be completed.

Potential Phase II RFI work may include:

- Additional soil or sediment sampling to further define the extent and concentration levels of hazardous waste constituents in these media;

- Sampling of existing wells where such monitoring wells are appropriately positioned to assess a particular SWMU or AOC with soil contamination; and

- Installation of additional monitoring wells where the existing monitoring well network can not adequately characterize potential groundwater impacts from a SWMU or AOC with soil contamination.

A technical memorandum, presenting the Phase I RFI data and recommendations of the QRA will be prepared and submitted to the U.S. EPA. After a review of the technical memorandum, the need for implementing a Phase II RFI will be evaluated in light of the overall objectives of the Corrective Action process.

This QAPjP is intended to fully address the scope of the Phase I RFI. To the extent that the potential Phase II RFI is comparable to the Phase I RFI, this QAPjP is expected to apply; however, specific review of any proposed Phase II RFI activities and this QAPjP will be required to assess its applicability and the need to provide further information in a "Phase II RFI QAPjP Addendum."

1.1.3 QAPjP Preparation Guidelines and History

As explained above, this Phase I RFI QAPjP has been prepared in accordance with the "Region 5 Model RCRA Quality Assurance Project Plan", dated May 1993. A pre-QAPjP meeting was held in Chicago on January 17, 1995. CWM-Vickery submitted a document describing a proposed grouping of SWMUs and outline the project objective on February 17, 1995, and received comments from U.S. EPA on April 11, 1995. The timing of this receipt did not allow the comments to be incorporated in the first draft of this QAPjP submitted in April 1995. "Version 0" of the QAPjP (August 1995) was revised in response to the February 27, 1996 comments received on "Version 0." Additionally, comments addressed during the March 25, 1996 meeting were incorporated into this QAPjP for Revision 1, dated May 1996. Therefore, the current version of the Phase I RFI QAPjP will be referenced as "Revision 2".

1.2 Site/Facility Description

1.2.1 Location, Facility Size, and Surroundings

As described in Section 2.1 of the Phase I RFI WP, the CWM-Vickery TSD Facility is located in a rural, unincorporated area of Sandusky County in the north-central part of Ohio.

1.2.2 Natural & Manmade Features and Topography

The natural and manmade features of the CWM-Vickery TSD Facility are described in Sections 2.1 and 3.1 of the Phase I RFI WP.

1.2.3 Local Geology & Hydrogeology

Information concerning the site's geology, soil, groundwater resources, surface hydrology and drainage is presented in Sections 3.2 and 3.3 of the Phase I RFI WP.

1.3 Site/Facility History

1.3.1 General History

The CWM-Vickery TSD Facility provides for the treatment, storage and disposal of liquid hazardous wastes. The site began as Don's Oil Service which started operations at this facility in 1958 and in 1970 changed its name to Ohio Liquid Disposal (OLD). Waste Management, Inc. (WMI) acquired the facility in 1978 and later transferred it to CWM (a wholly owned subsidiary of WMI).

The facility began as an oil recovery facility to provide hauling services for waste oil from neighboring industries to a central facility and to recover the oil for eventual resale. As time went on, the facility started to accept various industrial wastes and stored them in surface impoundments. In 1964, the facility was granted permission by the State of Ohio to accept chemical process waste. More surface impoundments were constructed to hold these wastes. As the inventory of wastes increased the site began searching for a suitable means to dispose of the waste. In 1972, old was granted permission to drill a test hole to evaluate the subsurface

conditions for the possible location of an injection well. After a number of years of applying for the approval to use the injection well, being denied, and appealing, an approval was finally granted to inject waste into the subsurface wells on-site. A total of 7 injections wells were drilled on-site throughout the history of the facility (Injection wells 1, 1A, 2, 3,4, 5 and 6).

During the history of the facility, a total of 12 surface impoundments existed. These surface impoundments were constructed between the years 1964 through 1975. As injection of wastes began, the surface impoundments were closed. Between the years of 1979 to 1992, all of the surface impoundments were closed. Details of these closures can be found in Section 6.0 of the Report on Current Conditions (December 1994, Revised April 1994). Injection wells 1, 1A and 3 were plugged and abandoned due to mechanical and physical failures. Presently, Injection Wells 2, 4, 5 and 6 are active on-site.

Additional activities at the site included treatment, storage and disposal of wastes. Landfarming and oil recovery were the most prevalent of these activities.

In order to provide for the disposal of the wastes generated during the closure of the surface impoundments and other treatment facilities, CWM-Vickery was granted an approval to construct a Toxic Substances Control Act (TSCA) closure cell. The closure cell was built between 1986-1988. Waste from a temporary waste pile was finally given an approval to be moved into the closure cell in 1990. The waste in the closure cell is comprised of stabilized wastes generated during the closure of the surface impoundments, and specific site facilities detailed in the 1984 Consent Decree. Five of the surface impoundments were certified clean closed (i.e., Ponds 4, 5,7, 11 and 12) by the State of Ohio Environmental Protection Agency (OEPA).

Presently, the CWM-Vickery TSD Facility receives a large variety of liquid hazardous wastes. The most common types include; pickle liquors, acid wastes, caustic wastes, neutral wastes, and other aqueous wastes including landfill leachate. The facility does not accept radioactive wastes, infectious wastes, explosive or shock sensitive wastes, air reactive wastes, compressed gases, reactive wastes that generate dangerous quantities of toxic or explosive gases when acidified, bulk ignitable wastes, bulk wastes containing >5% VOCs, or wastes that the facility deems can not be managed properly.

1.3.2 Past Data Collection Activities

The CWM-Vickery TSD Facility has been subject to a number of hydrogeologic and geologic investigations since 1983. The following summaries are based on a review of reports and supporting documents submitted by consultants and information obtained from the project files of the U.S. EPA and the State of Ohio.

1.3.2.1 Hydrogeologic Assessment (1983)

This assessment was completed by Bowser-Morner, Inc. and is summarized in their report titled "Hydrogeologic Assessment, Northern Ohio Treatment Facility, Vickery, Ohio", dated May 3, 1983. The purpose of this assessment was to perform a hydrogeologic study and analysis of existing groundwater quality data. The work was done in accordance with the special terms and conditions set forth by the Hazardous Waste Facilities Approval Board (HWFAB) in the site permit issued December 1981. The hydrogeologic investigation was based on a comprehensive soil boring and superficial rock coring program integrated with data available in published and unpublished literature. Water quality data was summarized and evaluated utilizing regression analysis.

The report summarized that the natural soil conditions are good to excellent for the containment of the types of waste handled at the site. A statistical analysis of the groundwater quality data indicated that most of the parameters except for hardness, sulfates and chlorides were below federal drinking water standards at the time of the analysis. Of these parameters, hardness and sulfate concentrations were attributed to the natural groundwater and the mineralogy of the rock formation through which it flows. The reasons for the elevated chloride levels were not determined as part of this study. The study recommended additional testing, analysis and installation of new monitoring wells.

1.3.2.2 Geohydrologic Review (1983)

This review was completed by Golder Associates (Golder) and described in their report titled "Geotechnical and Geohydrologic Data Review, Vickery, Ohio Chemical Waste Management Facility", dated June 20, 1983. The report was requested by CWM-Vickery in conjunction with the OEPA, to perform a thorough review and study of all the geotechnical and geohydrologic

data available. The report summarized the geologic and hydrogeologic conditions at the site. This included details on the types of deposits, structural features, permeability (vertical and horizontal), water level data and the groundwater flow directions and velocities. An overall understanding of the hydrogeological system at the site was developed with the data available to the date of the report. This was summarized by Golder as an interim step in defining the aquifer parameters and more quantitatively understanding the system. Additional studies and continuing studies were to be directed toward providing these data and information needed to accurately assess the potential for groundwater contamination at the site. In conclusion, Golder stated that the site is considered to have characteristics favorable for locating a hazardous waste facility.

1.3.2.3 Summary of Hydrogeologic Conditions (1983)

This summary was completed by Golder and described in their report titled "Summary and Characterization of Site Hydrogeologic Conditions" dated September 29, 1983. The purpose of this report was to present a more detailed discussion and interpretation of site hydrogeology, based on the results of published data and previous studies at the site by others, and the most recent results of field investigations at the site. A summary of hydrogeologic conditions was made by Golder which include:

- The site is underlain by some 40 ft. to 50 ft. of lacustrine clay and glacial till overburden. A series of carbonate deposits extend from the overburden to depths of about 600 ft. Underlying the carbonate deposits is a sequence of sedimentary rocks which extends to the Precambrian basement rock at a depth of about 2,900 ft.

- The water table in the overburden is close to the ground surface. Although all of the overburden below the water table is saturated, it is not considered an aquifer because of its very low hydraulic conductivity.

- The uppermost aquifer at the site is in the carbonate rocks of the Salina Group ("Big Lime" Formation). This confined aquifer and potentiometric surface is about 10 ft. to 15 ft. below ground surface.

- The ambient water quality in the carbonate aquifer is poor due to naturally high total dissolved solids (TDS) and sulfate content. The base of the carbonate aquifer is considered

to be the base of potable water in Ohio. The groundwater in the sedimentary rocks beneath the carbonate aquifer is generally a brine water.

- Groundwater level monitoring at the site indicates that on-site pumping has created a cone of depression in the upper portion of the shallow dolomite aquifer. This cone of depression may impede off-site migration of water in the upper portion of the dolomite.

- The direction of groundwater flow in the overburden is generally downward. The rate of flow to the underlying dolomite is less than 0.07 ft./yr. and is controlled by the low hydraulic conductivity of the soil.

- The natural groundwater gradient in the dolomite aquifer (disregarding the effects of on-site pumping) is thought to be directed toward the northwest. There is currently no data available regarding the vertical gradients within the dolomite, but it is possible that there is a slight upward flow component.

- Additional hydrogeologic information is provided in Appendix C of the Phase I RFI WP. This information includes water level hydrographs for all monitoring wells on-site 1986 to 1995, monitoring well construction details, precipitation data for 1995, two reports which discuss tritium analysis, and hydrogeological vertical flow nets. This information was provided to U.S. EPA's consultant Dr. Wayne Pettyjohn to substantiate vertical flow of groundwater within the lacustrine and glacial till zone on-site.

1.3.2.4 Additional Studies

Several additional studies have been performed since the above have been completed. These studies and investigations have centered on describing certain specific areas at the facility. A list of previous studies is provided in Table 3-1 of the Phase I RFI WP.

1.3.3 Current Status

Based on reports and documents reviewed for the site, and a current assessment of all available information, the following target compounds and source area release mechanisms have been targeted for further investigation.

- Past Facility Operations. The potential for releases to the soil and groundwater at the facility from past operations vary depending on the nature of the SWMU. SWMUs with adequate secondary containment have a low potential for releases to the soil and groundwater. However, before the mid-1980's most of the SWMUs at the facility did not have adequate secondary containment and releases to the soil were not uncommon. All of these releases were cleaned up immediately following the knowledge of there occurence.

  Most of the medium-size historical releases (50 to 5,000 gallons) resulted from failures of the polyvinyl chloride (PVC) waste transfer lines which carried liquid waste between the former surface impoundments, tanks, filter buildings and pumphouses. These releases may have impacted the surface soil but had little effect on the groundwater because of the low permeability of the clay soil. The releases were immediately remediated.

- Surface Impoundments. The former unlined surface impoundments posed a risk to soil and groundwater. The increased hydraulic head created when the surface impoundments were filled with liquid wastes may have contributed to deeper contamination of soil beneath the surface impoundments. Typically, several feet of contaminated clay were removed from the surface impoundments during closure activities.

  Studies performed at the site have statistically evaluated concentrations in the monitoring wells at the site. It has been concluded that one isolated location (L-19) has been contaminated with 1,2-dichloroethane. Migration of 1,2-dichloroethane contamination to the bedrock aquifer is not likely because of the low permeability of the glacial/lacustrine clay.

- Drainage System. Several large releases of liquid hazardous waste to Little Raccoon Creek and Meyers Ditch have been documented. In 1979, a spill of up to 96,000 gallons of hazardous waste from the transfer line between surface impoundment 7 and 11 reached Meyers Ditch. The waste was reported to have been pumped out. On March 3, 1986, approximately 75,000 gallons of Waste Pile leachate was accidentally released to Little Raccoon Creek through surface water flow control gate G-1 at the Leachate Retention Pond. Other releases have occurred to the surface water, one as recently as April 1993. All releases were remediated immediately after occurrence. An evaluation of the aquatic communities in Little Raccoon and Raccoon Creeks was completed to determine the effects of the 1993 spill, if any. A report was completed by ENSR in August 1993 detailing the results of the

evaluation. This report is provided as Appendix C. Due to the nature of the wastes which were released, an analysis of the streambed sediment for such constituents as, metals, PCBs and SVOCs should be made to characterize this medium.

Although remediated at the time, historical releases of contaminants as described above may have resulted in the some contamination of on-site soils and CWM-Vickery TSD Facility buildings. At this time, these soils will be evaluated to determine if they constitute a secondary source of contamination, potentially affecting human and environmental targets in the area of the CWM-Vickery TSD Facility.

1.4 Project Objectives

The Data Quality Objectives (DQOs) for this Phase I RFI reflect the quality of data needed to support decisions made during the RFI. These DQOs are determined based on the end usage of the data and directing the RFI toward the CMS.

The CWM-Vickery Phase I RFI DQOs, or project reporting limits (PRLs) presented within this QAPjP, are the highest analytical level achievable by the laboratory to support a QRA. These PRLs are deemed adequate as most of the documented SWMUs are believed to represent minimal environmental concerns.

If unexpected situations arise during the performing of the Phase I RFI, DQOs may be changed to reflect the type and use of data needed. However, the overall project objectives for this RFI will not change as movement of the RFI to the CMS in a timely manner is the ultimate project objective. The mechanism for movement through the RFI will be that any detection above the PRL or "non-detect", for which the PRL is above EPA Region 5 DQL, will be defined as potential contamination for risk assessment.

1.4.1 Specific Objectives by Activity/Media

The purpose of the Phase I RFI is to collect sufficient information to evaluate whether releases have occurred at 53 SWMUS (organized into 9 groups) and 10 AOCs. If releases have occurred, the Phase I RFI will provide information on the nature of these releases (i.e., constituents and concentrations) and may provide some information on the vertical extent of contamination.

Constituent and concentration data will be used to quantitatively assess whether unreasonable health risks are associated with the releases.

The specific objectives of the data collection at the CWM-Vickery TSD Facility are as follows:

Field screening of VOCs will be performed for the following purposes: i) general characterization of possible contaminant levels through casual screening of soil cores; ii) selection of samples for laboratory analysis through a specified headspace screening of soil samples; and iii) monitoring of ambient and work-space atmospheres for worker health and safety. This data collection activity will be performed on-site using an HNu or Photoionization Detector (PID). The documentation of instrument calibration, in accordance with procedures specified by the manufacturer, and frequency is specified in Section 6 of this QAPjP.

At two of the SWMU Groups (Groups A and C), where clean closure has not been performed, samples of the residual materials and the native soils adjacent to and underlying the SWMUs will be collected and analyzed for Appendix IX parameters using SW-846 methods to characterize the nature of these materials, and to determine whether there has been a release of hazardous waste or hazardous constituents into these soils. This data would serve as the basis for reducing parameter lists for Phase II RFI work, and will be used in a QRA. As such, a confirmation level of DQOs will be required.

At six of the SWMU Groups (Groups D, E, F, G, H, and I) and four of the AOCs (A, B, C, and F) soil samples will be collected and analyzed for Appendix IX parameters using SW-846 methods to determine whether or not there has been a release of hazardous waste or hazardous waste constituents into the native soils adjacent to or underlying the SWMU or AOC. Where field observations indicate that contamination is present in the uppermost native soil, additional soil samples will be collected at greater depths to characterize the vertical extent of migration. These data will be used in a QRA. As such, a confirmation level of DQOs will be required.

At SWMU Group B, a water sample will be collected from the capillary drainage layer that underlies the TSCA Closure Cell and analyzed for Appendix IX parameters using SW-846 methods. This activity will be performed as part of the Phase I RFI groundwater sampling. This cell was built "over" clean closed SWMUs #4, 5 and 7. There is continual inward flow to the drainage layer, and the groundwater flowing into it has traveled through the clean closed soils of

the former SWMUs. These data will be used in a QRA. As such, a confirmation level of DQOs will be required.

At AOC H, sediment samples will be collected from Meyers Ditch and Little Raccoon Creek and analyzed for Appendix IX parameters using SW-846 methods to characterize residual effects of the single large release of processed acid wastewater that reached this drainage way. These data will be used in a QRA. As such, a confirmation level of DQOs will be required.

At three SWMU's within Group I (No. 43, 44, and 45) soil samples will be collected and analyzed for chloride, VOCs, SVOCs and metals as an indicator of leakage from these SWMUs. The SWMUs are used exclusively for the management of sanitary waste produced at three of the on-site buildings. The facilities wastewater contained in these SWMUs is processed on site in the facility's sanitary wastewater treatment system and injected into the deepwell.

Groundwater samples will be collected from 10 existing monitoring wells (L17, L19A, L20, L25 and L26, MW14R, MW15R, MW20R, MW22R, and MW24R) to confirm the validation of recent historical groundwater monitoring data from these wells. These monitoring wells are located within the main facility area and positioned to be able to characterize possible releases (if any) from land-based SWMUs and AOCs that still contain residual (stabilized) waste materials. If analytical soil results indicate potential groundwater impacts, the extent of these impacts will be determined in Phase II.

Confirmation of analytical quality assures that DQOs are met and is integral to supporting a QRA. Assurance of analytical quality will be achieved through the full documentation of SW-846 analytical methods, sample preparation steps, data packages and data validation procedures necessary to provide defensible data. QC will be sufficient to define the precision and accuracy of these procedures at every step. The sampling and analysis program is summarized in Table 1-1.

1.4.2 Project Target Parameters and Intended Data Usages

The target parameters for field monitoring for the Phase I RFI at the CWM-Vickery TSD Facility are VOCs as detectable using an HNu. As described above, these data will be used for the following purposes: i) general characterization of possible contaminant levels through casual

screening of soil cores; ii) selection of samples for laboratory analysis through a specified headspace screening of soil samples; and iii) monitoring of ambient and work-space atmospheres for worker health and safety.

The target parameters for laboratory analysis for the Phase I RFI project at the CWM-Vickery TSD Facility are the Appendix IX VOCs, SVOCs, pesticides (organochlorine and organophosphate), PCBs, herbicides, metals, cyanide, sulfide, chloride and dioxins/furans, and they are listed in Table 1-2 through Table 1-8.

Intended usages for the laboratory data are to determine the presence or absence of contamination. The procedure for data comparison will be presented as follows:

- On-site soil sample metal data will be compared to background concentrations. All other on-site soil sample data will be compared to U.S. EPA Region 9 Industrial PRGs.

- Groundwater sample metal data will be compared to background concentrations. All other groundwater sample data will be compared to U.S. EPA Region 5 DQLs.

- Sediment sample data will be compared to Ecotox thresholds. If Ecotox thresholds are not available, the data be compared to DQLs.

Phase II samples will be collected at every Phase I location where analytical results meet any of the above conditions.

For the Phase I RFI, project reporting limits (PRLs), which are the lowest reliably quantifyable level achievable by the laboratory, have been established. Given the constraint of using SW-846 GC-MS methods that are most appropriate for broad-scan initial site characterization purposes, the PRLs have been established as close as possible to EPA Region 5's data quality levels (DQLs). The PRLs and DQLs are shown in Tables 1-2 through 1-8.

All RFI data (Phase I and Phase II) will also be used in a quantitative risk assessment (QRA) at the completion of the RFI. Non-detected analyte data will be reported at the laboratory's Method Detection Limit (MDL), which will be lower than the Project Reporting Limit (PRL). Non-detect results will be used in the QRA at ½ the MDL. If the results of the QRA determine the

need for a CMS, the data will also be used to assess feasibility of using certain remediation technologies.

1.4.3 Data Quality Objectives

DQO level one will be used for field instrument analysis. These include HNu field screening of soils and pH, specific conductance/conductivity, and temperature for water samples. The SOPs will be followed by field personnel.

DQO level three will be used for analysis of samples for VOCs, SVOCs, pesticides, PCBs, herbicides, dioxins, furans, metals, cyanide, sulfide and chloride. The U.S. EPA procedures will be followed by the laboratory and SOPs for each analysis is provided in Appendix A.

DQO level three will be used for all geotechnical testing analysis. The ASTM procedures will be followed by the laboratory and the SOPs are provided in Appendix A.

1.5 Sample Network Design and Rationale

The sample network design and rationale is fully described in detail in the FSP in Section 5 of the Phase I RFI WP. Sample matrices, analytical parameters and frequencies of sample collection for the 10 SWMU groups and the 10 AOCs are summarized in Table 1-1. As described above, it is possible that additional soil samples will be collected at locations where field observations indicate that the uppermost native soil is contaminated. The person making such decisions will be the Rust Field Team Leader whose responsibilities are described in Section 2 of this QAPjP.

Maps showing intended soil, sediment and groundwater sampling locations are included as Figures in the FSP in Section 5 of the Phase I RFI WP as follows:

- SWMU Group A -- Figure 5-7
- SWMU Group C -- Figure 5-8
- SWMU Group D -- Figure 5-9
- SWMU Group E -- Figure 5-10
- SWMU Group F -- Figure 5-11

- SWMU Group G -- Figure 5-12
- SWMU Group H -- Figure 5-13
- SWMU #15 -- Figure 5-14
- SWMU #20 -- Figure 5-15
- SWMU #28 -- Figure 5-16
- SWMU #41 -- Figure 5-17
- SWMU #42 -- Figure 5-18
- SWMU #43 -- Figure 5-19
- SWMU #44 & #45 -- Figure 5-20
- AOC A -- Figure 5-21
- AOC B -- Figure 5-22
- AOC C -- Figure 5-23
- AOC F -- Figure 5-24
- AOC H -- Figure 5-26
- AOC I -- Figure 5-27
- Groundwater Sampling -- Figure 5-28

Groundwater samples will be collected from the capillary drain, which underlies SWMUs in Group B (Section 5.9.2 of the WP) and from ten on-site groundwater monitoring wells (Section 5.11 of the WP). No sampling is proposed in AOC J (Section 5.10.10 of the WP).

It is possible that some of the sampling locations will be changed on the basis of field observations or conditions. For example, on-site observations may show that the intended sampling location at a SWMU suspected of releasing liquids to the ground surface is not along a flow path away from the source, or that there is an area of stained soil which would more fully characterize the impacts of the release. In these cases, sampling locations would be changed to provide data more representative of site conditions. On the other hand, certain sampling locations may need to be moved due to overhead or underground obstructions that either limit accessibility to the location or create undue safety hazards to the field crew. The person making such decisions will be the Rust Field Team Leader whose responsibilities are described in Section 2 of this QAPjP. All changes to the Phase I RFI will be documented in the field log book.

1.6 Project Schedule

As agreed during the October 15, 1997 meeting, Phase I RFI field activities are targeted to begin in April 1998, pending U.S. EPA's approval of the QAPjP. A Task Bar Chart for project activities as a function of time following this approval is presented in Figure 1-1.

SECTION 2
PROJECT ORGANIZATION AND RESPONSIBILITY

At the direction of the U.S. EPA RCRA Project Manager (PM), Rust will have overall responsibility for the Phase I RFI. Rust will perform the field investigation, evaluate the data, and prepare the Phase I RFI report. Project management will also be provided by Rust in concert with the CWM-Vickery. The various quality assurance, field, laboratory and management responsibilities of key project personnel are defined below.

2.1 Project Organization Chart

A Project Organization Chart is presented in Figure 2-1. It shows the roles, individuals and lines of authority for the Phase I RFI, and includes all of the individuals discussed below.

2.2 Management Responsibilities

U.S. EPA RCRA Project Manager

Thomas W. Matheson will be the U.S. EPA RCRA PM. He will have overall responsibility for all phases of the RFI/CMS.

CWM Vickery Project Manager

Steve Lonneman will be the CWM-Vickery Project Manager (PM). He will be responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The CWM-Vickery PM's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The CWM-Vickery PM will report directly to the U.S. EPA RCRA PM and will provide the major point of contact and control for matters concerning the project. The CWM-Vickery PM will:

- Define project objectives;
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task;

- Acquire and apply technical and corporate resources as needed to ensure performance within budget and schedule constraints;
- Review the work performed on each task to ensure its quality, responsiveness, and timeliness;
- Review and analyze overall task performance with respect to planned requirements and authorizations;
- Approve all reports (deliverables) before their submission to U.S. EPA Region 5;
- Ultimately be responsible for the preparation and quality of interim and final reports; and
- Represent the project team at meetings and public hearings.

Rust Project Director

Edward Need, P.G. will serve as the Rust project director (PD) and will be responsible for all technical elements of the sampling. The Rust PD:

- Reviews and approves Field Operating Procedures;
- Provides senior technical oversight and coordination of the overall project;
- Assures that approved procedures meet QA/QC objectives of the project; and,
- Responsible for implementation of recommendations made by the QA/QC manager.

Rust Project Manager

Michael Bedard, P.E. will serve as the Rust PM and will be responsible for management of Rust field staff and project costs. The Rust PM's responsibilities include:

- Day to day direction of field staff and subcontractors;

- Resolution of any problems related to personnel, material or equipment; and,

- Communication of project progress to Rust PD and CWM PM.

Martha Costello will serve as Project Health and Safety Coordinator and will coordinate required training and safety documentation.

The Rust Field Team Leader will coordinate all daily field activities performed by the field sampling team, drilling subcontractor, and GPR Subcontractor. The Field Team Leader will also be responsible for sample collection and shipment of samples to the laboratory and the preparation of daily reports. The Field Team Leader will report directly to the Rust PM.

2.3 Quality Assurance Responsibilities

Rust QA/QC Officer

Michael Christopher will serve as QA/QC manager and be responsible for all procedures and tasks pertaining to quality assurance on this project. The QA/QC Manager's responsibilities include:

- Monitoring project activities to verify compliance with QA/QC Plans;

- Implementing routine QA/QC audits for all technical deliverables; and,

- Preparation and review of all corporate QA/QC guidance documents that pertain to the Phase I RFI.

Rust Data Validator

Tony Noce will be the Rust Data Validator. Data validation will be performed following U.S. EPA contract laboratory program, national functional guidelines for organic data review (EPA 540/R-941012, February 1994) and U.S. EPA contract laboratory program, and national functional guidelines for inorganic data review (U.S. EPA 540/R-94013, February 1994). All

organic and inorganic data will be evaluated and validated according to EPA Region 5 Data Validation Criteria.

U.S. EPA Region 5 Quality Assurance Manager (RQAM)

EPA RQAM has the responsibility to review and approve all QAPjP. Additional U.S. EPA responsibilities for the project include:

- Conducting external Performance and System Audits of GP Environmental's, Triangle's and/or Rust's laboratories; and,

- Reviewing and evaluating analytical field and laboratory procedures.

2.4 Laboratory Responsibilities

Samples collected during the Phase I RFI will be sent to the following laboratories:

1) GP Environmental Services
   202 Perry Parkway
   Gaithersburg, Maryland 20877
   (301) 926-6802

   This laboratory will be used for analysis of all organic and inorganic parameters except dioxins/furans.

GP Environmental Services Project Manager

The GP Environmental Services PM, Ken Ives, will report directly to the Rust PM and will be responsible for the following:

Ensuring all resources of the laboratory are available on an as-required basis;

- Coordinating with Triangle Laboratories for performance of dioxins/furans analysis; and,

- Over viewing of final analytical reports.

GP Environmental Services Laboratory Manager

GP Environmental Services Laboratory Manager, Marty Sadoughi, will report to the GP Environmental Services PM and will be responsible for the following:

- Coordinating laboratory analyses;
- Supervising in-house chain-of-custody;
- Scheduling sample analyses;
- Overseeing data review;
- Overseeing preparation of analytical reports; and
- Approving final analytical reports prior to submission to Rust/CWM-Vickery

GP Environmental Services Quality Assurance Manager

GP Environmental Services QA Manager, Elsa Tai, has the overall responsibility for data after it leaves the laboratory. The GP Environmental Services QA Manager will communicate data issues through the GP Environmental Services Project Manager. In addition, the GP Environmental Services QA Manager will:

- Review and approve the QAPjP;
- Overview laboratory QA;
- Overview QA/QC documentation;
- Conduct detailed data review;
- Determine whether to implement laboratory corrective actions, if required and also be responsible for formally approving corrective actions;

- Define appropriate laboratory QA procedures; and
- Prepare laboratory Standard Operation Procedures (SOP).

GP Environmental Services Sample Custodian

GP Environmental Services Sample Custodian will report to the GP Environmental Services Laboratory Manager. Responsibilities of the GP Environmental Services Sample Custodian will include:

- Receiving and inspecting the incoming sample containers;
- Recording the condition of the incoming sample containers;
- Signing appropriate documents;
- Verifying COC and its correctness;
- Notifying laboratory manager and laboratory supervisor of sample receipt and inspection;
- Assigning a unique identification number and customer number, and entering each into the sample receiving log;
- With the help of the Laboratory Manager, initiating transfer of the samples to appropriate lab sections; and
- Controlling and monitoring access/storage of samples and extracts.

The GP Environmental Services Sample Custodian is Chris Lyons.

GP Environmental Services Technical Staff

GP Environmental Services technical staff will be responsible for sample analysis and identification of corrective actions. The staff will report directly to the GP Environmental Services Laboratory Manager.

2) Triangle Laboratories, Inc.
801 Capitola Drive
Durham, North Carolina 27713
(919) 544-5729

This laboratory will be used for laboratory analysis of dioxins/furans.

Triangle Laboratories Project Manager

Triangle Laboratories' PM, Mary McDonald, will report to Ken Ives, the GP Environmental Services PM, and will be responsible for the following:

- Ensure that the needed resources are available for the project;
- Coordinate with GP Environmental Services for the completion of the dioxin analysis; and,
- Over viewing final analytical report.

Triangle Laboratories Laboratory Management Team

The Triangle Laboratories Laboratory Management Team consists of Belen Rueda, Amy Bederlea, and Azor Gatchetchiladze. The team reports to Mary McDonald and is responsible for the following:

- Coordination of dioxin analysis;
- Supervising in-house COC;
- Scheduling sample analysis;
- Dioxin analysis;
- Data review analysis;
- Preparation of dioxin analytical reports; and,
- Approval of final analytical reports prior to submission to Ken Ives (GP Environmental Services).

Triangle Laboratories QA Manager

The Triangle Laboratories QA Manager is Patty Ragsdale. The QA Manager has the overall responsibility for the data after it leaves the laboratory.

Triangle Laboratories Sample Custodian

The sample custodian will report to the Laboratory Manager. The responsibilities of the sample custodian will include:

- Receive and inspect sample containers;
- Record conditions of sample containers;

- Sign appropriate documents;
- Verify COC and its correctness;
- Sample receipt and inspect notification;
- Assignment of identification receiving log;
- Transferring of samples to appropriate lab section; and,
- Sample control.

The Triangle Laboratories Sample Custodian is Bill Hurst.

3) Rust Environment & Infrastructure
   11785 Highway Drive, Suite 100
   Cincinnati, Ohio 45241
   (513) 483-5300

   This laboratory will be used for analysis of geotechnical parameters (e.g., Atterberg Limits, percent moisture, etc.).

The Laboratory Quality Assurance Manager for the Rust-Cincinnati Geotechnical Laboratory is Dr. Steven Zhou. Dr. Zhou will have the responsibility for supervising the analysis and assuring the data is of the quality required for this project.

2.5 Field Responsibilities

Rust Field Team Leader

The Rust Field Team Leader will be responsible for leading and coordinating the day-to-day activities of the various resource specialists under his supervision. The Rust Field Team Leader

will be a highly experienced environmental professional and will report directly to the Rust PM. Specific Field Team Leader responsibilities include:

- Provision of day-to-day coordination with the CWM-Vickery PM on technical issues in specific areas of expertise;
- Developing and implementing field-related WPs, assurance of schedule compliance, and adherence to management-developed study requirements;
- Coordinating and managing field staff including sampling, drilling, and supervising field measurement;
- Implementing QC for technical data provided by the field staff including field measurement data;
- Adhering to work schedules provided by the Rust PM;
- Authoring, writing, and approving of text and graphics required for field team efforts;
- Coordinating and overseeing of technical efforts of subcontractors assisting the field team;
- Identifying problems at the field team level, resolving difficulties in consultation with the CWM-Vickery PM, implementing and documenting corrective action procedures, and provision of communication between team and upper management; and,
- Participating in preparation of the final report.

Rust Field Technical Staff

The technical staff for this project will be drawn from Rust's pool of corporate resources. The technical team staff will be utilized to gather and analyze data, and to prepare various task reports and support materials. All of the designated technical team members are experienced professionals who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

Geophysical Survey System, Inc. (GSSI) will perform ground penetrating radar services. GSSI is a designer and manufacturer of ground penetrating radar systems and offers field survey services.

Bowser-Morner, Inc will be retained as the drilling subcontractor. Bowser-Morner, Inc. has provided drilling services on several projects at the facility and is familiar with all site requirements. The drilling subcontractor will be responsible for providing all drilling equipment, sampling equipment and decontamination of the drilling and sampling equipment.

SECTION 3
QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective for this project is to develop and implement procedures for field sampling, COC, laboratory analysis, and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, COC, laboratory instrument calibration, laboratory analysis, reporting of data, internal QC, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPjP. The purpose of this section is to address the specific objectives for precision, accuracy, completeness, representativeness and comparability. This section also describes the level of QC effort (i.e., the kind and frequency of QC samples) for the investigative program described in this QAPjP.

3.1 Precision

Precision is a measure of the degree to which two or more measurements are in agreement. The precision of field measurements (HNu screening for VOCs) will be assessed through replicate measurements; however, because VOCs will be "lost" as part of an initial measurement, the subsequent replicate measurement is expected to be biased "low". This is due to the fact that the measurement is completed from an uncontrolled sampling point, i.e., not from a jar or a bag. Thus, no formalized assessment (i.e., the calculation of relative percent difference) is planned.

Analytical precision will be assessed through the calculation of the relative percent difference (RPD) for the concentrations of spiked analytes in two replicate samples. The equation for calculating precision for this project can be found in Section 12 of this Phase I RFI QAPjP. Field effects on analytical precision will be assessed through the collection and measurement of field duplicates at a rate of 1 duplicate per 10 analytical samples. The total number of field duplicates being collected for this project is shown in Table 1-1. Laboratory effects on analytical precision will be assessed through the use of laboratory duplicate samples and matrix spike/matrix spike duplicate (MS/MSD) samples. The total number of MS/MSD samples being collected for this

project is shown in Table 1-1. Precision control limits for laboratory analysis are given in Tables 3-1 through 3-7.

3.2 Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference value. The accuracy of field measurements (HNu screening for VOCs) will be assessed through evaluation of calibration records maintained during the course of the field operations. The procedures for routine calibration of the HNu are described in Section 6 of this Phase I RFI QAPjP. Thus, no formalized assessment (i.e., the calculation of percent recovery) is planned.

Analytical accuracy will be assessed through the calculation of the percent recovery (%R) of a known amount of selected analytes spiked into a designated sample. The equation for calculating accuracy in this project can be found in Section 12 of this Phase I QAPjP. Field effects on accuracy will be assessed through evaluation of sampling documentation showing adherence with all sample handling, preservation and holding times requirements. Laboratory effects on accuracy will be assessed through evaluation of surrogate recoveries in each ORGANIC sample analyzed, and through the analysis of MS for the determination of percent recoveries. The total number of MS samples being collected for this project is shown in Table 1-1. Accuracy control limits for laboratory analysis are given in Tables 3-1 through 3-7.

3.3 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. The calculation of completeness is described in Section 12 of this QAPjP. By their nature, the field screening measurements of VOCs are considered to be 100 percent complete. It is expected that GP Environmental Services will provide data meeting QC acceptance criteria for 80 percent or

more for soil samples and 90 percent for water samples using SW-846 methods. If this objective would not be met due to difficulties and/or problems in the laboratory, then additional samples will be taken and analyzed to meet the objective.

3.4 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the FSP is followed and that proper sampling techniques are used, proper analytical procedures are followed and holding times of samples are not exceeded.

3.5 Comparability

Comparability is an expression of the confidence with which one data set can be compared with another. Comparability is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the FSP is followed and that proper sampling techniques are used. The sampling activities will be audited by the Rust QA officer to ensure proper procedures are being utilized. This QA will be used to ensure comparability of data collected. Comparability within the laboratory will be assured by the use of proper techniques and methodologies as documented in this QAPjP. Any subsequent sampling events will be expected to produce comparable results.

3.6 Level of Quality Control Effort

Field blank, trip blank, field duplicate, laboratory duplicate, MS and MSD samples will be analyzed to assess the quality of the data resulting from the field sampling programs. Field blanks will consist of analyte-free, HPLC-grade water placed in sample containers at the site

using the same (decontaminated) equipment that will be used to collect the samples. Field blanks are used to check for contamination which may have been introduced as a result of the sampling procedures and/or from ambient field conditions. Field blanks will be collected at the rate of one per 10 or fewer aqueous investigative samples.

Trip blanks will consist of deionized water placed in sample containers in the laboratory. These samples will accompany the other (empty) sample containers to the site, be kept with them in the field, and accompany the filled samples containers back to the laboratory. Trip blanks are used to assess the potential for VOC contamination of samples due to contaminant migration during shipment and storage. One trip blank will accompany each cooler of aqueous VOC samples shipped to the laboratory.

Field duplicate samples will consist of distinct samples obtained from the same sampling point or location. They are analyzed to check for sampling and analytical reproducibility. Duplicate samples will be collected at the rate of one per 10 or fewer investigative samples.

MS samples (which are prepared in the laboratory from extra investigative sample volume collected in the field) provide information about the effect of the sample matrix on the preparation and measurement methodology. The extra volumes required are triple the normal volume for VOC analysis and double the normal volume for other organics analysis. These extra volumes are in addition to the normal volume requirements for the investigative sample. All MS for organic analyses are performed in duplicate and are hereinafter referred to as MS/MSD samples. MS/MSD samples will be collected (for organics analysis) at the rate of one per 20 or fewer investigative samples. A MS and laboratory duplicate (LD) will be analyzed for inorganic parameter analysis. These analyses must be performed on an aliquot from the original investigative sample container; the samples will be designated in the field as MS samples but no extra volume is required. The MS/LD analyses will be performed at the rate of one per 20 or fewer investigative samples.

The number of field duplicate, field blank, trip blank, MS, LD, and MSD samples to be collected for the Phase I RFI at CWM-Vickery are listed Table 1-1. Sampling procedures are specified in the FSP (Section 5 of the Phase I RFI WP).

SECTION 4
SAMPLING PROCEDURES

The sampling procedures to be used in the Phase I RFI at the CWM-Vickery TSD Facility will be consistent with the purpose of this project. The FSP outlines all the sampling procedure information. The FSP is located in Section 5 of the Phase I RFI WP. Table 4-1 presents the sampling and analysis objectives rationale.

The sample containers will be provided by GP Environmental Services, who will prepare them in accordance with current U.S. EPA guidance (i.e., "Specification and Guidance for Contaminant Free Sample Containers," April 1992). Table 4-2 presents the sample containers, preservatives and holding times for this project.

Please refer to Section 5 of the Phase I RFI WP for the following information:

- Sample Containers - Section 5.2.3.3
- Obtaining Contaminant-Free Sample Containers - Section 5.2.3.3
- QC Sample Procedures - Section 5.2.5
- Field Blank Collection - Section 5.2.5.1.3
- Field Duplicate Collection - Section 5.2.5.1.1
- MS/MSD Collection - Section 5.2.5.1.2
- Trip Blank Preparation - Section 5.2.5.1.4
- Sampling Equipment Decontamination - Section 5.5
- Subsurface Soil Sampling Collection Procedures - Section 5.7.1
- Surface Soil Sampling Collection Procedures - Section 5.7.2
- Sediment Sampling Collection Procedures - Section 5.7.3
- Test Pit Sampling Procedures - Section 5.7
- Groundwater Sampling Procedures - Section 5.11

SECTION 5
CUSTODY PROCEDURES

It is the U.S. EPA Region 5 policy to follow the U.S. EPA Region 5 custody, or COC protocols as described in "NEIC Policies and Procedures," EPA-330/9-78DDI-R, Revised June 1985. This custody is in three parts: Sample collection, Laboratory analysis, and Final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area.

A sample or evidence file is under your custody if they:

- Are in your possession;
- Are in your view, after being in your possession;
- Are in your possession and you place them in a secure location; and,
- Are in a designated secure area.

5.1 Field Custody Procedures

Field logbooks will provide the means of recording the activities performed during data collection. As such, entries will be described in as much detail as possible so that persons going to the facility could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound, field survey books or notebooks. Field logbooks will be assigned to field personnel, but will be stored in the document control center when not in use. Each field logbook will be identified by the project-specific document number.

The title page of each field logbook will contain the following:

- Person to whom the logbook is assigned;
- Field logbook number;
- Project name;
- Project start date; and
- End date.

Entries into the field logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the site, field sampling or investigation team personnel and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in ink, signed, and dated and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark which is signed and dated by the sampler. Whenever a sample is collected, or a measurement is made, a detailed description of the location of the station, which includes compass and distance measurements, shall be recorded. The number of the photographs taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in Section 5.0 of the Phase I RFI WP. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. Sample identification number will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

The sample packaging and shipment procedures summarized below will ensure that the samples will arrive at the laboratory with the COC intact.

a) The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.

b) All bottles will be identified by use of labels with sample numbers, sampling locations, date/time of collection, and type of analysis. The sample numbering system is presented in Section 6.0 of the Phase I RFI WP.

c) Sample labels are to be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a

pencil was used to fill out the sample label because the ballpoint pen would not function in freezing weather.

d) Samples are accompanied by a properly completed COC form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to a mobile laboratory, to the permanent laboratory, or to/from a secure storage area. An example COC form is shown in Figure 5-1 of the Phase I RFI WP.

e) Samples will be properly packaged on ice at 4°C for shipment and dispatched to the laboratories specified in Section 2.4 of this QAPjP as appropriate for the analyses specified in Section 2.4 of this QAPjP, with a separate signed custody record enclosed in and secured to the inside top of each sample box or cooler. Shipping containers will be locked and secured with strapping tape and custody seals for shipment to the laboratory. The custody seals will be signed by the field team leader or his designee before attaching to the front right and back left of the cooler. The custody seals are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.

f) Whenever samples are collected to be split, a separate sample receipt will be prepared for those samples and marked to indicate with whom the samples are being collected. The person relinquishing the samples to the facility or agency will be requested to sign the sample receipt. If the representative is unavailable or refuses to sign, this will be noted in the "Received By" space.

g) All shipments will be accompanied by the COC Record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler for returning to the sampling office.

h) If the samples are sent by common carrier, a bill of lading should be used. Receipts of bills of lading will be retained as part of the permanent documentation. If sent by mail, the package will be registered with return receipt requested. Commercial carriers are

not required to sign off on the custody form as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

i) Samples will generally be transported to the laboratory by overnight courier but no later than 72 hours from time of sample collection.

5.2 Laboratory Custody Procedures

Laboratory custody procedures for sample receiving and log-in; sample storage and numbering; tracking during sample preparation and analysis; and storage of data are described in Section 7 of the GP Environmental Services QAPjP which has been excerpted and attached to this QAPjP as Appendix B. Similar information for Triangle Laboratories and Rust are provided in Appendix A.

5.3 Final Evidence Files

Custody of final evidence files will be maintained by the Rust PM for a period of 10 years. The files will be kept in a secured, limited access area and under the custody of the Rust PM, and offered to U.S. EPA prior to disposal. The final evidence files will contain at a minimum:

- Field Logbooks;
- Field Data and Deliverables;
- Photographs;
- Drawings;
- Soil Boring Logs;
- Laboratory Data Deliverables;
- Data Validation Reports;
- Data Assessment Reports;
- Progress Reports, and,
- All Custody Documentation.

SECTION 6
CALIBRATION PROCEDURES AND FREQUENCY

This section describes the calibration procedures and the frequency at which these procedures will be performed for both field and laboratory instruments.

6.1 Field Instrument Calibration

The HNu Model PI 101 will be calibrated daily prior to use and will be recalibrated every 25 samples. In addition, the PID will be calibrated if the probe assembly is removed from the readout assembly, if the ion chamber is cleaned, if the ultra-violet (UV) light is changed, or if the PID appears to be working erratically.

All calibration procedures will be documented in the field logbook. Each entry shall include the following information:

- Date;
- Time;
- Weather Conditions;
- Calibrating Personnel;
- Condition of Battery;
- Type of Calibration Gas;
- Concentration of Calibration Gas;
- Gas Cylinder Pressure;
- Span Setting; and,
- Pertinent Comments.

The PID is calibrated in the following manner:

1) Attach the probe extension to the probe. The probe extension must be used during the calibration procedure.

2) Attach the probe to the readout assembly. Align the 12 pin interface tabs before locking the probe to readout assembly with the threaded coupling.

3) Turn the function switch to the battery position. The needle should be in the green region on the readout. If it is not, recharge the battery. Make note of the battery's condition in the PID Calibration Log.

4) Turn the function switch to the standby position. If necessary, set the zero point with the zero potentiometer.

5) Attach the regulator to the isobutylene cylinder (calibration gas). Make note of the isobutylene concentration and the cylinder pressure in the PID Calibration Log. Do not use cylinders with pressures less than 30 pounds per square inch (psi). Low cylinder pressure can effect the calibration results.

6) Attach the probe extension to the regulator with a ¼ inch diameter tubing as described in PID Manufacturer's manual. The probe extension and the ¼ inch diameter tubing should be clean. Dirty extensions and ¼ inch diameter tubing can effect the calibration results.

7) Turn the function switch to the 0-200 ppm range.

8) Initiate gas flow by fully opening the valve on the regulator. The regulator sets and controls the flow rate of the gas at a value preset at the factory. Allow the gas to flow until a steady reading is obtained.

9) If the reading is the same as concentration indicated on the span gas bottle, then no adjustment is necessary. If the reading has changed from the concentration indicated on the span gas bottle, unlock and adjust the span control knob until the desired reading is obtained. Lock the span control knob and make note of the span setting in the PID Calibration Log.

6.2 Laboratory Instrument Calibration

GP Environmental Services, Triangle Laboratories and Rust E&I-Cincinnati Geotechnical Laboratory's calibration procedures and requirements are found in their SOPs which are included in Appendix A. Table 6-1 presents the calibration of the laboratory equipment for this project.

The laboratory maintains a sample logbook for each instrument which will contain the following information: instrument identification, serial number, date of calibration, analyst, calibration solutions run and the samples associated with these calibrations.

SECTION 7
ANALYTICAL PROCEDURES

The samples collected during the Phase I RFI field operations at CWM-Vickery will be analyzed by GP Environmental Services, 202 Perry Parkway, Gaithersburg, Maryland 20877, 301-926-6802 (chemical analysis for all organic and inorganic parameters except dioxins/furans); Triangle Laboratories, Inc., 801 Capitola Drive, Durham, North Carolina 27713, (919) 544-5729 (chemical analysis of dioxin); and Rust Environment & Infrastructure Geotechnical Laboratory, Suite 100, 11785 Highway Drive, Cincinnati, Ohio 45241, 513-733-9374 (geotechnical analyses).

7.1 Field Measurements

Field measurements will be limited to qualitative screening of VOCs using an HNu. Two types of screening will be performed -- for general information purposes and for selection of samples for laboratory analysis. Where the purpose is to obtain general information on the subsurface materials (i.e., comparable to noting the color and texture of the soil), the HNu probe tip will be drawn along the edge of the soil core as the sampling device is opened. The rate of movement will balance the need to obtain and observe a valid instrument response with the need to take measurements before excessive loss of VOCs occurs. Where the purpose is to select samples for laboratory analysis, the head-space screening procedure described in the FSP (Section 5 of the Phase I RFI WP) will be followed. This procedure involves immediate collection of possible samples in containers appropriate for laboratory analysis, with a portion of sample material placed in a plastic bag for head-space screening after a specified time allowance for volatilization.

7.2 Laboratory Analytical Procedures

GP Environmental Services will analyze the samples collected in the field for Appendix IX VOCs, SVOCs, pesticides (organochlorine and organophosphate), PCBs, herbicides, metals, cyanide, sulfide, and chloride as detailed in Table 1-1 using the analytical and preparatory methods listed in Table 7-1. The parameters comprising these analytical suites and the reporting limits that will be used by GP Environmental Services are shown in Tables 1-2 through 1-7. Triangle Laboratories will analyze the samples collected in the field for dioxins/furans using the analytical and preparatory methods listed in Table 7-1. The parameters comprising this analytical suite and the reporting limits that will be used by Triangle Laboratories are shown in Table 1-8. Table 7-1 shows the laboratories' SOP numbers, the titles of the methods, and the SW-846 (3rd Edition) methods on which SOPs are based. The SOPs are included in the Phase I RFI QAPjP as Appendix A.

7.3 Geotechnical Analytical Procedures

The Rust Geotechnical Laboratory will analyze the samples collected in the field for cation exchange capacity, Atterberg limits, moisture content, grain-size distribution (sieve and hydrometer), total organic carbon (TOC), and soil pH using the methods listed in Table 7-2.

SECTION 8
INTERNAL QUALITY CONTROL CHECKS

8.1 Field QC Checks

QC checks to assess field sampling precision and bias will be made by collecting field duplicates and field blanks (aqueous samples only) for laboratory analysis. Collection of these samples will be in accordance with the procedures described in the FSP at the frequency specified in Section 3 of this Phase I RFI QAPjP.

8.2 Laboratory Quality Control Checks

The GP Environmental Services laboratory uses an internal QC program to ensure the reliability and validity of the analysis performed at the laboratory. Each SOP includes a QC section which addresses the minimum QC requirements for the procedure.

The specific QC requirements applicable to the analyses included in the Phase I RFI are included in the laboratories' SOPs in Appendix A and are summarized in Table 8-1. The storage blank, method blank, and laboratory control samples listed in Table 8-1 are defined as follows:

- Storage Blank: a blank prepared and stored in a refrigerated area to determine whether additional contaminants are present;
- Method Blank: a matrix blank carried through the complete sample preparation and analytical procedure to document contamination resulting from the analytical process; and,
- Laboratory Control Sample: a known matrix spiked with one or more chemicals representative of the target analytes that is used to document laboratory performance.

All data obtained will be properly recorded. The data package will include a full deliverable package capable of allowing the recipient to reconstruct QC information and compare it to QC criteria. Any samples analyzed which are in non-conformance with the QC criteria will be reanalyzed by the laboratory, if sufficient volume is available and if sample holding times are not exceeded.

SECTION 9
DATA REDUCTION, VALIDATION, AND REPORTING

The data generated during the Phase I RFI will be reduced and validated prior to reporting. Data will not be disseminated by the laboratory until it has been subjected to the procedures summarized below.

9.1 Data Reduction

9.1.1 Field Data Reduction Procedures

Field data pertaining to the Phase I RFI will only be from direct read instrumentation for qualitative screening of VOCs by PID, and all data will be recorded into the field logbook immediately after the measurements are taken. Therefore, field data reduction will be minimal. If errors are made, results will be legibly crossed out, initialed and dated by the field member, and corrected in a space adjacent to the original (erroneous) entry. Later, when these readings are tabulated or transferred to boring logs for inclusion in the Phase I RFI report, the Field Team Leader will proof the table and logs to determine whether any transcription errors have been made.

9.1.2 Laboratory Data Reduction Procedures

The exact procedures for data collection and reduction vary depending on the analytical method. For most analyses, these procedures are fully automated. For soil samples, all analyses will be performed on samples as-received, and final results will be corrected to dry weight basis. The only exception is dioxins/furans, which will be analyzed and reported "as received." If any QA-induced reanalysis is performed, the analyst will determine which of the two results to

report, and the reason for this choice will be explained in the case narrative. Raw data for both analyses will be included in the final data package.

9.2 Data Validation

9.2.1 Procedures to Evaluate Field Data

Procedures to evaluate field data for this project primarily include checking the calibration records for the HNu. This task will be the responsibility of the Rust QA Officer, who will otherwise not participate in making any of the field measurements, or in adding notes, data or other information to the field logbook.

9.2.2 Procedures to Validate Laboratory Data

Procedure to validate laboratory data will be similar to the U.S. EPA Contract Laboratory Program's "National Functional Guidelines for Organic Data Review" (EPA 540/R-94/012, February 1994) and "National Functional Guidelines For Inorganic Data Review" (EPA 540/R-94/013, February 1994). The data validation will be performed according to the SOP titled "Data Validation Procedures for EPA Level III Data." This SOP is presented in Appendix A. All organic and inorganic data will be validated by the Rust Data Validator who is identified in Section 2 of this Phase I RFI QAPjP.

The overall completeness of the data package will be evaluated by the Rust Data Validator. Completeness checks will be administered on all data to determine whether deliverables specified in the Phase I RFI WP and Phase I RFI QAPjP are present. At a minimum, deliverables will include sample chain-of-custody forms, analytical results, QC summaries, and supporting raw data from instrument printouts. The reviewer will determine whether all required items are present and will request copies of missing deliverables.

9.3 Data Reporting

9.3.1 Field Data Reporting

Field data will be reported using summary tabulations of the HNu readings and as information included on boring logs.

9.3.2 Laboratory Data Reporting

GP Environmental will assemble the completed laboratory data packages and forward them to the Rust Project Manager. The completed data package will comprise the following sections:

1. Data Summary
2. Volatiles Package
3. Semi-volatiles Package
4. Organochlorine Pesticides Package
5. Organophosphorus Pesticides Package
6. Herbicides Package
7. Metals and Cyanides Package
8. Wet Chemistry Package
9. Subcontractor Data Package (Dioxins/Furans)

Each of the above sections (except the data summary) will be a "stand-alone" document, containing all information necessary to perform a complete data validation. The format will be "CLP-like," and all information required by CLP will be present, in the order required by CLP, although the exact format of forms may differ somewhat from CLP. For non-CLP analyses, e.g., herbicides, the report format will be analogous to comparable CLP methods, and will include all information necessary to perform complete data validation. Each section will include final

calculated results, plus all raw data, instrument printouts, logbook pages, etc., necessary to completely reconstruct the analysis.

Each of the above sections (except the data summary) will include a case narrative. The narrative will be prepared by a senior analyst or supervisor, and will discuss the analysis in narrative format. At a minimum, the narrative will include the following:

1. Date
2. Laboratory Work Order Number
3. Number and Type of Samples Received
4. Analyses Performed
5. Any Deviations from the Analytical Protocol
6. Any QA Problems Encountered, and What Action Was Taken
7. Discussion of Any Technical Problems, Action Taken, and Potential Effect on Data.

Each narrative will be signed by the person preparing the narrative, and the completed data package will be signed by the laboratory manager, or his designee.

Dioxins/furans data packages will be prepared by Triangle Laboratories in essentially the same manner as described above for other data packages. The package format will be "CLP-like," including summarized sample results and QA data, plus all raw data, instrument printouts, etc., necessary to completely reconstruct and validate the reported results. The dioxins/furans package will include an analysis narrative conforming to the requirements above. The package will be forwarded to the GP Environmental Project Manager, who will verify completeness of the package, and ensure that it is incorporated into the final data package.

SECTION 10
PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the FSP and QAPjP. The audits of field and laboratory activities include two independent parts: internal and external audits.

10.1 Field Performance and System Audits

10.1.1 Internal Field Audits

The internal audits of field activities including sampling and field measurements will conducted by the Rust QA Officer. These audits will verify that all established procedures are being followed. The initial field audit will be conducted during the first week of field operations. If a substantial number of corrective action issues are identified during this initial audit, or if the field operations extend beyond 12 weeks, follow-up audits will be scheduled and performed to ensure that deficiencies are corrected and to verify that QA procedures are maintained throughout the field operations.

The audits will include examination of field sampling records, field measurement records, field instrument operating records, instrumentation calibration records, sample collection, sample handling, sample packaging, sample documentation, maintenance of QA procedures, and chain-of-custody procedures. The results of these audits will be reported in the next monthly QA report to management as described in Section 14 of this Phase I RFI QAPjP. If these audits identify non-conformance with the FSP and Phase I RFI QAPjP that affect data quality, the emergency Corrective Action procedures described in Section 14 of this Phase I RFI QAPjP (including notification of the U.S. EPA RCRA PM) will be implemented.

10.1.2 External Field Audits

External field audits may be conducted by the U.S. EPA RCRA PM or his designee. External field audits may be conducted at any time during the field operations. These audits may or may not be announced and are at the discretion of the U.S. EPA. External field audits will be conducted according to the field activity information presented in the Phase I RFI QAPjP.

10.2 Laboratory Performance and Systems Audits

10.2.1 Internal Laboratory Audits

The internal laboratory audit will be conducted by the Rust QA Officer or his designee. An initial laboratory audit will be conducted during the first month following approval of this QAPjP by U.S. EPA. Subsequent system audits will be performed on an annual basis and subsequent performance audits will be performed on a quarterly basis as necessary based on the duration of the Phase I RFI.

The internal lab system audits will include an examination of laboratory documentation on sample receiving, sample log-in, sample storage, COC procedures, sample preparation and analysis, instrument operating records, etc. The performance audits will involve preparing blind QC samples and submitting them along with project samples to the laboratory for analysis throughout the project. The Rust QA Officer will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable QC performance.

10.2.2 External Laboratory Audits

An external audit will be conducted by U.S. EPA Region 5 Central Regional Laboratory (CRL). An external audit will be conducted at least once prior to the initiation of the sampling and

analysis activities. These audits may or may not be announced and are at the discretion of the U.S. EPA. External laboratory audits will include (but not be limited to) review of laboratory analytical procedures, laboratory on-site audits, and/or submission of performance evaluation samples to the laboratory for analysis.

SECTION 11
PREVENTATIVE MAINTENANCE

11.1 Field Instrument Preventative Maintenance

The field equipment for this project includes HNu meters and pH, conductivity, and temperature instruments. Specific preventative maintenance procedures to be followed for field equipment are those recommended by the manufacturer. Field instruments will be checked and calibrated daily before use. Calibration checks will be documented in field notebooks. Critical spare parts such as lamps and batteries will be kept on-site to reduce downtime. Backup instruments and equipment will be available on-site or within 1 day shipment to avoid delays in the field schedule.

11.2 Laboratory Instrument Preventative Maintenance

As part of their QA/QC programs, routine preventative maintenance is conducted by GP Environmental Services, Triangle Laboratories, and Rust to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees will regularly perform routine scheduled maintenance and repair of all instruments. All maintenance that is performed will be documented in each of the laboratories' operating records. All of the laboratories' instruments will be maintained in accordance with manufacturer's specification.

The schedules for preventive maintenance for each laboratory's instrumentation are included in each of the laboratory SOPs attached as Appendix A, and are summarized in Table 11-1.

SECTION 12
SPECIFIC ROUTINE PROCEDURES
USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

12.1 Precision Assessment

To assess the precision of analytical procedures, extra volumes of environmental samples designated in the field as the MS and MSD samples for organics are spiked with known amounts of the analyte or analytes to be evaluated. Laboratory Duplicates (LD) will be collected for inorganics. As specified in Section 3 of this Phase I QAPjP, MS/MSD/LD samples will be collected at the rate of one MS/MSD for every 20 or fewer investigative samples. The duplicate spiked and unspiked samples are analyzed, and the difference in the amount of the analyte detected in the two samples is compared to determine the relative percent difference (RPD). Daily control charts are plotted for the spiked compounds and kept on instrument, matrix, and analyte specific bases. The RPD is calculated according to the following formula:

$$\text{(Organics)RPD} = \frac{\text{amount in Spike 1 - amount in Spike 2}}{0.5(\text{amount in Spike 1 + amount in Spike 2})} \times 100$$

$$\text{(Inorganics)RPD} = \frac{\text{amount in Sample - amount in Lab Duplicate}}{0.5(\text{amount in Sample + amount in Lab Duplicate})} \times 100$$

12.2 Accuracy Assessment

To assess the accuracy of analytical procedures, an environmental sample designated in the field as the MS sample is spiked with a known amount of the analyte or analytes to be evaluated. As specified in Section 3 of this Phase I RFI QAPjP, MS samples will be collected at the rate of one MS for every 20 or fewer investigative samples. The spike sample is analyzed, and the increase

in concentration of the analyte observed in the spiked sample (due to the addition of a known quantity of the analyte) compared to the reported value of the same analyte in the unspiked sample determines the percent recovery. Daily control charts are plotted for each commonly analyzed compound and kept on instrument, matrix, and analyte specific bases. The percent recovery for a spiked sample is calculated according to the following formula:

$$\%R = \frac{\text{(amount in Spiked Sample - amount in Sample)}}{\text{(known amount added)}} \times 100$$

12.3 Completeness Assessment

Completeness is the ratio of the number of valid sample results to the total number of planned sample analyses for a specific matrix and analytical procedure. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness} = \frac{\text{(number of valid measurements)}}{\text{(number of measurements planned)}} \times 100$$

SECTION 13
CORRECTIVE ACTION

Corrective action is the process of identifying, recommending, approving and implementing measures to counter unacceptable procedures or out-of-quality-control performance which can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation and data assessment. All corrective action proposed and implemented will be documented in the regular QA reports to management. Corrective action should only be implemented after approval by the CWM-Vickery PM, or his designee. If immediate corrective action is required, an approval will be secured by telephone from the CWM-Vickery PM with notification to the U.S. EPA RCRA PM, and the situation will be documented in an additional memorandum.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the Rust PM. The Rust PM will involve other Rust and/or laboratory management as appropriate to the situation, and notify the CWM-Vickery PM, who in turn will notify the U.S. EPA RCRA PM. If the problem is analytical in nature, information on these problems will be promptly communicated to the U.S. EPA QA Section. Implementation of corrective action will be confirmed in writing through the same channels.

Any non-conformance with the established QC procedures in the Phase I RFI QAPjP or FSP will be identified and corrected in accordance with the Phase I RFI QAPjP. The CWM-Vickery PM, or his/her designee, will issue a non-conformance report for each non-conformance condition.

13.1 Field Corrective Action

Corrective action in the field can be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the Phase I RFI QAPjP, etc.), or when sampling procedures and/or field analytical procedures require modification due to unexpected conditions. In general, the field team (e.g., Rust Field Team Leader, Rust Field Staff, CWM-Vickery PM) may identify the need for corrective action. The Rust Field Staff in consultation with the Rust Field Team Leader will recommend a corrective action. The CWM-Vickery PM will approve the corrective measure which will be implemented by the Rust Field Staff. It will be the responsibility of the Rust Field Team Leader to ensure the corrective action has been implemented.

If the corrective action will supplement the existing sampling plan using existing and approved procedures in the Phase I RFI QAPjP (i.e., additional soil borings), corrective action approved by the CWM-Vickery PM will be documented. If corrective actions result in fewer samples (or analytical fractions), in alternate locations, or in other situations that would cause project quality assurance objectives not to be achieved, all levels of project management including the Rust Project Manager, the CWM-Vickery PM, and the U.S. EPA RCRA PM must concur with proposed action.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The Rust QA Officer will identify deficiencies and recommended corrective action to the CWM-Vickery PM. Implementation of corrective actions will be performed by the Rust Field Team Leader and Field Staff. Corrective action will be documented in QA reports and be distributed to each of the PMs (Rust, CWM-Vickery and the U.S. EPA RCRA PM).

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by the U.S. EPA RCRA PM.

13.2 Laboratory Corrective Action

Corrective action in each of the laboratory's may occur prior to, during and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with lab analysts and section leaders, it may be necessary for the QA Manager (GP Environmental Services, Triangle Laboratories, or Rust) from each of the laboratories to approve the implementation of corrective action.

The submitted standard SOPs specify some conditions during or after analysis that may automatically trigger corrective action or optional procedures. These conditions may include dilution of samples, additional sample extract cleanup, automatic reinjection/reanalysis when certain quality control criteria are not met, etc. In these situations, the bench chemist will identify the need for corrective action. The GP Environmental Services Laboratory Manager, or the Triangle Laboratories Laboratory Manager in consultation with the laboratories' technical staff, will approve the required corrective action to be implemented by the laboratory staff. The QA Manager from either laboratory will ensure implementation and documentation of the corrective action.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in each of the laboratories' (GP Environmental Services, Triangle Laboratories or Rust) corrective action forms (signed by analyst, section leader and

quality control coordinator), and the narrative data reports sent from the laboratories to the Rust Data Validator.

If corrective action does not rectify the situation, the laboratory will contact the Rust PM. If the non-conformance causes project objectives not to be achieved, it will be necessary to inform all levels of project management including the Rust Project Manager, the CWM-Vickery PM and the U.S. EPA RCRA PM to concur with the corrective action.

13.3 Corrective Action During Data Validation and Data Assessment

The need for corrective action may be identified during either the data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory.

These actions are dependent upon the ability to mobilize the field team, whether the data to be collected is necessary to meet the required quality assurance objectives (e.g. the holding time for samples is not exceeded, etc.) When the Rust Data Validator identifies a corrective action situation during data assessment, the CWM-Vickery PM will be responsible for approving the implementation of corrective action, including resampling if necessary.

SECTION 14
QUALITY ASSURANCE REPORTS TO MANAGEMENT

The deliverables associated with the tasks identified in the Phase I RFI WP and the monthly progress reports will contain separate QA sections in which data quality information collected during the task is summarized. Those reports will be the responsibility of the Rust PM and will include the Rust QA Officer report on the accuracy, precision, and completeness of the data, the results of the performance and system audits, and any corrective action needed or taken during the project.

14.1 Contents of Project QA Reports

QA reports that accompany a deliverable will summarize all pertinent information relating to the activities and findings described in that deliverable (i.e., a summary of information contained in the monthly reports as relevant to the deliverable). The monthly QA reports will contain on a routine basis all results of field and laboratory audits, all information generated during the past month reflecting on the achievement of specific data quality objectives, and a summary of any corrective actions that were implemented (including their impacts to the project). The status of the project with respect to the project schedule in the Phase I RFI QAPjP will be determined. Whenever necessary, updates on training provided, changes in key personnel, anticipated problems in the field or lab (that could bear on data quality), and proposed solutions to those problems will be reported. Detailed references to modifications of the Phase I RFI QAPjP will also be highlighted. All QA reports will be prepared in written, final format by the Rust PM or his designee.

In the event of an emergency, or in case it is essential to implement corrective action immediately, QA reports can be made by telephone to the individuals specified in the Corrective Action Section of this Phase I RFI QAPjP (including the U.S. EPA RCRA PM). However, these

events, and their resolution will be addressed thoroughly in the next issue of the monthly QA report.

14.2 Frequency of QA Reports

QA Reports will be prepared on a monthly basis and will be delivered with the monthly progress report. The monthly reports will continue without interruption until the project has been completed. The frequency of any emergency reports that must be delivered verbally cannot be estimated at the present time. QA reports accompanying project deliverables will be attached to and incorporated in those deliverable and submitted concurrently.

14.3 Individuals Receiving/Reviewing QA Reports

The monthly QA report will be sent to the individuals identified as having management responsibilities in Section 2.2 of this Phase I RFI QAPjP.

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
Group A:											
SWMU #1	Soil	Grid Nodes	13'-15'	24	2			1	1	28	VOC
SWMU #2				24	2			1	1	28	SVOC
SWMU #3				24	2			1	1	28	Pesticides, PCBs, Herbicides
SWMU #8				24	2			1	1	28	Metals, Cyanide, Sulfide
SWMU #16				3						3	Geotechnical Testing
				24						24	Qualitative Screening of Gross VOC Vapors
	Stabilized Waste Material	Select	13'	10	1			1	1	13	VOC
				10	1			1	1	13	SVOC
				10	1			1	1	13	Pesticides, PCBs, Herbicides
				10	1			1	1	13	Metals, Cyanide, Sulfide
				10	1					11	Geotechnical Testing
				10						10	Qualitative Screening of Gross VOC Vapors
Group B:											
SWMU #4	See Groundwater Sampling (end of this table)										
SWMU#5											
SWMU #7											
SWMU #10											
SWMU #11											
SWMU #17											
SWMU #53											
Group C:											
SWMU #6	Soil	Grid Nodes	13'	18	2			1	1	22	VOC
SWMU #9				18	2			1	1	22	SVOC
SWMU #19				18	2			1	1	22	Pesticides, PCBs, Herbicides
				18	2			1	1	22	Metals, Cyanide, Sulfide
				2						2	Geotechnical Testing
				18						18	Qualitative Screening of Gross VOC Vapors
	Stabilized Waste Material	Select	13'	5	1					6	VOC
				5	1					6	SVOC
				5	1					6	Pesticides, PCBs, Herbicides
				5	1					6	Metals, Cyanide, Sulfide
				1						1	Geotechnical Testing
				5						5	Qualitative Screening of Gross VOC Vapors

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
Group D:											
SWMU #12	Soil	Grid Nodes	2.5'	33	4			2	2	41	VOC
SWMU #13				33	4			2	2	41	SVOC
SWMU #14				33	4			2	2	41	Pesticides, PCBs, Herbicides
				33	4			2	2	41	Metals, Cyanide, Sulfide
				4	1					5	Geotechnical Testing
				33						33	Qualitative Screening of Gross VOC Vapors
Group E:											
SWMU #50	Soil		Surface	3				1	1	5	VOC
SWMU #51				3				1	1	5	SVOC
SWMU #52				3				1	1	5	Pesticides, PCBs, Herbicides
				3				1	1	5	Metals, Cyanide, Sulfide
				1						1	Geotechnical Testing
				3						3	Qualitative Screening of Gross VOC Vapors
Group F:											
SWMU #31	Soil		Surface	20	2			1	1	24	VOC
SWMU #32				20	2			1	1	24	SVOC
SWMU #33				20	2			1	1	24	Pesticides, PCBs, Herbicides
SWMU #34				20	2			1	1	24	Metals, Cyanide, Sulfide
SWMU #35				2						2	Geotechnical Testing
SWMU #36				20						20	Qualitative Screening of Gross VOC Vapors
SWMU #37											
SWMU #38											
SWMU #39											
SWMU #40											
Group G:											
SWMU #23	Soil		13' (#23)	14	1			1	1	17	VOC
SWMU #27			Surface	14	1			1	1	17	SVOC
SWMU #29			(#27, 29 & 30)	14	1			1	1	17	Pesticides, PCBs, Herbicides
SWMU #30				14	1			1	1	17	Metals, Cyanide, Sulfide
				2						2	Geotechnical Testing
				14						14	Qualitative Screening of Gross VOC Vapors

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
Group H:											
SWMU #46	Soil		Surface	4	1					5	VOC
SWMU #47				4	1					5	SVOC
SWMU #48				4	1					5	Pesticides, PCBs, Herbicides
SWMU #49				4	1					5	Metals, Cyanide, Sulfide
				4	1					5	PCDD/PCDF (3)
				1						1	Geotechnical Testing
				4						4	Qualitative Screening of Gross VOC Vapors
Group I:											
SWMU #15	Soil	Grid Node	2' - 4'	12	1			1	1	15	VOC
				12	1			1	1	15	SVOC
				12	1			1	1	15	Pesticides, PCBs, Herbicides
				12	1			1	1	15	Metals, Cyanide, Sulfide
				12	1			1	1	15	PCDD/PCDF (3)
				2	1					3	Geotechnical Testing
				12						12	Qualitative Screening of Gross VOC Vapors
SWMU #20	Soil		10'	1	1			1	1	4	VOC
				1	1			1	1	4	SVOC
				1	1			1	1	4	Pesticides, PCBs, Herbicides
				1	1			1	1	4	Metals, Cyanide, Sulfide
				1						1	Geotechnical Testing
				1						1	Qualitative Screening of Gross VOC Vapors
SWMU #41	Soil		Surface	3	1			1	1	6	VOC
				3	1			1	1	6	SVOC
				3	1			1	1	6	PCBs
				3	1			1	1	6	Metals
				1						1	Geotechnical Testing
				3						3	Qualitative Screening of Gross VOC Vapors

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
SWMU #42	Soil		0'-4'	2	1			1	1	5	VOC
				2	1			1	1	5	SVOC
				2	1			1	1	5	PCBs
				2	1			1	1	5	Metals
				1						1	Geotechnical Testing
				2						2	Qualitative Screening of Gross VOC Vapors
SWMU #43	Soil		4'-8' Base of Vault	2						2	VOC
				2						2	SVOC
				2						2	Chloride
				2						2	Metals
				1						1	Geotechnical Testing
				2						2	Qualitative Screening of Gross VOC Vapors
SWMU #44 SWMU #45	Soil	Select	6'-8'	2						2	VOC
				2						2	SVOC
				2						2	Chloride
				2						2	Metals
				1						1	Geotechnical Testing
				2						2	Qualitative Screening of Gross VOC Vapors
AOC A:											
AOC A	Soil		Surface	18	2			1	1	22	VOC
				18	2			1	1	22	SVOC
				18	2			1	1	22	Pesticides, PCBs, Herbicides
				18	2			1	1	22	Metals, Cyanide, Sulfide
				2						2	Geotechnical Testing
				18						18	Qualitative Screening of Gross VOC Vapors
AOC B:											
AOC B	Soil		Surface	2	1			1	1	5	VOC
				2	1			1	1	5	SVOC
				2	1			1	1	5	Pesticides, PCBs, Herbicides
				2	1			1	1	5	Metals, Cyanide, Sulfide
				1	1					2	Geotechnical Testing
				2						2	Qualitative Screening of Gross VOC Vapors

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
AOC C:											
AOC C	Soil		Surface	1						1	VOC
				1						1	SVOC
				1						1	Pesticides, PCBs, Herbicides
				1						1	Metals, Cyanide, Sulfide
				1						1	Geotechnical Testing
				1						1	Qualitative Screening of Gross VOC Vapors
AOC F:											
AOC F	Soil		Surface	2	1			1	1	5	VOC
				2	1			1	1	5	SVOC
				2	1			1	1	5	Pesticides, PCBs, Herbicides
				2	1			1	1	5	Metals, Cyanide, Sulfide
				1						1	Geotechnical Testing
				2						2	Qualitative Screening of Gross VOC Vapors
AOC H:											
AOC H	Soil	Spill Sites	Surface	6	1			1	1	9	VOC
				6	1			1	1	9	SVOC
				6	1			1	1	9	Pesticides, PCBs, Herbicides
				6	1			1	1	9	Metals, Cyanide, Sulfide
				2	1					3	Geotechnical Testing
				6						6	Qualitative Screening of Gross VOC Vapors
	Sediments	Meyers Ditch and Little Raccoon Creek		11	1			1	1	14	VOC
				11	1			1	1	14	SVOC
				11	1			1	1	14	Pesticides, PCBs, Herbicides
				11	1			1	1	14	Metals, Cyanide, Sulfide
				11	1			1	1	14	Qualitative Screening of Gross VOC Vapors
AOC I:											
AOC I	Soil	Estimated 5 Locations	Test Pits	10	1			1	1	13	VOC
				10	1			1	1	13	SVOC
				10	1			1	1	13	Pesticides, PCBs, Herbicides
				10	1			1	1	13	Metals, Cyanide, Sulfide
				10						10	Qualitative Screening of Gross VOC Vapors

TABLE 1-1
SAMPLING AND ANALYSIS PROGRAM SUMMARY
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Investigative Samples	Field Duplicates	Field Blanks	Trip Blanks	Matrix Spike	Matrix Spike Duplicate (1)	Sample Total	Test Parameters (2)
Monitoring Wells and Capillary Drain	Groundwater	Capillary Drain		11	2 (4)	1	2	1	1	18	VOC
		L17		11	2	1	2	1	1	18	SVOC
		L19A		11	2	1	2	1	1	18	Field Parameters (5)
		L20		11	2	1	2	1	1	18	Pesticides, PCBs, Herbicides
		L25		11	2	1	2	1	1	18	Metals, Cyanide, Sulfide
		L26		11	2	1	2	1	1	18	PCDD/PCDF
		MW-14R									
		MW-15R									
		MW-20R									
		MW-22R									
		MW-24R									
Background Samples											
Background Samples	Soil	See Note 6	Surface 8'-10'	10	1			1	1	13	Metals

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Note:

(1) - Matrix Spike Duplicate is Lab Duplicate for inorganics.

(2) - Geotechnical testing will include cation exchange capacity, Atterberg Limits, moisture content, grain size distribution, soil pH and total organic carbon (loss on ignition).

(3) - PCDD/PCDF will be analyzed in the soil if the sample indicates PCBs above the Project Reporting Limit

(4) - One field duplicate from capillary drain, one from a monitoring well.

(5) - Field Parameters - pH, Temperature, and Specific Conductivity (to assess well stabilization during purging) and Turbidity (of the collected sample).

(6) - Background soil samples will be collected from areas of the facility that are not associated with waste management activities.

AOC - Area of Concern

SWMU - Solid Waste Management Unit

VOC - Volatile Organic Compound

SVOC - Semi-Volatile Organic Compound

PCB - Polychlorinated Biphenyl

PCDD - Polychlorinated Dibenzo-p-Dioxin

PCDF - Polychlorinated Dibenzo Furans

pH - Hydronium Ion Concentration

TABLE 1-2
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX VOLATILE ORGANIC COMPOUNDS BY METHOD 8260B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Acetone	10	10	2,000,000	610
Acetonitrile	100	100	390,000	220
Acrolein	20	20	1,300,000	730
Acrylonitrile	20	20	1,330	3.7
Allyl Chloride	5	5	3,300,000	1800
Benzene	5	0.20	1,400	0.39
Bromodichloromethane	5	5	1,400	0.18
Bromoform	5	5	56,000	8.5
Bromomethane	10	2	15,000	8.7
2-Butanone (MEK)	10	10	N/A	1900
Carbon disulfide	5	5	16,000	21
Carbon tetrachloride	5	5	470	0.17
Chlorobenzene	5	5	160,000	39
2-Chloro-1,3-butadiene (chloroprene)	10	10	N/A	N/A
Chloroethane	10	10	1,100,000	710
Chloroform	10	1	530	0.16
Chloromethane (methyl chloride)	10	10	2,000	1.5
Dibromochloromethane	5	5	5,300	1
1,2-Dibromo-3-chloropropane	100	1	320	0.048
1,2-Dibromoethane	5	1	5	0.00076
Dibromomethane	5	5	650,000	370
trans-1,4-Dichloro-2-butene	100	100	8	0.0012
Dichlorodifluoromethane	5	5	110,000	390
1,1-Dichloroethane	5	5	840,000	810
1,2-Dichloroethane	1	1	440	0.12
1,1-Dichloroethene	5	5	38	0.046
1,2-Dichloroethene (trans)	5	5	170,000	120
1,2-Dichloropropane	5	1	680	0.16
cis-1,3-Dichloropropene	5	1	510	0.081
trans-1,3-Dichloropropene	5	1	510	0.081
1,4-Dioxane	20	20	14,000	1
Ethylbenzene	5	5	2,900,000	1300
Ethyl methacrylate	5	5	340,000	550
2-Hexanone	1	10	N/A	N/A
Isobutyl alcohol	50	50	20,000,000	11000
Methacrylonitrile	10	3	1,300	1
Methylene chloride	1	1	11,000	4.3
Methyl iodide	5	5	N/A	N/A
Methyl methacrylate	5	5	5,200,000	2900
4-Methyl-2-pentanone (MIBK)	10	10	5,200,000	2900
Pentachloroethane	5	5	N/A	N/A
Propionitrile	50	50	N/A	N/A

TABLE 1-2
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX VOLATILE ORGANIC COMPOUNDS BY METHOD 8260B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Styrene	1	1	2,200,000	1600
1,1,1,2-Tetrachloroethane	1	1	4,800	0.43
1,1,2,2-Tetrachloroethane	5	5	900	0.055
Tetrachloroethene	5	5	7,000	1.1
Toluene	5	5	1,900,000	720
1,1,1-Trichloroethane	5	5	3,200,000	1300
1,1,2-Trichloroethane	1	1	1,400	2
Trichloroethene	1	1	7,100	1.6
Trichlorofluoromethane	5	5	710,000	1300
1,2,3-Trichloropropane	5	5	7	31
Vinyl acetate	10	10	65,000,000	37000
Vinyl chloride	5	2	5	0.02
Xylenes (total)	5	5	980,000	1400
1,4-Dichlorobenzene	10	1	7,400	0.47

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Notes:

µg - microgram

kg - kilogram

L - Liter

N/A - DQL Not Available

TABLE 1-3
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX SEMI-VOLATILE ORGANIC COMPOUNDS BY METHOD 8270B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Acenapthene	330	10	360,000	370
Acenaphthylene	330	10	N/A	N/A
Acetophenone	330	10	5,600,000	3,700
2-Acetylaminoflourene	660	20	N/A	N/A
4-Aminobiphenyl	660	20	N/A	N/A
Aniline	330	10	19,000	11
Anthracene	330	10	19,000	1,800
Aramite	165	5	18,000	2.7
Benzo(a)anthracene	330	1	610	0.092
Benzo(b)flouranthene	99	3	610	0.092
Benzo(k)flouranthene	99	3	6,100	0.92
Benzo(ghi)perylene	330	3	N/A	N/A
Benzo(a)pyrene	150	3	61	0.0092
Benzyl alcohol	330	10	20,000,000	11,000
bis(2-Chloroethoxy)methane	330	10	N/A	N/A
bis(2-Chloroethyl)ether	330	10	74	0.0098
bis(2-Chloroisopropyl)ether	330	10	6,300	0.96
bis(2-ethylhexyl)phthalate	330	3	32,000	4.8
4-Bromophenyl phenyl ether	330	10	N/A	N/A
Butyl benzyl phthalate	330	10	13,000,000	7,300
4-Chloroaniline	330	10	260,000	150
Chlorobenzilate	660	2	1,600	0.25
4-Chloro-3-methylphenol	330	10	N/A	N/A
2-Chloronapthalene	330	10	5,200,000	2,900
2-Chlorophenol	330	10	330,000	180
4-Chlorophenyl phenyl ether	330	10	N/A	N/A
Chrysene	330	1	24,000	9.2
cis/trans-Diallate	330	10	7,300	1.1
Dibenzofuran	330	10	260,000	150
Di-n-butyl phthalate	330	10	N/A	3,700
Dibenz(a,h)anthracene	150	3	61	0.0092
1,2-Dichlorobenzene	330	10	2,300,000	370
1,3-Dichlorobenzene	330	10	2,800,000	N/A

TABLE 1-3
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX SEMI-VOLATILE ORGANIC COMPOUNDS BY METHOD 8270B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
3,3'-Dichlorobenzidine	660	20	990	0.15
2,4-Dichlorophenol	330	10	200,000	110
2,6-Dichlorophenol	330	10	N/A	N/A
Diethyl phthalate	330	10	52,000,000	29,000
Dimethoate	99	3	13,000	7.3
p-(Dimethylamino)azobenzene	330	10	N/A	N/A
7,12-Dimethylbenz(a)anthracene	330	10	N/A	N/A
3,3'-Dimethylbenzidine	330	10	48	0.0073
a,a-Dimethylphenethylamine	330	10	N/A	N/A
2,4-Dimethylphenol	330	10	1,300,000	730
Dimethyl phthalate	330	10	>100000000	370,000
1,3-Dinotrobenzene	33	1	6,500	3.7
4,6-Dinitro-2-methylphenol	1,650	50	N/A	N/A
2,4-Dinitrophenol	1,650	50	130,000	73
2,4-Dinitrotoluene	330	10	130,000	73
2,6-Dinitrotoluene	330	10	65,000	37
Di-n-octyl phthalate	330	10	1,300,000	730
Diphenylamine	330	10	1,600,000	910
Ethyl methanesulfonate	660	20	N/A	N/A
Fluoranthene	330	10	2,600,000	1,500
Fluorene	330	10	300,000	240
Hexachlorobenzene	200	3	280	0.042
Hexachlorobutadiene	330	3	5,700	0.86
Hexachlorocyclopentadiene	330	10	450,000	260
Hexachloroethane	330	10	32,000	4.8
Hexachloropropene	330	10	N/A	N/A
Indeno(1,2,3-cd)pyrene	330	1	610	0.092
Isodrin	660	20	N/A	N/A
Isophorone	330	10	470,000	71
Isosafrole	660	10	N/A	N/A
Methapyrilene	3,300	100	N/A	N/A
3-Methylcholanthrene	330	10	N/A	N/A
Methyl methansulfonate	495	15	N/A	N/A

TABLE 1-3
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX SEMI-VOLATILE ORGANIC COMPOUNDS BY METHOD 8270B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
2-Methylnaphthalene	330	10	N/A	N/A
4-Methylphenol	330	10	330,000	180
2 or 3-Methylphenol	330	10	3,300,000	1,800
Naphthalene	330	10	800,000	240
1,4-Naphthoquinone	330	10	N/A	N/A
1-Naphthalamine	330	10	N/A	N/A
2-Naphthalamine	330	10	N/A	N/A
2-Nitroanaline	1,650	10	3,900	2.2
3-Nitroanaline	1,650	50	N/A	N/A
4-Nitroanaline	660	20	N/A	N/A
Nitrobenzene	330	10	33,000	18
2-Nitrophenol	330	10	N/A	N/A
4-Nitrophenol	1,650	50	N/A	N/A
4-Nitroquinoline-1-oxide	1,320	40	N/A	N/A
n-Nitrosodi-n-butylamine	330	10	82	0.012
n-Nitrosodiethylamine	660	20	3	0.00045
n-Nitrosodimethylamine	165	5	9	0.0013
n-Nitrosodiphenylamine	330	10	91,000	14
n-Nitrosodi-n-propylamine	165	5	63	0.0096
n-Nitroso-n-methylethylamine	330	10	20	0.0031
n-Nitrosomorpholine	330	10	N/A	N/A
n-Nitrosopiperidine	660	20	N/A	N/A
n-Nitrosopyrrolidine	330	10	210	0.032
5-Nitro-o-toluidine	330	10	N/A	N/A
Pentachlorobenzene	330	10	52,000	29
Pentachloronitrobenzene	660	20	1,700	0.26
Pentachlorophenol	330	10	2,500	0.56
Phenacetin	660	20	N/A	N/A
Phenanthrene	330	10	N/A	N/A
Phenol	330	10	39,000,000	22,000
1,4-Phenylenediamine	330	10	12,000,000	6,900
2-Picoline	330	10	N/A	N/A
Pronamide	330	10	4,900,000	2,700

TABLE 1-3
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX SEMI-VOLATILE ORGANIC COMPOUNDS BY METHOD 8270B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Pyrene	330	10	2,000,000	1,100
Pyridine	330	10	65,000	37
Safrole	330	10	N/A	N/A
1,2,4,5-Tetrachlorobenzene	330	10	20,000	11
2,3,4,6-Tetrachlorophenol	330	10	2,000,000	1,100
Tetraethyl dithiopyrophosphate	330	10	33,000	18
Thionazine	660	20	N/A	N/A
o-Toluidine	330	10	N/A	N/A
1,2,4-Trichlorobenzene	330	10	620,000	190
2,4,5-Trichlorophenol	330	10	6,500,000	3,700
2,4,6-Trichlorophenol	66	2	40,000	6.1
o,o,o-Triethyl phosphorothioate	330	10	N/A	N/A
1,3,5-Trinitrobenzene	132	4	3,300	1.8

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Notes:
µg - microgram
kg - kilogram
L- Liter
N/A - DQL Not Available

TABLE 1-4
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX ORGANOCHLOIDE PESTICIDES / PCBs BY METHOD 8081
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Aldrin	1.34	0.04	26	0.004
alpha BHC	1.01	0.03	71	0.011
beta BHC	2.01	0.06	250	0.037
delta BHC	3.02	0.09	N/A	N/A
gamma BHC/Lindane	1.34	0.04	340	0.052
Chlorodane	4.69	0.14	340	0.052
4,4'-DDD	3.69	0.11	1,900	0.28
4,4'-DDE	1.34	0.04	1,300	0.2
4,4'-DDT	4.02	0.04	1,300	0.2
Dieldrin	0.67	0.005	28	0.0042
Endosulfan I	4.69	0.14	3,300	1.8
Endosulfan II	1.34	0.04	3,300	1.8
Endosulfan Sulfate	22.11	0.66	N/A	N/A
Endrin	2.01	0.06	20,000	11
Endrin aldehyde	7.71	0.23	N/A	N/A
Heptachlor	1.01	0.03	99	0.015
Heptachlor epoxide	27.81	0.32	49	0.0074
Hexachlorophene	1650	50	20,000	11
Kepone	660	20	25	0.0037
Methoxychlor	58.96	1.76	330,000	180
Toxaphene	80.4	0.86	400	0.061
Arochlor 1016	16.75	0.50	NA	NA
Arochlor 1221	16.75	0.50	NA	NA
Arochlor 1232	16.75	0.50	NA	NA
Arochlor 1242	21.78	0.65	NA	NA
Arochlor 1248	33.5	1.00	NA	NA
Arochlor 1254	33.5	1.00	NA	NA
Arochlor 1260	33.5	1.00	NA	NA

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Notes:

BHC - Benzene Hexachloride
DDD - Dichlordiphenyldichloroethane
DDE - Dichlorodiphenylethane
DDT - Dichlorodiphenyltrichloroethane
N/A - DQL Not Available
µg - microgram
kg - kilogram
L - Liter

TABLE 1-5
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX ORGANOPHOSPHATE PESTICIDES BY METHOD 8141A
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
Disulfoton	4.69	0.7	2,600	1.5
Phorate	2.68	0.4	13,000	7.3
Parathion (Ethyl Parathion)	4.02	0.6	390,000	229
Methyl parathion	8.04	1.2	16,000	9.1
Famphur	660	20.0	N/A	N/A

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Notes:

µg - microgram

kg - kilogram

L - Liter

N/A - DQL Not Available

TABLE 1-6
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX ORGANOCHLORINE HERBICIDES BY METHOD 8150B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
2,4-D	20	1.0	650,000	370
Dinoseb	14	0.7	65,000	37
2,4,5-TP (Silvex)	2	0.1	520,000	290
2,4,5-T	2	0.1	650,000	370

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Notes:

2,4-D - 2,4 - Dichlorophenoxyacetic Acid

2,4,5 - TP (Silvex) 2-(2,4,5 -Trichlorophenoxy) Propionic Acid

2,4,5 - T - 2,4,5 - Trichlorophenoxyacetic Acid

µg - microgram

kg - kilogram

L - Liter

TABLE 1-7
REPORTING LIMITS AND DATA QUALITY LEVELS
APPENDIX IX METALS AND INORGANICS
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT		DATA QUALITY LEVEL (DQL)		ANALYTICAL METHOD
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)	
Antimony	170	1.7	31,000	15	7041
Antimony	500	5.0	31,000	15	6010A
Arsenic	300	3.0	320	0.038	6010A
Barium	1000	10.0	5,300,000	2,600	6010A
Beryllium	100	1.0	140	0.016	6010A
Cadmium	500	5.0	38,000	18	6010A
Chromium	500	5.0	210,000	180	6010A
Cobalt	1000	10.0	N/A	N/A	6010A
Copper	1000	10.0	2,800,000	1,400	6010A
Lead	100	1.0	400,000	4	6010A
Mercury	200	0.2	23,000	11	7471A
Nickel	2000	20.0	1,500,000	730	6010A
Selenium	200	2.0	380,000	180	6010A
Silver	100	1.0	380,000	180	6010A
Thallium	300	3.0	6,100	2.9	6010A
Tin	1000	10.0	46,000,000	22,000	6010A
Vanadium	200	2.0	540,000	260	6010A
Zinc	500	5.0	23,000,000	11,000	6010A
Chloride	25,000	N/A	N/A	N/A	300.0
Cyanide	1000	5.0	380,000	6.2	9010A
Sulfide	5000	1,000.0	N/A	N/A	376.1

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Notes:
*** - The Graphite Frunance Atomic Absorption methods will be employed as a backup to the Inductively Coupled Plasma method**
µg - microgram
kg - kilogram
L - Liter
N/A - Not Applicable

TABLE 1-8
REPORTING LIMITS AND DATA QUALITY LEVELS
POLYCHLORINATED DIBENZO - P - DIOXINS & DIBENZO FURANS BY METHOD 8280
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETERS	PROJECT REPORTING LIMIT (PRL)		DATA QUALITY LEVEL (DQL)	
	SOIL (µg/kg)	WATER (µg/L)	SOIL (µg/kg)	GROUNDWATER (µg/L)
TCDD/TCDF (incl. 2378-TCDD) (1)	1.0	0.01	N/A	4.5 E-07
PeCDDs/PeCDFs	2.5	0.25	N/A	N/A
HxCDDs/HxCDFs	2.5	0.25	N/A	N/A
HpCDDs/HpCDFs	2.5	0.25	N/A	N/A
OCDD/OCDF	5.0	0.50	N/A	N/A

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Notes:

(1) DQL above is for 2378-TCDD isomer only.

(2) This analysis will be performed by Triangle Laboratories, Inc., 801 Capitola Drive, Durham, NC 27713

TCDD - Tetrachloro Dibenzo-p-Dioxin

TCDF - Tetrachloro Dibenzo Furan

PeCDD - Polychlorinated Dibenzo-p-Dioxin

PeCDF - Polychlorinated Dibenzo Furans

HxCDD - Hexachloro Dibenzo-p-Dioxin

HxCDF - Hexachloro Dibenzo Furan

HpCDD - Heptachloro Dibenzo-p-Dioxin

HpCDF - Heptachloro Dibenzo Furan

OCDD - Octachloro Dibenzo-p-Dioxin

OCDF - Octachloro Dibenzo Furan

µg - microgram

kg - kilogram

L - Liter

TABLE 3-1
PRECISION AND ACCURACY CRITERIA
APPENDIX IX VOLATILE ORGANIC COMPOUNDS BY METHOD 8260B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Benzene	11	21	76-127	66-142
Chlorobenzene	13	21	75-130	60-133
1,1-Dichloroethene	14	22	61-145	59-172
Toluene	13	21	76-125	59-139
Trichloroethene	14	24	71-120	62-137

SURROGATE COMPOUND	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
4 Bromofluorobenzene	N/A	N/A	86-115	74-121
1, 2 DichloroEthane - d4	N/A	N/A	80-120	70-121
Toluene - d8	N/A	N/A	88-110	81-117

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Note:
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable

TABLE 3-2
PRECISION AND ACCURACY CRITERIA
APPENDIX IX SEMIVOLATILE ORGANIC COMPOUNDS BY METHOD 8270B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Acenapthene	31	19	46-118	31-137
4-Chloro-3-methylphenol	42	33	23-97	26-103
2-Chlorophenol	40	50	27-123	25-102
1,4-Dichlorobenzene	28	27	36-97	28-104
2,4-Dinitrotoluene	38	47	24-96	28-89
4-Nitrophenol	50	50	10-80	11-114
n-Nitrosodi-n-propylamine	38	38	41-116	41-126
Pentachlorophenol	50	47	9-103	17-109
Phenol	42	35	12-110	26-90
Pyrene	31	36	26-127	35-142
1,2,4-Trichlorobenzene	28	23	39-98	38-107

SURROGATE COMPOUND	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Nitrobenzene - d5	N/A	N/A	35-114	23-120
2-Fluorobiphenyl	N/A	N/A	43-116	30-115
p-Terphenyl-d14	N/A	N/A	33-141	18-137
Phenol - d6	N/A	N/A	10-94	24-113
2-Fluorophenol	N/A	N/A	21-100	25-121
2, 4, 6 - Tribromophenol	N/A	N/A	10-123	19-122

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Note:
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable

TABLE 3-3
PRECISION AND ACCURACY CRITERIA
APPENDIX IX ORGANOCHLORINE PESTICIDES / PCBs BY METHOD 8081
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Aldrin	22	43	40-120	34-132
gamma BHC/Lindane	15	50	56-123	46-127
Dieldrin	18	38	52-126	31-134
Endrin	21	45	56-121	42-139
Heptachlor	20	31	40-131	35-130

SURROGATE COMPOUND	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Tetrachloro-m-xylene (TCMX)	N/A	N/A	62-122	8-205
Decachlorobiphenyl (DCB)	N/A	N/A	20-116	11-212

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Note:
BHC - Benzene Hexachloride
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable
(1) Advisory Surrogate minimum 10% recovery used as action limit.
(2) Two surrogates are run for Method 8081, but only one surrogate must actually be quantified.
The analyst may pick the appropriate surrogate based on the properties of the sample.
(3) A recovery of less than 10 percent will require rejection of the associated analytical results.
A recovery of 10 to 23 percent will require that the associated analytical results be qualified as estimated.

TABLE 3-4
PRECISION AND ACCURACY CRITERIA
APPENDIX IX ORGANOPHOSPHORUS PESTICIDE COMPOUNDS BY METHOD 8141
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Ethyl parathion	25	50	75-125	65-140

SURROGATE COMPOUND	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Tributylphosphate	N/A	N/A	25-125	20-150

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Note:
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable

TABLE 3-5
PRECISION AND ACCURACY CRITERIA
APPENDIX IX ORGANOCHLORINE HERBICIDES BY METHOD 8150B
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
2,4-D	25	50	50-125	40-135
2,4,5-TP (Silvex)	25	50	50-125	40-135
2,4,5-T	25	50	50-125	40-135

SURROGATE COMPOUND	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
2, 4 - DCAA	N/A	N/A	10-160	10-160

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Note:

2,4-D - 2,4 - Dichlorophenoxyacetic Acid

2,4,5 - TP (Silvex) 2-(2,4,5 -Trichlorophenoxy) Propionic Acid

2,4,5 - T - 2,4,5 - Trichlorophenoxyacetic Acid

2,4,5 - DCAA - 2,4 - Dichlorophenoxyacetic Acid

TABLE 3-6
PRECISION AND ACCURACY CRITERIA
APPENDIX IX METALS AND INORGANICS
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	METHOD	PRECISION (RPD)		ACCURACY (%R)	
		Water	Soil	Water	Soil
Antimony	6010A	20	20	75-125	75-125
Arsenic	6010A	20	20	75-125	75-125
Barium	6010A	20	20	75-125	75-125
Beryllium	6010A	20	20	75-125	75-125
Cadmium	6010A	20	20	75-125	75-125
Chromium	6010A	20	20	75-125	75-125
Cobalt	6010A	20	20	75-125	75-125
Copper	6010A	20	20	75-125	75-125
Lead	6010A	20	20	75-125	75-125
Mercury	7471A	20	20	75-125	75-125
Nickel	6010A	20	20	75-125	75-125
Selenium	6010A	20	20	75-125	75-125
Silver	6010A	20	20	75-125	75-125
Thallium	6010A	20	20	75-125	75-125
Tin	6010A	20	20	75-125	75-125
Vanadium	6010A	20	20	75-125	75-125
Zinc	6010A	20	20	75-125	75-125
Cyanide	9010A	20	20	75-125	75-125
Chloride	300.0	20	N/A	75-125	N/A
Sulfide	376.1	20	20	75-125	75-125

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Note:
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable

TABLE 3-7
PRECISION AND ACCURACY CRITERIA
POLYCHLORINATED DIBENZO - P - DIOXINS & DIBENZO FURANS BY METHOD 8280
RFI PHASE I QAPjP
CWM-VICKERY

NATIVE SPIKE	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
2, 3, 7, 8 - TCDD	50	50	50-150	50-150
1, 2, 3, 7, 8 - PECDD	50	50	50-150	50-150
1, 2, 3, 4, 7, 8 - HXCDD	50	50	50-150	50-150
1, 2, 3, 4, 6, 7, 8 - OCDD	50	50	50-150	50-150
2, 3, 7, 8 - TCDF	50	50	50-150	50-150
1, 2, 3, 7, 8 - PECDF	50	50	50-150	50-150
1, 2, 3, 4, 7, 8 - HXCDF	50	50	50-150	50-150
1, 2, 3, 4, 6, 7, 8, 9 - OCDF	50	50	50-150	50-150

INTERNAL STANDARD	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
13c12 - 2, 3, 7, 8 TCDD	N/A	N/A	40-120	40-120
13c12 - 1, 2, 3, 6, 7, 8 - HXCDD	N/A	N/A	40-120	40-120
13c12 - OCDD	N/A	N/A	25-120	25-120
13c12 - 2, 3, 7, 8 - TCDF	N/A	N/A	40-120	40-120
13c12 - 1, 2, 3, 4, 6, 7, 8 - HPCDF	N/A	N/A	40-120	40-120

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Note:
TCDD - Tetrachloro Dibenzo-p-Dioxin
PECDD - Pentachloro Dibenzo-p-Dioxin
HXCDD - Hexachloro Dibenzo-p-Dioxin
OCDD - Octachloro Dibenzo-p-Dioxin
TCDF - Tetrachloro Dibenzo Furan
PECDF - Pentachloro Dibenzo Furan
HXCDF - Hexachloro Dibenzo Furan
OCDF - Octachloro Dibenzo Furan
HPCDF - Heptachloro Dibenzo Furan
Internal Standards also serve as the Surrogate.
RPD - Relative Percent Difference
%R - Percent Recovery
N/A - Not Applicable

TABLE 3-8
PRECISION AND ACCURACY CRITERIA
CHLORIDE BY METHOD 300.0
RFI PHASE I QAPjP
CWM-VICKERY

PARAMETER	PRECISION (RPD)		ACCURACY (%R)	
	Water	Soil	Water	Soil
Chloride	20	25	80-120	75-125

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Note:
RPD - Relative Percent Difference
%R - Percent Recovery

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
Group A:					
SWMU #1 SWMU #2 SWMU #3 SWMU #8 SWMU #16	Surface Impoundments 1, 2, 3, 9 and the waste pile contained waste oils, oily sludges, inorganic acids and pickle liquors; and fixed sludges, structures and soils, respectively. PCBs, D004-D011 metals, VOCs, PAHs and phenols are the potential waste constituents that have been identified as part of this SWMU group. Based on the historical usage and the above potential constituents, samples have been proposed to characterize the impact to the soil. Monitoring well MW-15R is located downgradient of this SWMU group and data from this monitoring well provides useful information for the characterization of groundwater. Recent historical data generated as part of the RCRA and TSCA monitoring programs will be validated during the Phase I RFI to assess the groundwater quality in the area adjacent to the SWMUs in this group. Groundwater samples will be collected to support this validation. Further characterization of the groundwater will be completed as part of the Phase II RFI, if appropriate. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Grid Nodes	13-15	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
		Soil	Select	13	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
		Groundwater	MW-15R		VOC SVOC pH (Field) Specific Conductivity (Field) Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide PCDD/PCDF

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
Group B:					
SWMU #4 SWMU #5 SWMU #7 SWMU #10 SWMU #11 SWMU #17 SWMU #53	Surface Impoundments 4, 5, 7, 11 and 12 contained waste oils, oily sludges, waste acids, caustics, pickle liquors and phenols. The leachate retention pond (SWMU#17) contained surface water runoff from the waste pile. The TSCA closure cell (SWMU #53) was built over the area where Surface Impoundments 4, 5 and 7 were located. PCBs, D004-D011 metals, VOCs, PAHs, dioxins and phenols are the potential waste constituents that have been identified as part of this group. Based on historical records and the above potential constituents, a groundwater sample will be collected under the closure cell from the capillary drain. Water from this drain is in contact with surrounding soils and provide a mechanism to assess the soils without disturbing the integrity closure cell. Monitoring wells MW-14R, MW-15R and MW-22R are located downgradient of the SWMUs in this group and provide data on the groundwater in these areas. Recent historical data generated as part of the RCRA and TSCA monitoring programs will be validated in the Phase I RFI to assess the groundwater quality around this SWMU group. Groundwater samples will be collected to support this validation. Further characterization of the groundwater will be completed as part of the Phase II RFI, if appropriate. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Groundwater	Capillary - Drain Sump MW-14R MW-15R MW-22R		VOC SVOC pH (Field) Specific Conductivity (Field) Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide PCDD/PCDF

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
Group C:					
SWMU #6 SWMU #9 SWMU #19	Surface Impoundment 6 contained waste acids, acid sludges, pickle liquors, phenol wastes and sludges from Surface Impoundment 9. Surface Impoundment 10 contained aqueous sludges and phenols wastes. The history of the Old Drum Storage Pad is uncertain, but it is believed to have contained organics and PCBs. PCBs, pesticides, D004-D011 metals, VOCs, PAHs, and phenols are the potential waste constituents that have been identified as part of this SWMU group. Based on historical records and the above potential constituents, samples will be collected to characterize the impact to the soil, if any. Monitoring well MW-20R is located downgradient of the SWMUs in this group. Recent historical data generated as part of the RCRA and TSCA monitoring programs will be validated in the Phase I RFI to assess the groundwater quality around this SWMU group. A groundwater sample will be collected to support this validation. Further characterization of the groundwater will be completed as part of the Phase II RFI, if appropriate. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Grid Nodes	13	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
		Soil	Select	13	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
		Groundwater	MW-20R		VOC SVOC pH (Field) Specific Conductivity (Field) Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide PCDD/PCDF
Group D:					
SWMU #12 SWMU #13 SWMU #14	The North, East and South Landfarms contained oily and plating sludges. In addition the waste history of the landfarms indicated that metal hydroxide sludges was present at the North and East Landfarms, but absent at the South Landfarm. PCBs, D004-D011 metals, VOCs, PAHs and phenols are the potential waste constituents that have been identified as part of this SWMU group. Based on historical records and the above potential constituents, samples will be collected confirm the removal of residual wastes. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for the additional assessment of groundwater, further characterization of the groundwater will be completed as part of the Phase II RFI . All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Grid Nodes	2.5	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
Group E:					
SWMU #50 SWMU #51 SWMU #52	The injection wells that comprise this SWMU group were used to inject aqueous acidic wastes and brines into the Mt. Simon Sandstone. These wells were decommissioned due to casing failures at depths greater than 2000 feet below ground surface. Acids, D004-D011 metals, and VOCs are the potential waste constituents that have been identified as part of this SWMU group. Based on historical records and the above potential constituents, samples will be collected to confirm contamination does not exist in the surficial soils. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for the additional assessment of groundwater, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
Group F:					
SWMU #31 SWMU #32 SWMU #33 SWMU #34 SWMU #35 SWMU #36 SWMU #37 SWMU #38 SWMU #39 SWMU #40	The filtered acid tanks and pump houses contain filtered acidic wastes. Acids, D004-D011 metals, phenols and VOCs are the potential waste constituents that have been identified as part of this SWMU group. Based on historical records and the above potential constituents, samples will be collected at selected locations to characterize the impact to soil, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for the additional assessment of groundwater, further characterization of the groundwater will be completed as part of the Phase II RFI, All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing
Group G:					
SWMU #21 SWMU #22 SWMU #23 SWMU #24 SWMU #25 SWMU #26 SWMU #27 SWMU #29 SWMU #30	These SWMUs are grouped together based on their active status within the treatment process. These SWMUs handle pickle liquors, acids and brines. Acids, D004-D011 metals and VOCs are the potential waste constituents that have been identified as part of this SWMU group. Based on the historical record and the above potential constituents, samples will be collected at selected locations to characterize the impact to soil, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select (#23)	13' (#23) Surface (#27, 29 & 30)	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
Group H:					
SWMU #46 SWMU #47 SWMU #48 SWMU #49	The injection wells that comprise this SWMU group are used to inject aqueous wastes and brines into the Mt. Simon Sandstone at depths greater than 2,000 feet below ground surface. Acids, D004-D011 metals, and VOCs are the potential waste constituents that have been identified as part of this SWMU group. Based on the historical record and the above potential constituents, surface soil samples will be collected at selected locations confirm no releases have occurred. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI	Soil	Select	Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide PCDD/PCDF(1) Geotechnical Testing Qualitative Screening of Gross VOC Vapors
Group I:					
SWMU #15	The oil recovery area was used to recover oil bearing waste waters and light oil sludges which were mixed and sent to an oil/water separator. Cyanide, PCBs, D004-D011 metals, PAHs and VOCs are the potential waste constituents that have been identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected with the intent on confirming the remedial activities. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Grid Nodes	2' - 4'	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide PCDD/PCDF(1) Geotechnical Testing Qualitative Screening of Gross VOC Vapors
SWMU #18	The Old W-Tank Farm was "cleaned-closed" in 1992 and used to store aqueous wastes, oily wastes, odorous wastes and phenolic wastes prior to treatment. PCBs, D004-D011 metals, phenols and VOCs are the potential waste constituents that have been identified as part of this SWMU. During the "clean" closing of the unit, samples were collected to characterize the soils. The historical data from this "clean" closure will be submitted as part of the Phase I RFI. No sampling is proposed.	-	-	-	

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
SWMU #20	The Lab Waste Tank is active and used to store unused tanker samples and lab wastes prior to disposal. No F-solvents are stored in this tank. PCBs, PAHs, D004-D011 metals, phenols and VOCs are the potential waste constituents that have been identified as part of this SWMU. Based on the historical record and the above potential constituents, a sample will be collected to confirm there has been no release to the soils. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	10	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
SWMU #28	The Sluice Pit is inactive, but it is not closed. The Sluice Pit is an underground storage tank that is used to hold the acidic rinse water derived from the backflushing of the leaf filters. Various acids and D004-D011 metals are the potential waste constituents that have been identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	8 to 10	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
SWMU #41	The Drum Storage Pad is active and used as a 90 day storage area. Drums of filters, filtered materials and solids are staged in this area to await shipment to the off-site disposal facility. Various acids, D004-D011 metals, phenols and VOCs are the potential waste constituents that have been identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected to a characterize the impact to the surface soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil Surface		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
SWMU #42	The Waste Oil Lube Tank has been closed and removed. While in service, the Waste Oil Lube Tank received waste lube oil derived from on-site machinery. VOCs, SVOCs and TPH are the potential waste constituents that have identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the surface soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	Surface to 4	VOC SVOC PCBs Metals Geotechnical Testing Qualitative Screening of Gross VOC Vapors
SWMU #43	The Wastewater Treatment Plant treats septic wastes pumped out of the cesspits located at the maintenance building and the truck unloading facility. Septic waste is the potential constituent that has been identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected to confirm the SMWU has not leaked. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	4 to 8	VOC SVOC Chloride Metals Geotechnical Testing Qualitative Screening of Gross VOC Vapors
SWMU #44 SWMU #45	These cesspits are located at the maintenance building and the truck unloading facility. Septic waste is the potential constituent that has been identified as part of this SWMU. Based on the historical record and the above potential constituents, samples will be collected to confirm the cesspits have not leaked. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	6 to 8	VOC SVOC Chloride Metals PCBs Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
AOC A:					
	Approximately two dozen emergency/maintenance tanks are found at various locations along the above ground transfer piping system. The tanks are used to store filtered acidic waste when the above ground transfer piping needs to be drained. Acids, D004-D011 metals, and VOCs are the potential waste constituents that have been identified as part of this AOC. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the surface soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil	Select	Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
AOC B:					
	Seven roll-off boxes were staged on the soil south of the Drum Storage Pad and 100 drums were staged at the northwest corner of the North Parking lot. The roll-off boxes and the drums contained debris from the demolition of the W-Tanks. Acids, D004-D011 metals, PCBs, phenols and VOCs are the potential waste constituents identified as part of this AOC. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the surface soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
AOC C:					
	The decontaminated Pug Mill is stored on the concrete pads of the Hay Mill west of Injection Well No. 5. The Pug Mill was used to solidify and fix sludges. Samples will be collected to confirm no impact to the soils from the staged pug mill has occurred. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
AOC D&E:					
	Borrow Pit #1 & 2 were used for soils to increase the height of the dikes around Surface Impoundments 11 & 12 and for clay and fill material for the closure cell. Borrow Pit #1 was incorporated into the "clean closure" of Surface Impoundments 11 & 12 and Borrow Pit # 2 has been allowed to fill will surface water and is used as a wildlife habitat. No sampling is proposed.	-	-	-	-
AOC F:					
	This AOC consists of the truck Sampling area, the truck scales, receiving trailer and the UST which is used to collect rain and snowmelt from under the former truck sampling area. Various acids, D004-D011 metals, phenols and VOCs are the potential waste constituents identified as part of this AOC. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the surface soils, if any. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil		Surface	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors
AOC G:					
	The roll-off staging area consists of the area where roll-off containers are staged. These containers contain sludge from the filter press building and are removed for off-site disposal. The roll-off pad was build in 1991 with concrete berms to surround the pad. No releases are recorded and therefore no sampling is proposed.	-	-	-	-
AOC H &I:					
	Above ground transfer piping system and some remnants of the underground transfer piping system exist across the entire facility. When in service, the transfer piping carried acidic wastes. Acids, D004-D011 metals, phenols and VOCs are the potential waste constituents that have been identified as part of this AOC. Based on the historical record and the above potential constituents, samples will be collected to characterize the impact to the surface soils, if any. Soil sampling will also support the groundwater assessment. If soil sample results indicate the need for additional groundwater assessment, further characterization of the groundwater will be completed as part of the Phase II RFI. All data collected will be used to support a quantitative risk assessment at the completion of the Phase II RFI.	Soil H-Surface I-Testpits		Surface Testpits	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide Geotechnical Testing Qualitative Screening of Gross VOC Vapors

TABLE 4-1
SAMPLING AND ANALYSIS PROGRAM OBJECTIVE RATIONALE
RFI PHASE I QAPjP
CWM-VICKERY

SWMU Groups & AOCs	Sampling Rationale	Sample Matrix	Collection Location	Approximate Collection Depth (ft bgs)	Test Parameters (1)
AOC J:					
	The area around monitoring well L-19 has been added as an AOC. This area has had an historical presence of 1,2-dichloroethane in the groundwater within the well. Investigations have been completed to document and determine the extent of this contaminant. Historical reports will be submitted in the Phase I RFI. No sampling is proposed.	-	-	-	-
Drainage Ditches: Meyers Ditch	Sediment samples will be collected along Meyer's ditch ending at the final flow control gate before entering Little Racoon Creek to confirm no releases from the transfer piping has migrated towards the creek.	Sediment		-	VOC SVOC Pesticides, PCBs, Herbicides Metals, Cyanide, Sulfide

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Note:
Geotechnical testing will include cation exchange capacity, Atterberg Limits, moisture content, grain size distribution, soil pH and total organic carbon (loss on ignition).
AOC - Area of Concern
SWMU - Solid Waste Management Unit
VOC - Volatile Organic Compound
SVOC - Semi-Volatile Organic Compound
PCB - Polychlorinated Biphenyl
PCDD - Polychlorinated Dibenzo-p-dioxins
PCDF - Polychlorinated Dibenzo Furans
(1) - PCDD/PCDF will be analyzed in the soil only if the soil indicates PCBs above the Project Report Limit.
(2) - MW - 24R is the upgradient monitoring well and will be sampled as part of this program.

TABLE 4-2
SAMPLE CONTAINERS, PRESERVATIVES and HOLDING TIMES
RFI PHASE I QAPjP
CWM-VICKERY

Parameter	Media[1]	Container	Preservation	Maximum Holding Time[2]
Volatile Organics	Water[6]	(2) 40 mi VOA Vials with Teflon© lined septum	4 drops HCL, Cool to 4°C	14 days
	Soil	(1) 3" brass sleeve with Teflon © cap seals	Cool to 4°C	14 days
Semi-Volatiles, Pesticides, PCBs, Herbicides	Water[6]	(5) 1 L amber glass with Teflon© liner	Cool to 4°C	47 days[1]
	Soil	(2) 4 oz. wide mouth glass with Teflon© liner	Cool to 4°C	54 days[4]
Metals[5]	Water	1 L polyethylene with polyethylene liner	50% HNO_3, pH <2. Cool to 4°C	6 months
Metals, Cyanide, Sulfide, Chloride	Soil	(1) 4 oz. wide mouth glass with Teflon© liner	Cool to 4°C	6 months
Cyanide	Water	1 L polyethylene with polyethylene liner	NaOH. pH > 12. Cool to 4°C	14 days
Sulfide	Water	1 L polyethylene with polyethylene liner	Zinc Acetate, Cool to 4°C	7 days
PCDD, PCDF	Soil	(1) 4 oz. wide mouth glass with Teflon© liner	Cool to 4°C	54 days[4]
	Water[6]	1 L narrow-mouth amber glass with Teflon© liner	Cool to 4°C	47 days[3]
Geotechnical Parameters	Soil	(1) 16 oz. wide mouth glass with Teflon© liner	Cool to 4°C	45 days

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Notes:
1. Water refers to subsurface water or surface water samples. Soil refers to samples from test pits, soil borings and streambed sediments.
2. Holding time refers to the number of days following the Validated Time of Sample collection by the laboratory.
3. Seven days until extraction and analysis within 40 days of extraction.
4. Fourteen days until extraction and analysis within 40 days of extraction. For PCDD/PCDF, 30 days until extraction and analysis within 40 days of extraction.
5. Mercury has a holding time of 28 days for both liquid and soil samples. Liquid samples will be preserved to pH <2 with 50% nitric acid and cooled to 4°C. Soil samples will be cooled to 4°C.
6. Matrix Spike/Matrix Spike Duplicate will require three times this sample volume.

L - liter
c - centigrade
oz - ounce
PCDD - Polychlorinated Dibenzo-p-Dioxins
PCDF - Polychlorinated Dibenzofurans
NaOH - Sodium Hydroxide
HCL - Hydrochloric Acid
HNO_3 - Nitric Acid

TABLE 6-1
CALIBRATION FOR LABORATORY EQUIPMENT
PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	# STANDARDS INITIAL CALIBRATION	ACCEPTANCE / REJECTION CRITERIA INITIAL CALIBRATION	FREQUENCY OF CALIBRATION	FREQUENCY OF INITIAL CALIBRATION VERIFICATION	ACCEPTANCE / REJECTION CRITERIA INITIAL CALIBRATION VERIFICATION	FREQUENCY OF CONTINUING CALIBRATION VERIFICATION	ACCEPTANCE / REJECTION CRITERIACONTINUING CALIBRATION VERIFICATION
Thermo Jarrell Ash ICAP 61e Trace	6010A	2		Daily	Once each calibration	+/-10% of True Value	Every ten samples	+/-10% of True Value
PS 200 Mercury Autoanalyzer	7470A	5	R > 0.995	12 hours or less	Once each calibration	+/- 10%	Every ten samples	+/- 10%
	7471A	5	R > 0.995	12 hours or less	Once each calibration	+/- 10%	Every ten samples	+/- 10%
Perkin-Elmer 8410 & HP 5890(s) Gas Chromatographs	8081	5	%RSD < 20%	Daily	As Needed (1)	< 20%	Beginning of each shift	%RSD < 15%
	8141	5	%RSD < 20%	Daily	Daily	+/- 15%	Daily, every 10 samples	+/- 15%
	8150	5	%RSD < 20%	Daily	Daily	+/- 15%	Every 12 hours or 10 samples	+/- 15%
HP 5970B GC/MS Selective Detector	8260A	5	%RSD < 30% (CCC) 1,1-Dichloroethene Chloroform 1,2-Dichloropropane Toluene Ethylbenzene Vinyl Chloride RF>0.10(SPCC) Chloromethane 1,1-Dichloroethane Bromoform RF>0.30(SPCC) 1,1,2,2-Tetrachloroethane Chlorobenzene	Every 12 hours	Every 12 hours	CCC < 30% RSD	Every 12 hours	CCC < 25%
	8270B	5	%RSD < 30% (CCC) acenaphtene 1,4-dichlorobenzene hexachlorobutadiene N-niroso-diphenylamine di-octylphthalate fluoranthene benzo(a)prene 4-chloro-3-methylphenol 2,4-dichlorophenol 2-nitrophenol phenol pentachlorophenol 2,4,6-trichlorophenol RF>0.05(SPCC) N-nitrosodipropylamine hexachlorocyclopentadiene 2,4-dinitrophenol 4-nitrophenol	Daily	As Needed (1)	CCC < 30% RSD	Every 12 hours	CCC < 30% RSD
HP 5890 GC	8141	5	%RSD < 20%	Daily	Daily	+/- 15%	Daily, every 10 samples	+/- 15%
HP 5890 HRGC VG/HRMS	8280	5	RRF < or = 15% RSD	Every 12 hours	Before anal. and as needed (1)	+/- 15%	Every 12 hours	+/-30%
Rapid Flow Auto-Analyzer	9010A	3	R > or = 0.995	Daily	Once each calibration	+/-15%	Every ten samples	+/-15%
Dionex 40001 Ion Chromotograph	300.0	6	R > or = 0.995	Daily	Daily	100 +/- 20%	Every 10 samples, end of run	100 +/- 20%

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Note:
(1) The minimum frequency for initial calibration verification is whenever the continuing calibration verification for any analyte exceeds the quality control limit.

TABLE 7-1
ANALYTICAL & PREPARATORY METHODS
RFI PHASE I QAPjP
CWM-VICKERY

GP Environmental Services SOP No.	Title	3rd Edition SW 846 Method No.
13.6	Volatile Organics	8260B
12.17	Soil Extraction for Semivolatile Organics (Sonication Extraction)	3550A
13.19	GC/MS Analysis of The Target Compound List and Appendix IX Semivolatile Organics	8270B
12.15	Continuous Liquid-Liquid Extraction for Pesticides/PCBs	3520B
12.16	Soil Extraction for Pesticides/PCBs Compounds (Sonication Extraction)	3550A
13.38	Organochlorine Pesticides and PCBs	8081
13.36	Organophosphorus Pesticides	8141A
13.35	Analysis of Herbicides	8150B
11.36	Acid Digestion of Surface and Ground Water Samples for Flame/ICP Analyses and Furnace Analysis of Antimony in Accordance with SW 846	3005A
11.35	Acid Digestion of Soil, Sludge, Sediment, and Other Solid Waste Samples for Flame/ICP and Furnace Analyses in Accordance with SW 846	3050A
11.62	Trace ICP Quantitation of HSL Metals	6010A
11.39	Cold Vapor Analysis for Mercury in Accordance with SW 846	7470A & 7471A
11.46	Method for Total Cyanide Analysis In Water and Soil	9010A
11.47	Analysis for Water and Soils for Sulfide According to MCAWW	376.1
11.48	Inorganic Anions	300.0
Triangle No. DSP224	Extraction of PCDD/PCDF from Solid Samples - 8280 and DFL M01.1	8280
Triangle No. DSP225	Acid/Base Cleanup of PCDD and PCDF Extracts - Method 8280	8280
Triangle No. DSP183	PCDDs and PCDFs by GC/MS Method 8280	8280

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Note:
GC/MS - Gas Chromatography/Mass Spectrometry
PCBs - Polychlorinated Biphenyls
ICP - Inductively Coupled Plasma
*** - The Graphite Furnance Atomic Absorption methods will be employed as a backup to the ICP methods**
HSL - Hazardous Substance List
MCAWW - Method for the Chemical Analysis of Waste and Water

TABLE 7-2
GEOTECHNICAL METHODS
RFI PHASE I QAPjP
CWM-VICKERY

ASTM METHOD NO.	TITLE
D4318	Atterberg Limits
D2216	Soil Moisture
D422	Particle Size Analysis
D4972	Soil pH
D2974	TOC
EPA 9080	Cation Exchange Capacity

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Note:

TOC - Total Organic Carbon (loss on ignition)

pH - Hydronium Ion Concentration

TAB. _ 8-1
GP ENVIRONMENTAL SERVICES
CONTROL LIMITS AND CORRECTIVE ACTIONS
RFI PHASE I QAPjP
CWM-VICKERY

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
8260B	**VOC**	Trip blank	One per cooler	Less than 4 cmpds. all with conc. less than 3 times the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field blank	1 per 10 samples or daily; whichever is more frequent	Less than 4 cmpds. all with conc. less than 3 times the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field duplicate	1 per 10 samples	Water - < 30% RPD Soils - < 40% RPD	Examine analytical results. If no problems then examine sampling procedures.
		Storage blank	1 per set of samples	Less than 4 cmpds. with conc. less than 3 times EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Method blank	1 per 12 per period	All compounds less than EQL.	Re-analyze blanks, if contaminants are still present then clean and recalibrate the instrument.
		Surrogate spikes	All analyses	See Table 3-1 to 3-7 for spiking compound, concentrations and control limits.	Re-analyze sample, and if recoveries are again outside of the limits then report both analyses and bias the data.
		MS/MSD analyses	1 pair for every 20 samples or less	See Table 3-1 to 3-7 for compounds, recovery limits and RPD.	BS/BSD. Recalibrate and re-analyze.
		LCS	1 per 20 samples or less	Does not violate any item listed below in Note 1.	Determine reason for loss of control and re-analyze.
8270B	**SVOC**	Field blank	1 per 10 samples or daily; whichever is more frequent	Less than 4 cmpds. all with conc. less than 3 times the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field duplicate	1 per 10 samples	Water - < 30% RPD Soils - < 40% RPD	Examine analytical results. If no problems then examine sampling procedures.
		Method blank	Per daily extraction-batch or 1 per 20 samples, whichever is more frequent	All cmpds. less than the EQL except phthalates which are less than 5 times the EQL.	Re-analyze and re-examine analytical results. If still present, re-extract and re-analyze all associated samples. Document all actions.
		Surrogate spikes	All analyses	See Table 3-1 to 3-7 for spiking compound, concentrations and control limits.	Re-analyze sample, and if recoveries are again outside of the limits then report both analyses and bias the data.
		MS/MSD analyses	1 pair for every 20 samples or less	See Table 3-1 to 3-7 for compounds, recovery limits and RPD.	BS/BSD. Recalibrate and re-analyze.
		LCS	1 per 20 samples or less	Does not violate any item listed below in Note 1.	Determine reason for loss of control and re-analyze.
8081	**Pesticides / PCBs**	Field blank	1 per 10 samples or daily; whichever is more frequent	Less than 4 cmpds. all with conc. less than 3 times the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field duplicate	1 per 10 samples	Water - < 30% RPD Soils - < 40% RPD	Examine analytical results. If no problems then examine sampling procedures.
		Method blank	Per daily extraction-batch or 1 per 20 samples, whichever is more frequent	All cmpds. less than the EQL.	Re-analyze. If still present clean instrument and recalibrate.
		Surrogate spikes	All analyses	See Table 3-1 to 3-7 for spiking compound, concentrations and control limits.	Re-analyze samples. If outside of criteria, then report both results and bias the data.
		MS/MSD analyses	1 per 20 samples or less	See Table 3-1 to 3-7 for compounds, recovery limits and RPD.	BS/BSD. Re-analyze and if recoveries are still outside of criteria, report both results.
		LCS	1 per 20 samples or less	Does not violate any item listed below in Note 1.	Determine reason for loss of control and re-analyze.
8150B	**Herbicides**	Field blank	1 per 10 samples or daily; whichever is more frequent	All cmpds. less than the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field duplicate	1 per 10 samples	Water - < 30% RPD Soils - < 40% RPD	Examine analytical results. If no problems then examine sampling procedures.

TABLE 8-1
GP ENVIRONMENTAL SERVICES
CONTROL LIMITS AND CORRECTIVE ACTIONS
RFI PHASE I QAPjP
CWM-VICKERY

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
8150B	**Herbicides**	Method blank	Per daily extraction-batch or 1 per 20 samples, whichever is more frequent	All cmpds. less than the EQL.	Re-analyze blanks. If containments are still present, then clean and recalibrate instrument.
		Surrogate spikes	All analyses	See Table 3-1 to 3-7 for spiking compound, concentrations and control limits.	Re-analyze sample, and if recoveries are again outside of the limits then report both analyses and bias the data.
		MS/MSD analyses	1 per 20 samples or less	See Table 3-1 to 3-7 for compounds, recovery limits and RPD.	BS/BSD. Re-analyze and if recoveries are still outside of criteria, report both results.
		LCS	1 per 20 samples or less	Does not violate any item listed below in Note 1.	Determine reason for loss of control and re-analyze.
8280	**Dioxins & Furans**	Method Blank	Each batch of up to 20 samples	No target analyte above PRL	Re-analyze and re-examine analytical results. If not contaminant free re-extract associated samples.
		MS/MSD analyses	Each batch of up to 20 samples	Refer to Table 3-1 to 3-7	BS/BSD. Asses for matrix interferences. Evaluate Blank Spike for method control.
		LCS	Each batch of up to 20 samples	Refer to Table 3-1 to 3-7	Re-analyze and re-examine analytical results. If not within limits, re-extract associated samples or qualify data.
		Internal Standard	Added to all field & batch QC samples	Refer to Table 3-1 to 3-7 (1)	If not within limits, re-extract.
		Column Performance Check (PC)	Begining & end of analytical sequence; every 12 hours of continuous operation	% Valley of 2, 3, 7, 8 - TCDD & 1, 2, 3, 4 - TCDD must be less than or equal to 25% for bracketing PCs.	Determine reason for > 25% and re-analyze samples to last passing PC.
		Continuing Calibration	Begining of analytical sequence; every 12 hours of continuous operation	Less than or equal to 30% Difference; S/N ratio of 2, 3, 7, 8 - TCDD must be greater than or equal to 50:1	If fails, recalibrate instrument and re-analyze samples.
6010 & 7000 Series	**Metals**	Field blank	1 per 10 samples or daily; whichever is more frequent	All cmpds. less than the EQL.	Examine analytical results, if there is not a problem and compound is present in samples then resample.
		Field duplicate	1 per set of 10 samples	Water - < 30% RPD Soils - < 40% RPD	Examine analytical results. If no problems then examine sampling procedures.
		Method blank	Daily or one per digestion batch, whichever is more frequent	All cmpds. less than the EQL.	Re-analyze. If problem still exists then redigest and re-analyze all associated samples.
		Lab duplicate	1 per digestion batch	If less than 5x CRDL, then +/-CRDL for water and +/-2x for CRDL for soils.	Re-analyze and re-examine analyses.
		Matrix Spike	1 per 10 samples or 1 per digestion batch	See Table 3-1 to 3-7.	Re-analyze and confirm results. Report analyses.
		LCS	1 per set of 10 samples	Recovery between 80-110%.	Re-analyze, if problem still exists then redigest and re-analyze associated samples.
9010A &	**Cyanide & sulfide**	Field blank	Daily	All cmpds. less than the EQL.	Re-analyze and examine field sampling procedures if necessary.
376.1		Field duplicate	1 per 10 samples	Water - < 20% Soils - < 30%	Examine analytical results. If no problems then examine sampling procedures.
		Method blank	Once per extraction procedure	All cmpds. less than the EQL.	Re-analyze and re-distill all associated samples if necessary.
		Lab duplicate	1 per 10 samples	Water - < 20% Soils - < 30%	Examine analytical data and re-analyze if necessary.
		Matrix Spike	1 per 10 samples or 1 per digestion batch	See Table 3-1 to 3-7.	Re-analyze and confirm results. Report analyses.
		LCS	1 per set of 10 samples	Recovery between 80-110%.	Re-analyze, if problem still exists then redigest and re-analyze associated samples.

TABLE 8-1

GP ENVIRONMENTAL SERVICES

CONTROL LIMITS AND CORRECTIVE ACTIONS

RFI PHASE I QAPjP

CWM-VICKERY

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
8141	**Organophosphorus Pesticides**	Field Blank	1 per 10 samples, or daily	Less than 4 cmpds, all less than 3x EQL	If cmpd present in samples, resample.
		Field Duplicate	1 per 10 samples	<30% RPD/<40% RPD (water/soil)	Examine analytical results & sampling procedures.
		Method Blank	1 per 20, minimum 1 per extraction batch	All cmpds below PRL	Re-analyze. If still present clean instrument and recalibrate.
		Surrogate Spike	All samples	Per Table 3-4	Re-analyze. If problem persists, report both results and qualify data.
		MS/MSD	1 per 20, or less	Per Table 3-4	Examine results. If no indication of analytical problem, qualify data.
		LCS	1 per 20, minimum 1 per extraction batch	Per Note 1, below	Troubleshoot and correct problem. Re-analyze.
300.0	**Chloride**	Field Blank	1 per 10 samples, or daily	Less than 3x EQL	If cmpd present in samples at <10x EQL, resample.
		Field Duplicate	1 per 10 samples	<30% RPD/<40% RPD (water/soil)	Examine analytical results & sampling procedures.
		Method Blank	1 per 20, minimum 1 per extraction batch	Below PRL	Re-analyze.
		MD/MS	1 per 20, or less	Per Table 3-8	Examine results. If no indication of anlytical problem, qualify data.
		LCS	1 per 20, minimum 1 per extraction batch	Per Note 1, below	Troubleshoot and correct problem. Re-analyze.

TAB. 3-1
GP ENVIRONMENTAL SERVICES
CONTROL LIMITS AND CORRECTIVE ACTIONS
RFI PHASE I QAPjP
CWM-VICKERY

Notes:

Field Blanks are collected on water samples only.
VOC - Volatile Organic Compound
SVOC - Semi-Volatile Organic Compound
PCBs - Polychlorinated Biphenyls
TCDD - Tetrachloro Dibenzo-p-Dioxins
EQL - Estimate Quantitation Limit
LCS - Laboratory Control Samples
RPD - Relative Percent Difference
QC - Quality Control
S/N - Signal To Noise Relation
CRDL - Contract Required Detection Limits
cmpds - compounds
conc. - concentration
MS/MSD - Matrix Spike / Matrix Spike Duplicate
BS/BSD - Blank Spike / Blank Spike Duplicate

(1) Samples having very complex matrices may not achieve the specified recoveries, but must meet 10:1 signal to noise criteria.

(2) The laboratory QC logbooks are for the recording of QC data (LCS results) by the analyst immediately after it is acquired. The data points are also immediately plotted by the analyst on Quality Control Charts in the QC logbooks. Control charts may also be generated automatically by the laboratory data management system. This allows the analyst to immediately ascertain the validity of the QC data and to take action, if required, in the event of an out of control situation. An analysis may be considered out of control whenever, at a minimum, any one of the following conditions is demonstrated by a control chart used to monitor that analysis:

- Any one point is outside of the control limits
- Any three consecutive points are outside the warning limits
- Any eight consecutive points are on the same side of the plotted mean
- Any six consecutive points are such that each point is larger (or smaller) than its immediate predecessor
- Any obvious cyclic pattern is seen in the data points

Quality Control Charts are periodically updated based on historical data. It is GP Environmental Services' policy to update Control Charts after every twenty new sample data points are accumulated. The recalculation of mean and standard deviation values are based upon the forty most recent data points.

Warning and control limits are based upon the following formulas:

Upper Control Limit (UCL)	$= \chi + 3\sigma$
Upper Warning Limit (UWL)	$= \chi + 2\sigma$
Lower Warning Limit (LWL)	$= \chi - 2\sigma$
Lower Control Limit (LCL)	$= \chi - 3\sigma$

where:

χ = mean percent recovery
σ = Standard deviation

TABLE 11-1
GP ENVIRONMENTAL SERVICES AND TRIANGLE LABORATORIES, INC.
PREVENTIVE MAINTENANCE SCHEDULE
RFI PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	ACTIVITY	FREQUENCY
Thermo Jarrell Ash ICAP 61e Trace	6010A	Change pump windings	Every 2 days
		Check profile of 5 ppm As	Daily
		-adjust profile to within +/- 0.3 nm	
		Clean sample introduction	Daily (end of day)
		-aspirate 2% soap solution	
		-follow with deionized water rinse	
		-aspirate air to dry	
		Clean Plasma Torch	Quarterly
		Check RF power supply output	Quarterly
		Clean Air filters	Quarterly
		Change deionized water in water recirculator.	Semi-annually
		Change all plastic tubing (gas lines and water lines)	Yearly
PS 200 Mercury Autoanalyzer	7470A 7471A	Drying tube - replace desiccant	Daily
		Clean and refill wash basin	Daily
		Perform test optics and record results	Daily
		Lubricate Autosampler Rails	Daily
		Replace pump tubing if needed	Weekly
		Align Autosampler if needed	Monthly
		Perform Instrumental Detection Limit Study	Quarterly
		Replace Liquid - Gas separator	Annual
		Clean Absorption Cell	Annual

TABLE 11-1
GP ENVIRONMENTAL SERVICES AND TRIANGLE LABORATORIES, INC.
PREVENTIVE MAINTENANCE SCHEDULE
RFI PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	ACTIVITY	FREQUENCY
Dionex 4000i Ion Chromatograph	300.0	Rinse hydroxide system to remove residual carbonates	Daily
		Prepare and degas eluents	Daily
		Check baseline stability, (pt eval)	Daily
		Check for spills in column and valve compartments	Weekly
		Clean dried eluent from surfaces and components	Weekly
		Check micromembrane suppressers for leaks	Weekly
		Check all lines for crimping	Weekly
		Check GPM pump seals and pistons	Monthly
		Replace regen system acid	Quarterly
		Clean conductivity detector and check cell constant	Quarterly
		Regenerate ATC	Annual
		Disassemble and clean GPM check valve	Annual
		Disassemble and clean ACM liquid valves and check piston o-rings	Annual
		Clean guard and separator columns	Annual
		Clean dust from GPM cooling fan and boards	As Needed
		Change gas cylinder (helium)	As Needed
		Replace guard column	As Needed
		Replace Separator column	As Needed
		Replace ATC	As Needed
		Replace micromembrane suppresser	As Needed
		Replace auto-regen cartridge	As Needed
		Replace gas & liquid lines	As Needed
Analytical Balance	3550 3550A	Clean the sample holder	Each Use
		Adjust the zero setting	Each Use
		Check the calibration of the scale through full range	Biweekly

TABLE 11-1
GP ENVIRONMENTAL SERVICES AND TRIANGLE LABORATORIES, INC.
PREVENTIVE MAINTENANCE SCHEDULE
RFI PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	ACTIVITY	FREQUENCY
Perkin-Elmer 8410 & HP 5890(s) Gas Chromatographs	8080A 8141 8150	Change septa	Daily
		Save the data files from previous day's run	Daily
		Check the carrier gas pressure and replace it if below 250 psi	Daily
		Check the gas indicator traps for water and replace if needed	Daily
		Back up the computer system software	Monthly
		Remove column and check for deposits	Monthly
		Replace glass wool and ferrules	Monthly
		Reinstall and check flow rate	Monthly
		Bake out electron capture detectors at 400 C for 4 hours	Monthly
		Check and clean the syringe and dip needle	Monthly
		Replace the gas line purifying devices	Quarterly
		Replace the printer ribbon	Quarterly
HP 5970B GC/MS Selective Detector	8260B 8270B	Check oil level in mechanical pump	Weekly
		Run Autotune	Weekly
		Back up data and tape unit	Weekly
		Check the condition of the carrier gas trap at each cylinder change	Weekly
		Inspect and refill the calibration gas vial with PFTBA (Perfluorotributylamine)	Quarterly
		Change the oil in the mechanical pump	Semiannual
		Change the oil in the turbomolecular pump	Semiannual
		Vacuum the dust from the grills of the two cooling fans as needed	Annual
		Filament replacement	Annual
		Source cleaning - repeller face, drawout lens face, quadruples, lens stack, electron focus, ion source chamber, and any other metal parts that appear dirty	Annual
		Replace electron multiplier	Annual
		Replace GC column (capillary/packed)	Annual

TABLE 11-1
GP ENVIRONMENTAL SERVICES AND TRIANGLE LABORATORIES, INC.
PREVENTIVE MAINTENANCE SCHEDULE
RFI PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	ACTIVITY	FREQUENCY
Rapid Flow Auto-Analyzer	9010A	Empty the sample cups	Each Use
		Check the fitting connections	Each Use
		Perform flow test	Each Use
		Make up new reagents and standards	Each Use
		Flush the system with distilled water	Each Use
		Perform the flow test	Each Use
		Check the pump fittings and connections	Weekly
		Check the pump rollers and clean the system with Kemwash	Weekly
		Change the pump tubes	Bimonthly
		Reset bubble phase	Bimonthly
		Check the transmission tubing and connections and change as needed	Bimonthly
		Lubricate the main speed reduction gear on the pump	Biannual
		Inspect and/or change the transmission tubing and sleeving	Biannual

TABLE 11-1
GP ENVIRONMENTAL SERVICES AND TRIANGLE LABORATORIES, INC.
PREVENTIVE MAINTENANCE SCHEDULE
RFI PHASE I QAPjP
CWM-VICKERY

INSTRUMENT	METHOD	ACTIVITY	FREQUENCY
HP 5890 HRGC VG/HRMS	8280	Inspect vacuum system pressures	Daily
		Inspect helium tank pressures and change if less than 300 psi	Daily
		Change injection port liner and septum	As needed
		Inspect water filters and change if necessary	Monthly
		Bake AutoSpec flight tube	Bi-monthly
		Clean ion source	Quarterly or as needed
		Clean source slit	Bi-annually or as needed
		Clean or replace split line	Bi-annually or as needed
		Inspect focus 2 assembly and clean if necessary	Bi-annually or as needed
		Bake out 70 style HRMS	Bi-annually or as needed
		Replace rotary pump oil	Bi-annually or as needed
		Check diffusion pump oil and add if needed	Bi-annually or as needed
		Change reservoir septum	Quarterly or as needed
		Change oxygen trap	Annually
		Full preventative maintenance visit by an engineer	As needed

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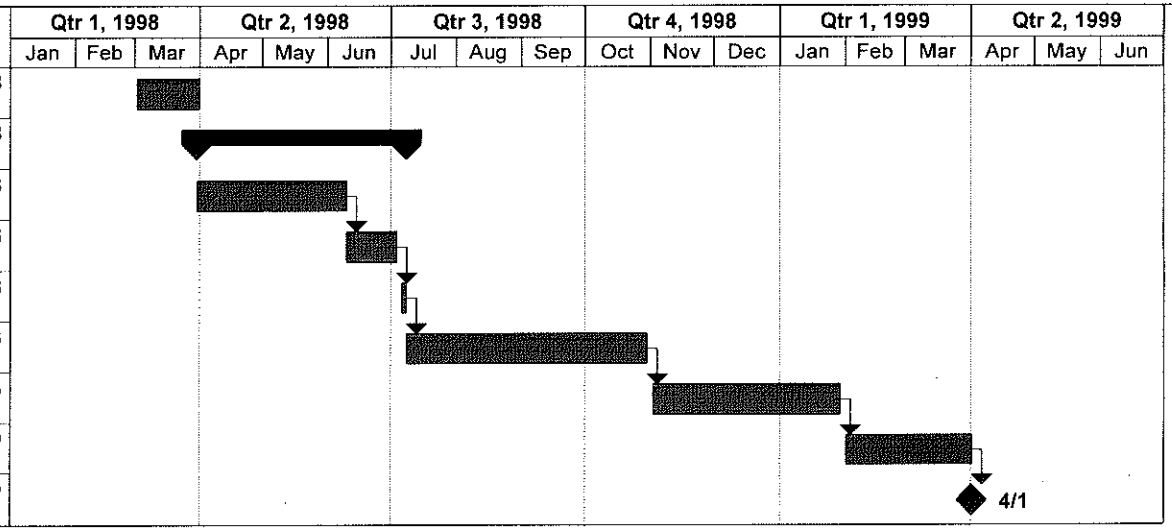
Notes:

Mn - Manganese
Na - Sodium
ATC - Anion Trap Column
RF - Radio Frequency
pt eval - Point Elevation
GPM - General Pump Module
ACM - Advanced Chrome Mod
ICP - Inductively Coupled Plasma
GC - Gas Chromatography
psi- Pounds Per Square Inch

Figure 1-1
RFI Phase I Schedule of Activities
CWM-Vickery

ID	Task Name	Start
1	**Mobilization**	3/2/98
2	**Field Investigation**	**3/31/98**
3	SWMU Groups A through I	3/31/98
4	Areas of Concern	6/10/98
5	Groundwater Sampling	7/6/98
6	**RFI Final Report**	7/8/98
7	**EPA Review**	11/2/98
8	**Address Comments**	2/1/99
9	**Submit Final Report**	4/1/99



Project: CWM-Vickery RFI QAPjP
Date: 11/14/97

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

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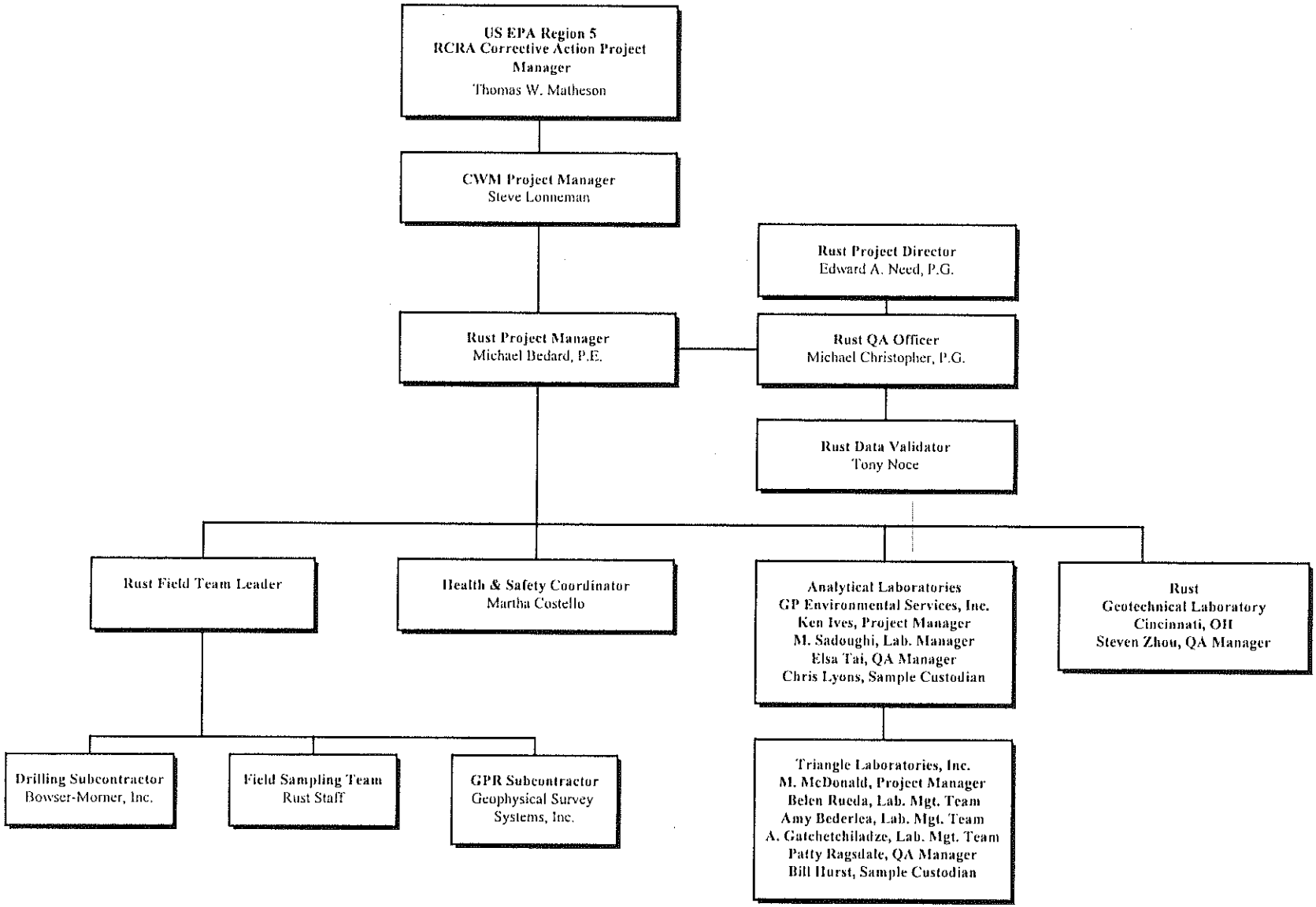

FIGURE 2-1
RFI PROJECT ORGANIZATION CHART
RFI PHASE I QAPjP
CWM-VICKERY

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APPENDIX A

Effective Date: October 1997
Version Number: 1
Initiated By :
Approved By :

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SOP No: 13.6

Title: Volatile Organics - Method 8260B

1.0 SCOPE AND APPLICATION

This method is used to identify and quantify purgeable compounds in waste water, soil, and various types of waste samples using GCMS methodology. The compounds listed below include the most common requested volatile parameters. Their respective retention time and quantitation ion are listed in Table 1 for the target compounds.

Target Compound List

1. Chloromethane
2. Bromomethane
3. Vinyl Chloride
4. Chloroethane
5. Methylene Chloride
6. Acetone
7. Carbon Disulfide
8. 1,1-Dichloroethene
9. 1,1-Dichloroethane
10. trans-1,2-Dichloroethene
11. Chloroform
12. 1,2-Dichloroethane
13. 2-Butanone
14. 1,1,1-Trichloroethane
15. Carbon Tetrachloride
16. Vinyl Acetate
17. Bromodichloromethane
18. 1,1,2,2-Tetrachloroethane
19. 1,2-Dichloropropane
20. trans-1,3-Dichloropropene
21. Trichloroethene
22. Dibromochloromethane
23. 1,1,2-Trichloroethane
24. Benzene
25. cis-1,3-Dicholoropropene
26. 2-Chloroethyl Vinyl Ether
27. Bromoform
28. 2-Hexanone
29. 4-Methyl-2-pentanone

30. Tetrachloroethene
31. Toluene
32. Chlorobenzene
33. Ethyl Benzene
34. Styrene
35. Total Xylenes

Appendix IX List

1. Acetonitrile
2. Acrylonitrile*
3. Allyl Chloride
4. 2-Chloro-1,3-butadiene
5. 1,2-Dibromo-3-chloropropane
6. Dibromomethane
7. 1,2-Dibromoethane
8. 1,2-Dichlorobenzene
9. 1,3-Dichlorobenzene
10. 1,4-Dichlorobenzene
11. trans-1,4-Dichloro-2-butene
12. Dichlorodifluoromethane
13. p-Dioxane*
14. Ethyl methacrylate
15. Isobutyl alcohol
16. Methacrylonitrile
17. Methyl iodide
18. Methyl methacrylate
19. Pentachloroethane
20. Propionitrile*
21. 1,1,1,2-Tetrachloroethane
22. Hexachloroethane
23. 1,2,4-Trichlorobenzene
24. Trichlorofluoromethane
25. 1,2,3-Trichloropropane
26. 1,1-Dichloropropylene
27. 1,4-Dioxane
28. Acrolein
29. Bromochloromethane
30. cis-1,2-Dichloroethene

*Poor purging efficiency resulting in high EDL.

Additional Compounds

1. MTBE
2. 2, 2 - Dichloropropane
3. 1, 3 - Dichloropropane
4. Isopropylbenzene
5. Bromobenzene
6. n - Propylbenzene
7. 2 - Chlorotoluene
8. 4 - Chlorotoluene
9. 1, 3, 5 - Trimethylbenzene
10. tert - Butylbenzene
11. 1, 2, 4 - Trimethylbenzene
12. sec - Butylbenzene
13. 4 - Isopropyltoluene
14. n - Butylbenzene
15. Hexachlorobutadiene
16. Naphthalene
17. 1, 2, 3 - Trichlorobenzene

TABLE 1

Comp No.	Compound Name	Retention Time, Min	Quantitation Ion
1)	*Fluorobenzene (IS)	8.14	96.0
2)	Chloromethane	2.49	50.0
3)	Bromomethane	3.10	94.0
4)	Vinyl Chloride	2.61	62.0
5)	Chloroethane	3.25	64.0
6)	Acrolein	4.37	56.0
7)	Acrylonitrile	5.69	53.0
8)	Methylene Chloride	5.49	84.0
9)	Acetone	4.57	43.0
10)	Carbon Disulfide	5.24	76.0
11)	1,1-Dichloroethane	4.69	96.0
12)	trans-1,2-Dichloroethene	6.06	96.0
13)	1,1-Dichloroethane	6.75	63.0
14)	1,2-Dichloroethene (cis)	7.73	96.0
15)	Chloroform	8.00	83.0
16)	1,2-Dichloroethane-d4	9.04	65.0
17)	1,2-Dichloroethane	9.18	62.0
18)	2-Butanone	7.57	72.0
19)	*1,4-Difluorobenzene (IS)	9.83	114.0
20)	1,1,1-Trichloroethane	8.63	97.0
21)	Carbon Tetrachloride	9.02	117.0
22)	Vinyl Acetate	6.98	43.0
23)	2-Chloroethylvinyl Ether	11.47	106.0
24)	Bromodichloromethane	10.77	83.0
25)	1,2-Dichloropropane	10.47	63.0
26)	cis-1,3-Dichloropropene	11.73	75.0
27)	Trichloroethene	10.24	130.0
28)	Dibromochloromethane	13.43	129.0
29)	1,1,2-Trichloroethane	12.73	97.0
30)	Benzene	9.22	78.0
31)	trans-1,3-Dichloropropene	12.55	75.0
32)	Bromoform	15.92	173.0
33)	*Chlorobenzene-d5 (IS)	14.49	117.0
34)	4-Methyl-2-Pentanone	11.61	43.0
35)	2-Hexanone	13.00	43.0
36)	Tetrachloroethene	13.30	164.0
37)	1,1,2,2-Tetrachloroethane	16.41	83.0
38)	Toluene	12.24	92.0

39)	Toluene-d8	12.14	98.0
40)	Chlorobenzene	14.55	112.0
41)	Ethylbenzene	14.75	106.0
42)	Styrene	15.61	104.0
43)	Xylene (total)	15.59	106.0
44)	Bromofluorobenzene	16.53	95.0

*Compound is Internal Standard. Compounds listed under each (IS) is quantified against that particular (IS).

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into a gas chromatograph by the purge and trap method.

2.2 An inert gas is bubbled through the solution at ambient temperature (at elevated temperatures for soil samples), and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences and contamination, under the analysis conditions, by analyzing method blanks.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett-Packard 5890 Gas Chromatographic Systems (GC) are employed for execution of this method. The GCs are complete with temperature programming capabilities, and all required accessories such as columns, gases, cooling valves and syringes. Sample introduction is accomplished through the use of purge and trap systems.

4.2 Purge and Trap System

The Tekmar 2000/3000 purge and trap system is coupled with the gas chromatographic system. The system is equipped with a Tekmar 2016 sixteen position autosampler, and a sample heating device for soil samples.

The purge and trap device consists of three separate modules. The sample purger, the trap and the desorber. The purging chamber accepts glass vessels capable of holding at least 5-ml of liquid samples or 5 grams of soil samples. The glass tubes are stored in an oven at 105°C to prevent contamination from organic vapors.

The trap utilized by the laboratory is 25 cm long and has an inside diameter of 0.105 in. Traps are marketed as VOCARB 3000 by vendors such as Supelco, and consist of graphitized carbon.

A complete description of the inner workings of this purge and trap model is available in the Tekmar 2000/3000 manual.

4.3 Mass Spectrometer

The HP-5970 Quadropole Mass Selective Detector is used as the detection device for Method 8260B. This system is capable of scanning from 35-260 amu every one second or less, using 70 volts (nominal) electron energy in the EI mode. After proper tuning, the system produces a mass spectrum that meets all the criteria in Table 4 when 50 ng of 4-Bromofluorobenzene (BFB) are injected into the gas chromatograph.

4.4 Data System

Each GC/MS system is attached to a dedicated 486 or pentium based computer equipped with Enviroquant software for automated acquisition and processing. The software generates total and extracted ion profiles of each compound and is capable of performing library searches on spectra using a full EPA/NIH Mass Spectral Data Library. Each system is attached to an internal laboratory computer network for additional data processing, storage and archiving.

4.5 Column

A Restek Megabore column, 60 meters in length, with a 0.53 mm internal diameter and 2.0 micron film thickness is used.

4.6 Microsyringes - 10 ul, 25 ul, 100 ul, 250 ul, 500 ul, and 1000 ul.

4.7 Luerlock syringe - 5 and 25 ml gas tight.

5.0 REAGENTS

5.1 Organic free reagent water.

5.2 Stock solutions.

5.3 Methanol, High purity grade, B & J Brand for Purge and Trap analysis.

6.0 PROCEDURE

6.1 Calibration

Five concentration levels are analyzed for each analyte and surrogate standards. A minimum five point curve is then created after all 5 points are analyzed. Calibration levels are analyzed at 5, 20, 50, 100, 150 and/or 200ug/l for all analytes and surrogate standards except for 2-Chloroethyl vinyl ether which is analyzed at 40, 100, 200, 300 and 400ug/l.

6.2 Instrumentation Parameters

The following set of operating conditions exist for method 8260B.

Electron energy:	70 volts (nominal)
Mass range:	35-260 amu
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan

Initial column temperature:	10° C
Initial column holding time:	4 min
Column temperature program:	8° C/minutes
Final column temperature:	190° C
Final column holding time:	1 min
Injector temperature:	220° C
Source temperature:	According to manufacturer's specifications
Transfer line temperature:	280° C (Preset to manufacturer)
Carrier gas:	Helium at about 8ml/min

6.3 Tuning

At the beginning of each day, each GC/MS system is injected with 50ng of BFB and tuned to meet the criteria listed in Table 4. The analysis must not commence unless the criteria are met. This requirement must be met for each 12 hour interval.

6.4 Calibration Requirements

Once tuning requirements are met, the initial or continuing calibration check must be established. The generation of response factors is the next step in establishing the calibration requirements for method 8260B. The instructions for determining the response factors are as follows:

6.4.1 Tabulate the area response of the quantitation ions (see Table 1) against the concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard with the retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x - Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

The average RF must be calculated for each compound. A system performance check should be completed before the calibration curve is used. Five compounds, the System Performance Check Compounds, or SPCCs, are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene (see Table 4). The minimum relative response factors for these compounds should be 0.1, 0.1, 0.1, 0.3 and 0.3. These compounds typically have RFs respectivly, of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Initial calibration is analyzed at a minimum of 5 levels. These levels are 5, 20, 50, 100, 150 and/or 200ug/l. The following compounds have higher initial calibration levels.

Acrolein	100	250	500	750	1000
Acrylonitrile	100	250	500	750	1000
2 - Chloroethyl Vinyl Ether	80	200	400	600	800

Using the RFs from the initial calibration, calculate the percent relative standard deviation (% RSD) for all compounds.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation

$\bar{X}$ = mean of 5 initial RFs for a compound

N = Number of calibration points

SD = standard deviation of average RFs for a compound

X_i = Response factor for each point

$$SD = \left[\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1} \right]^{1/2}$$

6.4.2 The % RSD for any compound should be 15% or less. If the % RSD for any compound is greater than 15%, one of the following options must be applied. However, the % RSD for calibration check compounds should be less than 30%. Meeting only the CCC and SPCC criteria is not substituted for successful calibration.

6.4.2.1 Construct calibration curve of area ratio (A/Ais) versus concentration using first regreation fit of the five calibration points. The analyst should not force the line through the origin, but have the intercept calculated from the five data points. The use of linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the s tandard. The regression calculation will generate a correlation coefficient (r). A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99. The regression will

produce the slope and intercept terms for a linear equation in the form

$$y = ax + b$$

where:

y = instrument response (peak area or height)
a = slope of the line
x = concentration
b = the intercept

In calculating sample concentration by internal standard method, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y-b)}{a}$$

which may be rearranged to solve for x, the concentration using internal standard quantitation, the regression equation is rearranged as shown below:

$$\frac{A_s C_{is}}{Ais} = aC + b$$

where:

A_s = Area of peak for target analyte in the sample

A_{is} = Area of peak for internal standard

C_s = Concentration of target analyte

C_{is} = Concentration of the internal standard

a = Slope of the line

b = The intercept

6.4.2.2 If the % RSD for one or more analytes exceeds 15%, the initial calibration may still be acceptable if the following conditions are met:

- The mean of the RSD value for all analytes in the calibration is less than or equal to 15%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total numbers of analytes.

- The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest of specific project.

6.4.3 Continuing (Daily) Calibration

The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a 50ppb calibration standard and verifying if all compound of interest meet the acceptance criteria for daily calibration. Daily calibration standard analysis must meet the relative response factor criteria for SPCC and non SPCC; % drift criteria of calibration check compounds (CCC) and non CCC. If SPCC and non SPCC criteria listed in Table 4 are not met, the system must be evaluated and corrective action must be taken before sample analyses begins. Potential problem include standard mixture degradation, injection port inlet contamination, contamination of front end of the analytical column, and active sites in the column or chromotographic system. After the criteria for relative response factor (RRF) are met, calculate the % drift of each compound to check the validity of the initial calibration.

Calculate the % drift using the following equation:

$$\% \text{ Drift} = \frac{C_1 - C_c}{C_1} \times 100$$

where:

C_1 = Calibration check compound standard concentration

C_c = Measured concentration

If the percent drift for each CCC is (>20% drift), and >35% for non CCC except up to 4 compounds could have % drift less than or equal to 50%, corrective action must be taken. After corrective action, if non source of the problem can be determined, a new five point calibration MUST be generated. This criteria must be met before sample analysis begins. If

the CCCs are not required analytes, then all required analytes must meet the 20% drift criterion.

The internal standard response and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. Tables 3 and 4 list SPCC and CCC compounds.

6.5 Retention Time Change

If the retention time for any internal standard changes by more than 30 sec. from the last check calibration or when an internal standard area changes by a factor of 2 (-50% to +100%), from the mid point standard of the most recent initial calibration, then all affected samples must be reanalyzed after the problem is corrected. Typical retention times for 8260A analytes under the parameters listed in Section 6.2 is provided on Table 1.

6.6 Qualitative Analysis

6.6.1 The compounds listed in Section 1 shall be identified by an analyst by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identification.

6.6.1.1 Relative relation time of the sample and standard must agree ± 0.05.

6.6.1.2 Correspondence of the sample component and standard component mass spectra.

6.6.2 The requirement for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectra at a relative intensity greater than 10% <u>must</u> be present in the sample spectrum. All ions specified must agree within ± 20% between the standard and sample spectra. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for.

6.7 Quantitative Analysis

When a compound is identified, quantification is based on the integrated abundance of the primary characteristics ion and the response and amount of the corresponding internal standard.

$$\text{Concentration (ug/L)} = \frac{(Ax)\ (Is)\ (D)}{(Ais)\ (Avg\ RF)\ (Vo)}$$

$$\text{Concentration (ug/kg)} = \frac{(Ax)\ (Is)\ (D)}{(Ais)\ (Avg\ RF)\ (W)\ (S)}$$

where:

Ax	=	Area of primary ion
Is	=	Amount of internal standard, ug/L
Ais	=	Area of ion for internal standard
Avg RF	=	Mean relative response factor for compound measured
Vo	=	Volume of sample purged, L
D	=	Dilution factor
W	=	Weight in Kg
S	=	Solid

6.8 For non-TCL components, a library search may be executed. Up to 20 non-target organic compounds shall be tentatively identified when required. Guidelines for making tentative identification:

6.8.1 Ions greater than 10% of the most abundant ion should be present in the sample spectrum.

6.8.2 Relative intensities of the major ions should agree within ± 20%.

6.8.3 Molecular ion present in the reference spectrum should be present in sample spectrum.

6.8.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.9 GC/MS Analysis

6.9.1 Water Samples

6.9.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

6.9.1.3 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples.

6.9.1.4 Adjust the purge gas (Helium) flow rate to approximately 40ml/min on the purge and trap device.

6.9.1.5 Remove the plunger from a 5ml syringe. Open the sample and carefully pour the sample into the syringe barrel to just short of overflowing. Compress the sample. Vent any residual air while adjusting the sample volume to 5.0ml.

6.9.1.6 Add 5.0ul of surrogate spiking solution and 5ul of internal standard solution (50 ppm each) through the valve bore of the syringe and load samples into the sample tube. Immediately after loading the sample, verify the pH of the samples using narrow range pH paper. Sample vials should not be opened to verify pH prior to loading into the purge unit.

6.9.1.7 For the matrix spike analysis, add 5ul of the matrix spike solution (50 ppm) to the sample to be purged. This will yield a final concentration of 50ug/L (ug/kg for soils) in the final sample.

6.9.1.8 The samples are analyzed with appropriate dilution when the concentration level of any analyte exceeds the calibration range. Dilutions are made in the 5ml gastight luer lock syringe by adding reagent water. Calculate the volume of reagent water needed for the dilution and add into a 4ml syringe. Dilution of samples should result in analysis with the highest concentration target analyte in the upper half of the calibration range. Using a suitable syringe, add the exact volume of sample into the reagent water in the 5ml syringe. Add 5ul of Internal Standard & Surrogate and analyze as discussed above.

If the dilute sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

6.9.1.10 The spiked sample is injected into a purging tube attached to the Purge & Trap device. Purge the sample for 11 minutes and desorb the contents of the trap at 200° for 2 minutes into the GC/MS.

6.9.1.11 Low Concentration Method: This method is applicable to water samples containing low levels of contaminants. The detection limits are generally improved by analyzing larger sample volume (25 ml). The detection limits of compounds with poor purging efficiency (such as ketones) do not significantly improve when low concentration method is utilized. The low concentration analytical procedure is virtually the same as low level water analysis except for concentration of the calibration, surrogate and internal standards. The following concentration levels and ranges are analyzed:

Calibration	-	2, 10, 20, 40, 60 ug/L
Surrogates	-	2, 10, 20, 40, 60 ug/L 10 in sample and QC ug/L
Internal Standards	-	10 ug/L
Matrix Spike/LCS	-	10 ug/L
Continuing Calibration	-	10 ug/L

Acceptance criteria for the initial and continuing calibrations is based on the evaluation of check compounds exclusively (Table 3). Criteria for percent RSD and difference in the initial and continuing calibrations are described in section 6.4. System performance check compounds are not monitored for low concentration method.

6.9.1.12 Cleaning of purge and trap cells.
Upon completion of volatile analysis, the purge and trap cells are disconnected from the ALS. The purge and trap cells are cleaned with deionized water and mild soap, and rinsed with deionized water. The purge and trap cells are then baked in an oven at 105° for at least four hours. Upon completion of baking, the purge and trap cells are placed in a container covered with aluminum foil.

6.9.2 Sediment/Soil and Waste Samples

6.9.2.1 Low Concentration method: Applicable for samples containing individual compounds of <1mg/kg. All granular/porous waste/sediment/soil samples can be analyzed using this method.

Weigh 5g of the sample into a glass sparge tube and record the weight to the nearest 0.1g. Add reagent water to a 5ml luerlock type syringe and adjust the volume to 5ml. Add 5ul of internal standard and 5ul of surrogate standard to the water. Connect the sparge tube with the sample to the purge & trap device and add the spiked water to the sample. Heat the sample to 40°C ±1°C and purge the sample for ul minutes. Desorb the trap at 200c for 2 minutes into the GCMS.

If the concentration level of any analyte exceeds the calibration range and is below 1mg/kg, the sample should be analyzed by weighing 1g of the sample. If the concentration level of any analyte is higher than 1mg/kg, then the high concentration method should be used.

6.9.2.2 High Concentration Method: The method is based on extracting the soil/sediment with methanol. Weigh 4gm of the sample into a 20ml vial using a top loading balance. Record the weight to the nearest 0.1g. Using a pipet, add 9.0ml methanol; then add 1.0ml of the surrogate spiking solution into the vial. Close the cap and shake for 2 minutes. Pipet approximately 1ml of the extract to a GC vial for storage, using a disposable pipet. Transfer approximately 1ml of the method blank to a separate GC vial for each set of samples. The standards, LCS and blanks should contain 100µl of a solvent to simulate the sample condition. 100ul of the extract is added to reagent water collected in a 5ml luerlock syringe. 5ul each of Internal Standard is added to the syringe. Proceed with the analysis as outlined in the water sample analysis. If further dilution is needed, a smaller extract volume is used and the same procedure is repeated.

A separate method blank containing 100ul methanol should be analyzed prior to a high concentration sample.

6.9.2.3 For matrix spike in the high concentration sediment/soil samples, 8.0ml of methanol, 1.0ml of surrogate spike solution, and 1.0ml of spike solution is added to a 4g sample. Cap and shake for 2 minutes. Add a 100µl aliquot of this extract to 5ml of organic free reagent water for purging.

6.9.2.4 Samples extracted through Toxicity Characteristic Leachate Procedure by zero headspace extractor are analyzed by this method. Only those compounds designated by the TCLP method are accounted for. Samples are analyzed at 10 times dilution in order to minimize the effects of acetic acid on the chromatography and purge and trap systems. TCLP compounds are listed on Table 7.

7.0 QUALITY CONTROL

7.1 Prior to initiating on going data, it is necessary that the GC/MS meets BFB abundance criteria (Table 5) every twelve (12) hour period for the method.

7.2 When twelve (12) hours have elapsed since the initial tune, the GC/MS must be retuned to continue the analysis.

7.3 If the retention time of the standard changes by more than 30 seconds, the GC system must be inspected for malfunction.

7.4 Surrogate recoveries must be evaluated by determining whether the concentrations fall inside the required recovery limits listed in Table 6.

7.5 A matrix spike and spike duplicate must be performed every 20 samples at the concentration equal to mid-level calibration (50ug/l). Table 2 lists the matrix spike compounds, concentration added, recovery limits and %RPD for soil and water matrices. TCLP samples are spiked with TCLP target compounds at 50ug/l concentration (see Table 7).

7.6 A method blank must be performed for each 12 hour time period.

7.6.1 A method blank for volatile analysis must contain less than or equal to CRQL. For methylene chloride, acetone, toluene and 2-butanone should be less than or equal to 5 times the CRQL. All other target analytes should be <PQL.

7.7 Lab Control Spikes (LCS) are analyzed per batch or every 20 samples whichever comes first. LCS compounds and their concentrations are listed on Table 8. LCS compound must be within the in-house established control limit. Statistical control limit are based on 20 data points. Data points used in the data set must not be selectively included or excluded. If recovery of LCS compound falls outside the established limit, corrective action must be taken. After corrective action, if LCS analyte recovery is still outside QC acceptance limits, all the associated samples batch must be reanalyzed if holding times have not elapsed. For specific clients and U.S. Army Corps programs, LCS should contain all target analytes. In-house established recovery limit for LCS should not exceed ± 20%.

8.0 SAFETY

8.1 Safety glasses, laboratory coats, and latex gloves must be worn.

8.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

8.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the administrative area.

8.4 Standard preparation should be handled under a hood.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition

TABLE 2

MATRIX SPIKE COMPOUNDS	CONC. ADDED	ACCEPTABLE RECOVERY RANGES WATER	%RPD	SOIL/SEDIMENT	%RPD
1,1-Dichloroethene	50	61-145	14	59-172	22
Trichlorethene	50	71-120	14	62-137	24
Chlorolenzene	50	75-130	11	60-133	21
Toluene	50	76-125	13	59-139	21
Benzene	50	76-127	13	66-142	21

TABLE 3

CALIBRATION CHECK COMPOUNDS

1 - 1,1-Dichloroethene

2 - Chloroform

3 - 1,2-Dichloropropane

4 - Toluene

5 - Ethylbenzene

6 - Vinyl chloride

TABLE 4

SYSTEM PERFORMANCE CHECK COMPOUNDS

1 - Chloromethane

2 - 1,1-Dichloroethane

3 - Bromoform

4 - 1,1,2,2-Tetrachloroethane

5 - Chlorobenzene

All other compounds must meet a minimum RRF of 0.010

TABLE 5

BFB KEY ION ABUNDANCE CRITERIA

Mass	Ions Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 6
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

SURROGATE COMPOUND	LOW/MEDIUM WATER	LOW/MEDIUM SOIL/SEDIMENT
4-Bromofluorabenzene	86-115	74-121
1,2-Dichloroethane-d_4	80-120	70-121
Toluene-d_8	88-110	81-117
1,2 - Dichlorobenzene - d_4	80-120	80-120

TABLE 7

TCLP Matrix Spike Recovery

Compound	Spike Added (ug/L)	% Recovery Lower Limit	% Recovery Upper Limit
Vinyl Chloride	50	50	125
1,1-Dichloroethene	50	50	125
Chloroform	50	50	125
1,2-Dichloroethane	50	50	125
2-Butanone	50	50	125
Carbon Tetrachloride	50	50	125
Trichloroethene	50	50	125
Benzene	50	50	125
Tetrachloroethene	50	50	125
Chlorobenzene	50	50	125

TABLE 8

Lab Control Std Recovery for Soil and Water

Compound	Internal Laboratory Limits Water	Internal Laboratory Limits Soil
Vinyl Chloride	69 - 176	55 - 144
1,1-Dichloroethene	72 - 101	58 - 91
Chloroform	88 - 124	71 - 109
1,2-Dichloroethane	88 - 124	50 - 117
1,1,1-Trichloroethane	88 - 129	62 - 105
Carbon Tetrachloride	76 - 120	77 - 110
Bromodichloromethane	75 - 127	70 - 113
Trichloroethene	74 - 120	72 - 111
Dibromochloromethane	88 - 123	76 - 106
Benzene	88 - 129	65 - 107
Bromoform	76 - 127	60 - 123

Units in ug/L or ug/Kg

Effective Date: July 1997
Version Number: 4
Initiated By : D. Hartman
Approved By :

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SOP No: 12.17

Title: Soil Extraction for Semivolatile Organics by Method 3550A (Sonication Extraction)

1.0 APPLICATION AND SCOPE

1.1 This method describes the procedure for extracting non-volatile and semi-volatile organic compounds from solids such as soils. Extracts are suitable for analysis by method 8270B.

2.0 SUMMARY OF METHOD

2.1 Method 3550 describes both a high level and low level technique. This SOP is based on the low level version of method 3550A.

2.1 A 30g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using sonication. The extract is separated from the sample by filtration. The extract is ready for cleanup following concentration.

3.0 INTERFERENCES

3.1 Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. These materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.0 APPARATUS AND MATERIALS

4.1 Mortar Model 155 Grinder, Fisher Scientific Company, or an equivalent brand and model.

4.2 Ultrasonic cell disrupter, Heat Systems - Ultra Sonic, Inc., Model W-385 (475 watt) Sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapped Microtip Probe.

4.3 Apparatus for Determining Percent Moisture

- Oven: drying
- Desiccator
- Crucibles: Porcelain

4.4 Pasteur Glass Pipets, Disposable, 1ml

4.5 Beakers, 400ml

4.6 Filtration Apparatus

- Conical funnel
- Filter paper: Whatman No. 41 or equivalent

4.7 Kuderna-Danish (K-D) Apparatus

4.7.1 Concentrator tube: 10ml graduated (Kontes K-570050-1025 or equivalent).

4.7.2 Evaporator Flask: 500ml (Kontes K-570001-0500 or equivalent).

4.7.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8 Solvent extracted Boiling Chips, approximately 10/40 mesh (Silicon Carbide or equivalent)

4.9 Heated Water Bath, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.10 Top-loading Analytical Balance, capable of accurately weighing 0.001 grams.

4.11 2ml and 12ml Vials and Caps

4.12 Glass Funnel

4.13 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C.

4.14 Spatula, Stainless steel or Teflon

4.15 Syringe, 1ml

4.16 Large disposable glass pipets

5.0 REAGENTS

5.1 Sodium Sulfate; Anhydrous and reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Methylene chloride: acetone (1:1, V:V)

5.3 Methylene chloride (B&J GC2 grade, or equivalent)

6.0 PROCEDURE

6.1 Sample Handling

6.1.1 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

6.2 Determination of Percent Moisture

In most cases sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed simultaneously with the portion used for analytical determination.

Immediately after weighing the sample for extraction, weigh 5-10g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\frac{\text{g of Sample - g of dry Sample}}{\text{g of Sample}} \times 100 = \%\ \text{moisture}$$

6.3 Determination of pH

Transfer 50g of sample to a 100ml beaker. Add 50ml of water and stir for 1 hour. Determine the pH of sample with pH paper. Discard this portion of sample. A lesser amount of sample may be used if an appropriate amount is unavailable. Adjust the amount of water proportionally.

6.4 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30g of sample into a 400ml beaker. Record the weight to be nearest 0.1g. Add 1-ml of surrogate standards to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, add 0.5ml of the matrix spiking standard. The amount added for the surrogate compounds should result in a final concentration of 3300μg/Kg of each base/neutral analyte and 6600 μg/Kg of each acid

analyte in the extract to be analyzed. All surrogate and spiking solutions must be added to the samples before any processing occurs. To ensure an efficient extraction, all samples must be dried by mixing with 60g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Immediately add 100ml of 1:1 methylene-chloride: Acetone.

6.5 Sonicator tuning procedure

The sonicator is to be tuned weekly, at a minimum, and whenever any of the components are changed or , at the discretion of the analyst. The following procedure is to be followed for tuning.

6.5.1 Turn the power output knob to zero.

6.5.2 Turn the sonicator mode switch to continuous mode.

6.5.3 Turn the sonicator power switch on.

6.5.4 Press and hold the sonicator tune switch on with one hand; use the other hand to turn the power output knob or the sonicator tuning knob as follows.

6.5.5 Slowly turn the power output knob toward 10 while watching the output power meter reading. When the meter reading reaches 50%, turn the tuning knob until the minimum meter deflection is observed. The minimum deflection can be determined by observing when the needle starts to go back up when turning the tuning knob in either direction. The tuning knob for the Tekmar sonicator is on the front panel of the generator. The tuning knob for the heat systems sonicator is on the back panel of the generator.

6.5.6 Proceed again with step (6.5.5) until reaching output level 10 (output level 5 for microtips), and adjust the tuning knob to achieve the minimum deflection. At this point, the sonicator is considered tuned and operational provided that minimum deflection is achieved and the sonicator power output meter reads less than 25% at the minimum.

6.5.7 If the tuning criteria can't be met, check for loose cable connections or loose horn to converter connection and tighten as necessary. Retune. If the tuning criteria still can't be met, try replacing horn and converter with backup unit. Retune. If the tuning criteria still can't be met, notify the supervisor immediately so that repairs and/or a loaner can be obtained. Place a sign on the sonicator stating "Out of order, do not use".

6.5.8 Release the sonicator tune switch, switch the sonicator mode switch to pulsed mode and switch the sonicator off.

6.5.9 Record the tuning in the appropriate sonicator maintenance logs and weekly checklist.

6.6 Place the bottom surface of the tip of the #207 3/4" disrupter horn approximately 1/2" below the surface of the solvent, above the sediment layer.

6.7 Sonicate for 3 minutes with the output control knob set at 10, the mode switch set on pulse, and the percent-duty cycle knob set at 50%. DO NOT use a microtip probe.

6.8 Decant and filter extracts through Whatman No. 41 filter paper, or centrifuge and decant extraction solvent.

6.9 Repeat the extraction two more times using two additional 100ml portions of solvent. Decant and filter the extraction solvent after each sonication. On the final sonication, pour the entire sample into the conical funnel and rinse with extraction solvent.

6.10 Assemble a Kuderna-Danish (K-D) Concentrator by attaching a 10ml concentrator tube to a 500ml evaporative flask.

6.11 Dry the extract by passing it through a drying column containing approximately 10cm of anhydrous Sodium Sulfate. Collect the dried extract in a K-D Concentrator. Wash the extractor flask and Sodium Sulfate Column with 100-125ml of extraction solvent to complete the quantitative transfer.

6.12 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder Column. Pre-wet the Snyder Column by adding approximately 1ml methylene chloride to the top. Place the K-D apparatus in a hot water bath (80-85°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 minutes. At the proper rate of distillation the balls of the column will actively chatter however, the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1ml, remove the K-D apparatus and allow to drain and cool for at least 10 minutes.

6.13 Remove the Snyder Column and rinse the flask and lower joints into the concentrator tube with 1-2ml of methylene chloride. The extract may be further concentrated and adjusted to 1.0ml using methylene chloride.

6.14 Transfer the concentrated extract to a clean 2ml vial. Seal the vial with a Teflon-lined lid and mark the level on the vial. Label with the sample number and fraction and store in the dark at 4°C.

7.0. QUALITY CONTROL

7.1 Method Blank

7.1.1 A method blank for a soil sample consists of purified solid matrix (NA_2SO_4) which is carried through the entire extraction. The method blank weight must be approximately equal to the sample weights being processed.

7.1.2 Method Blank

A method blank extraction must be performed once:

- daily, or
- each 20 samples in a case, including matrix spike or
- whenever samples are extracted by the same procedure.

7.2 Matrix Spike/Matrix Spike Duplicate

7.2.1 Matrix Spike/Matrix Spike Duplicate frequency of extraction

A matrix spike and matrix spike duplicate must be performed once:

- each 20 field samples in a case, or
- each 30 calendar day period during which field samples in a case are received.

7.3 Surrogate Spike

Each sample, matrix spike, matrix spike duplicate and blank are spiked with surrogate compounds prior to extraction.

8.0 SAFETY

8.1 Safety glasses, lab coat, and gloves should be worn at all times during extraction.

8.2 Label reagents, spikes, surrogate solutions with solution type, concentration, date, chemist's initials and shelf life.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition.

Effective Date: October 1997
Version No: 5
Initiated By:
Approved By:

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SOP No: 13.19

Title: SOP for Method SW8270B
GC/MS Analysis of Semivolatile Organics

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure describes the methodology used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water. Table 1 indicates compounds typically determined by this method and lists the method detection limit for each in water or soil. Table 2 lists additional semi-volatiles including the Appendix IX compounds which can be determined using 8270B methodologies. Table 4 lists semivolatile PAH compounds and their low concentration reporting limits.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation methods.

3.0 INTERFERENCE

3.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples and initiate corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between each use.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph/Mass Spectrometer

Hewlett Packard 5970 MSD System equipped with an autosampler is utilized. The HP 5970 MSD is a complete instrument composed of two modules: a Controller and a main frame GCMS.

4.1.1 Data System

Each GC/MS system is attached to a dedicated 486 or pentium based computer equipped with Enviroquant software for automated acquisition and processing. The software generates total and extracted ion profiles of each compound and is capable of performing library searches on spectra using a full EPA/NIH Mass Spectral Data Library. Each system is attached to an internal laboratory computer network for additional data processing, storage and archiving.

4.2 Columns

A 30 meter 0.25mm ID, 1.0μ meter RTX-5 (5% phenyl methyl silicon) Restek column is used.

4.3 Syringe: 10μl

5.0 QC CONDITION

5.1 The following GC parameters are established:

- Injection port temp: 250°C
- Interface temp: 300°C
- Initial temp: 40°C
- Initial time: 4 min.
- Rate at 15°C per min.
- Final temp: 310°C
- Final time: 20 min.
- Equilibrium time: .5 min.
- Septum purge flow on at .5ml/min.
- Septum purge flow on at .5 min.
- Flow rate at about 0.7ml/min.
- Splitless flow about 50ml/min.
- Injection type: "Splitless"
- Autosampler injection mode: "Fast"

- Sample Column 1μl

5.2 GC/MS Condition

5.2.1 Scanning from 35 to 500 amu in less than 1 second, using 70 volt (nominal) electron energy in the Electron Impact Ionization mode.

5.2.2 GCMS Tuning - to determine the system performance, 50ng of decafluorotriphenylphosphine (DFTPP) is injected and the mass spectrum is evaluated. The following criteria must be met before any further analysis is performed.

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

MASS	ION ABUNDANCE CRITERIA
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

The GC/MS tuning standard should also be used to assess GC column performance and injection inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and Pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

5.3 Calibration

5.3.1 Upon satisfactory completion of DFTPP analysis, at least 6 levels of calibration standards at 10, 20, 50, 80, 120 and 160ng are analyzed. Calibration standards must contain the following internal and surrogate standards.

5.3.1.1 Internal Standards - the following Internal Standards at 40μg/ml must be present in the Calibration Standard.

- 1,4-dichlorobenzene-d_4
- Naphthalene-d_8
- Acenaphthane-d_{10}
- Phenanthrene-d_{10}
- Chrysene-d_{12}
- Perylene-d_{12}

5.3.1.2 The following Surrogate Standards at 20, 50, 80, 120 and 160ng are analyzed.

- Phenol-d_6
- 2-Fluorophenol
- 2,4,6-Tribromophenol
- nitrobenzene-d_5
- 2-fluorobiphenyl
- p-terphenyl-d_{14}

5.4 After analyzing the initial Calibration Standard average RF (Response Factor) should be calculated for each compound. The percent relative standard deviation (%RSD) should be less than 15% for each compound. However, Calibration Check Compounds (CCC) must have a % RSD less than 30%. If the % RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The relative retention times of each compound in each calibration run should agree within 0.06 relative time units. System performance check compounds must have a minimum RF of 0.05. The CCC and SPCC compounds are listed as follows:

SPCC	CCC
N-nitroso-di-n-Propylamine	Acenaphthene
Hexachlorocyclopentadiene	1,4-Dichlorobenzene
2,4-Dinitrophenol	N-Nitrosodiphenylamine
4-Nitrophenol	Di-n-octylphthalate
	Fluoranthane
	Benzo(a)pyrene
	4-Chloro-3-methylphenol
	2,4-Dichlorophenol
	2-Nitrophenol
	Phenol
	Pentachlorophenol
	2,4,6-Trichlorophenol

5.5 Internal Standard responses and retention times in the calibration check, blanks and samples must be evaluated. Retention time variation for any internal standard must be less than 30 seconds from the 12 hour calibration check. Variation of the areas for internal standards must not vary by more than a factor of two or -50% to +100%.

5.6 A continuing calibration (daily) at 50ng concentration containing all semivolatile analytes, including all required surrogates must be analyzed every 12 hours. The following criteria must be met before sample analysis starts:

- System Performance Check Compounds (SPCCs): A system performance check must be made every 12 hour shift. For each SPCC compound in the daily calibration a minimum response factor of 0.05 must be obtained. All other non SPCC must have RF of 0.01.

- Percent drift for all CCC should be less than 20% Non CCC should have less than 35% except up to 4 compounds could have 50%.

$$\% \text{ drift} = \frac{C_1 - C_c}{C_1} \times 100$$

where:

C_1 = CCC standard concentration
C_c = Measured concentration

If the % difference criteria for each CCC is not met (>20% drift), corrective action must be taken, and if after corrective action criteria were not met a new five-point calibration must be generated.

- Retention time for Internal Standards ± 30 seconds.

5.7 Continuing Calibration Verification

For all U.S. Army Corps programs, samples must be bracketed by acceptable calibration verifications. If a calibration verification fails to meet the same criteria as the continuing calibration, all samples analyzed before the calibration verification must be reanalyzed.

6.0 SAMPLE ANALYSIS

6.1 Initially 0.5ml of Acid and Base Neutral extracts are combined and 10μl of 4000μg/ml internal standard is added to each mix. One μl of this extract is injected into the GCMS using the same parameters as the calibration standard. All samples must be injected within a 12 hour period starting with analysis of DFTPP.

6.2 Qualitative Analysis

6.2.1 Two criteria must be satisfied to verify compound identification.

6.2.1.1 Elution of sample component at the same GC relative retention time (RRT) $\pm$ 0.06 units.

6.2.1.2 Correspondence of the sample component and the standard component mass spectrum.

All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum. The relative intensity of these ions must agree $\pm$ 20% between the standard and sample spectra.

6.2.2 Library Search

6.2.2.1 When required, a search may be performed for the purpose of tentative identification. Only after visual comparison of sample spectra with the nearest library searches will the analyst assign a tentative identification. The analyst should use an approach similar to the 5 step identification listed for method SW8270 (pp-18), Sept. 1986.

6.3 Quantitative Analysis

6.3.1 When a compound is identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation is based on the internal standard technique. The internal

standard nearest the retention time of that given analyte, shall be used.

7.0 CALCULATIONS

The following information should be used throughout the quantitation process.

7.1 Response Factor

$$RF = \frac{(A_x C_{is})}{(A_{is} C_x}$$

where:

A_x = Area of the characteristic ion for the compound being measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_x = Concentration of the compound being measured (μg/ml)

C_{is} = Concentration of the specific internal standard (μg/ml)

7.2 % RSD and % Difference

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Average RF}} \times 100$$

$$\% \text{ Difference} = \frac{\text{AvgRF}_i\text{(Init. Calib.)} - \text{RF}_c\text{(Cont. Calib.)}}{\text{Avg RF}_1} \times 100$$

7.3 Sample Calculation

$$\text{Water Concentration } \mu\text{g/l} = \frac{(A_x)\ (I_s)\ (V_t)\ (\text{Dil})}{(A_{is})\ (\text{Avg RF})\ (V_o)\ (V_i}$$

$$\text{Soil Concentration } \mu\text{g/kg} = \frac{(A_x)\ (I_s)\ (V_t)\ (\text{Dil})}{(A_{is})\ (\text{Avg RF})\ (V_i)\ (W_s)\ (D)}$$

where:

I_s = Amount of internal standard injected (ng)

V_t = Volume of total extract

V_o = Initial volume

V_i = Volume of extract injected (ml)

W_s = Weight of sample extracted (G)

D = Percent solids

Dil = Dilution applied

Alternatively, the regression line fitted to the initial calibration may be used for determination of the extract concentration.

8.0 QUALITY CONTROL

8.1 Blank analysis - A method blank is analyzed with each analytical batch to examine the interferences and contamination from extraction and analysis. Concentration of the target compounds in the blank must be less than or equal to the PQL. If the above criteria are not met, reinjection or reextraction of the blank and the samples is required.

8.2 Surrogate analysis - Surrogate standard determinations are performed on all samples and blanks. The following range of recoveries is suggested.

SURROGATE COMPOUND	WATER	LOW/MEDIUM SOIL/SEDIMENT
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorphenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

8.2.1 If any surrogate recoveries in the method blank in either the BN or acid fraction are outside the surrogate spike recovery limits, corrective action should be taken. First, re-inject the blank - if no improvement is observed, reextraction should be considered. The blank and all samples associated with the blank should be reextracted.

8.2.2 If any surrogate recoveries in the sample in either the BN or acid fraction are outside the surrogate spike recovery limits, corrective action should be taken. First, re-inject the sample. If the surrogate recoveries fail to meet the criteria after re-analysis, re-extract the sample. If the surrogate compound recoveries meet acceptance criteria in the re-extraction/reanalysis, submit data from the re-extraction/reanalysis only if it met holding times. If not, submit both datas.

8.2.3 If the surrogate compound recoveries fail to meet the acceptance criteria in the re-extracion/reanalysis sample, then submit data from both analyses.

8.3 Matrix Spikes - A matrix spike and matrix spike duplicate are analyzed with each case of 20 samples. Recoveries of MS/MSD should be calculated and listed. The following range of recoveries are suggested:

MATRIX SPIKE RECOVERY LIMITS

FRACTION	MATRIX SPIKE COMPOUND	WATER	SOIL/ SEDIMENT
BN	1,2,4-Trichlorobenzene	39-98	38-107
BN	Acenaphthene	46-118	31-137
BN	2,4-Dinitrotoluene	24-96	28-89
BN	Pyrene	26-127	35-142
BN	N-Nitroso-Di-n-Prophylamine	41-116	41-126
BN	1,4-Dichlorobenzene	36-97	28-104
Acid	Pentachlorophenol	9-103	17-104
Acid	Phenol	12-89	26-90
Acid	2-Chlorophenol	27-132	25-102
Acid	4-Chloro-3-Methylphenol	23-97	26-103
Acid	4-Nitrophenol	10-80	11-114

8.4 Lab Control Sample

8.4.1 A laboratory control sample is extracted and analyzed routinely with each extracted batch. Calculated concentrations are compared with the amount added and results are used to demonstrate that the laboratory process for sample preparation and analysis is in control. Generation of in house statistical control limits must be based on 20 data points. Data set used to generate control limits must have been generated using the same analytical procedure and data sets must not be selectively included or excluded. Control limits must be recalculated on a periodic basis (minimum annual). If recovery falls outside in house control limits, and if the analyte is present in any of the samples, the laboratory must take corrective action. If after corrective action and reanalyses, LCS analyte recovery is still outside QC acceptance limits, the associated samples in the preparation batch must be re-extracted if sufficient sample exists and holding time have not elapsed. Soil and water laboratory established limits are listed in Table 3. For U.S. Army Corps programs, LCS must contain all target compound in the method. In-house established control limits should not exceed ± 20%.

8.5 Internal Standard Recoveries and Retention times - when internal standard recoveries (-50 to +100%) or retention time requirements, (0.06 RRT) are not satisfied, sample is reinjected and reanalyses results are submitted if they are acceptable. If both analyses are out of criteria, then both results are submitted.

8.6 All extracts must be analyzed within 40 days after completion of extraction.

8.7 Dilutions are performed on samples when the concentration of target analytes exceed the calibration range. Additional IS must be added to the diluted extract to maintain the required IS concentration. Dilution of extracts should result in analysis with the highest concentration target analyte in the upper half of the calibration range.

8.8 If the analytes of interest are not able to be determined due to interferences, GPC cleanup is performed. However, the experience of the analyst may prove invaluable in determining which cleanup methods or if additional are needed.

9.0 LOW CONCENTRATION PAHs

9.1 When requested low concentration PAHs can be analyzed using a modified 8270B method. Sample matrix should be reasonably free of interferences to allow low level detection of PAHs. Extraction procedures for water and soil matrices are the same as methods 3510, 3520, 3540 and 3550 except for surrogate and matrix spike standards levels added to the sample and quality control samples before extraction. Surrogate standard is added at 1.0ml of 0.5ug/ml of all base/neutral compounds. Matrix spike and lab control spike consist of 1.0ml of all PAH compounds at 0.5ug/ml concentrations. Both soil and water matrices receive the same amount of surrogate and matrix spike standards. Aqueous matrices are extracted under base/neutral condition only. Sample and quality control extracts are spiked at 5.0ug/ml internal standard before injection.

9.2 Six level calibration standards are analyzed at concentrations 0.1, 0.5, 1, 2.5, 5 and 10ug/ml. Percent Relative Standard Deviation (RSD) for all compounds must be less than 30 before any sample analysis begins. Continuing calibration must have percent difference less than 20 for all target compounds. All other criteria pertaining to low level semivolatile analysis apply to low concentration procedures. Table 4 lists the PAH compounds list that may be determined using low concentration procedure.

10.0 REFERENCES

10.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW846, 3rd Edition. Methods 525.1 and 525.2 for drinking water.

TABLE 1

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[b] ug/Kg
Phenol	108-95-2	10	330
bis (2-Chloroethyl) ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
bis (2-Chloroisopropyl) ether	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-dipropylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
bis (2-Chloroethoxy) methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	10	330
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	50	1600
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600

TABLE 1 (Cont)

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

Semivolatiles	CAS Number	Quantitation Limits** Water ug/L	Low Soil/Sediment[b] ug/Kg
Dimethylphthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
2,6-Dinitrotoluene	606-20-2	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl-phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-nitrosodiphenylamine	86-30-6	10	330
4-Bromophenyl-phenylether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Di-n-butylphthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Pyrene	129-00-0	10	330
Butylbenzylphthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	20	660
Benzo(a)anthracene	56-55-3	10	330
Chrysene	218-01-9	10	330
bis (2-Ethylhexyl) phthalate	117-81-7	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno (1,2,3-cd) pyrene	193-39-5	10	330
Dibenz (a,h) anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

TABLE 1 (Cont)

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

[b] Medium soil/sediment contract required quantitation limits (CRQL) for semivolatile TCL compounds are 60 times the individual low soil/sediment CRQL.

* Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment. Calculated on dry weight basis as required by the contract, will be higher.

TABLE 2

Appendix IX Compounds

1. Acetophenone
2. 2-Acetylaminofluorene
3. 4-Aminobiphenyl
4. Aniline
5. Chlorobenzilate
6. 4-Chlorophenyl phenyl ether
7. m-Cresol
8. Dimethoate
9. 4-Dimethylaminoazobenzene
10. 7,12-Dimethylbenz(a)anthracene
11. 3,3'-Dimethylbenzidine
12. a,a-Dimethylphenethylamine
13. 1,3-Dinitrobenzene
14. Diphenylamine
15. 1,4-Dioxane
16. Famphur
17. Hexachloropropene
18. Isodrin
19. Isosafrole(cis)
20. Kepone
21. Methapyrilene hydrochloride
22. 3-Methylcholanthrene
23. Methyl methane sulfonate
24. 1,4-Naphthoquinone
25. 1-Naphthylamine
26. 2-Naphthylamine
27. 4-Nitroquinoline-1-oxide
28. N-Nitrosodi-n-butylamine
29. N-Nitrosodiethylamine
30. N-Nitrosodimethylamine
31. N-nitrosomethylethylamine
32. N-Nitrosomorpholine
33. N-Nitrosopiperidine
34. N-Nitrosopyrrolidine
35. 5-Nitro-o-toluidine
36. Pentachlorobenzene
37. Pentachloronitrobenzene
38. Phenacetin
39. 1,4-Phenylenediamine
40. Phorate
41. 2-Picoline
42. Pronamide
43. Pyridine
44. Safrole
45. 1,2,4,5-Tetrachlorobenzene
46. 2,3,4,6-Tetrachlorophenol
47. Thionazin
48. o-Toluidine
49. o,o,o-Triethylphosphorothioate
50. sym-Trinitrobenzene
51. Methyl methacrylate
52. Ethyl methacrylate
53. Ethyl methane sulfonate
54. o-Anisidine
55. p-Cresidine
56. 5-Chloro-2-methylaniline
57. Phthalic anlydride
58. 2,4-Diaminotoluene
59. 1-Chloronaphthalene
60. Diallate
61. Disulfoton
62. Methylparathion
63. Ethylparathion
64. 4-Aminoazobenzene
65. 4,4-Oxydianiline
66. 3,3-Dimethoxybenzidine
67. Tetraethyldithiopyrophosphate
68. 2,6-Dichlorophenol
69. Aramite
70. Hexachlorophene

TABLE 3

SOIL AND WATER LABORATORY CONTROL SPIKE RECOVERY REPORT

Compound	Soil Internal QC Limits	Water Laboratory QC Limits
Phenol	45 - 91	18 - 109
2-Chlorophenol	49 - 91	21 - 110
1,4-Dichlorobenzene	43 - 95	14 - 122
N-Nitroso-Di-n-Propylamine	48 - 108	15 - 132
1,2,4-Trichlorobenzene	50 - 94	19 - 113
4-Chloro-3-methylphenol	53 - 90	19 - 108
Acenaphthene	54 - 90	18 - 118
2,4-Dinitrotoluene	57 - 102	17 - 132
4-Nitrophenol	D - 207	19 - 207
Pentachlorophenol	17 - 205	D - 213
Pyrene	32 - 140	23 - 136

Table 4

PAH Compounds

PAH	CAS Number	Water ug/L	Soil ug/kg
Naphthalene	91-20-3	0.07	2.30
Acenaphthylene	208-96-8	0.08	2.70
Acenaphthene	83-32-9	0.07	2.30
Fluorene	86-73-7	0.10	3.30
Phenanthrene	85-01-8	0.09	3.00
Anthracene	120-12-7	0.11	3.70
Fluoranthene	206-44-0	0.08	2.70
Pyrene	129-00-0	0.07	2.30
Benzo(a)anthracene	56-55-3	0.07	2.30
Chrysene	218-01-9	0.05	1.70
Benzo(b)fluoranthene	205-99-2	0.15	5.00
Benzo(k)fluoranthene	207-08-9	0.14	4.70
Benzo(a)pyrene	50-32-8	0.08	2.70
Indeno(1,2,3-cd)pyrene	193-39-5	0.12	4.00
Dibenz(a,h)anthracene	53-70-3	0.16	5.30
Benzo(g,h,i)perylene	191-24-2	0.15	5.00

Effective Date: May 1997
Version Number: 4
Initiated By : D. Hartman
Approved By :

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SOP No: 12.15

Title: Method 3520B, Continuous Liquid-Liquid Extraction for Pesticide/PCBs

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics such as organochlorine pesticides and PCBs from water, wastewater, groundwater and TCLP extracts. Extracts produced by this method may be analyzed by Methods 8080.

1.2 This method also describes concentration techniques suitable for preparing the extract for the appropriate method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated and exchanged into a solvent compatible with the step being employed.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifact and/or interferences to sample analysis. All materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.0 APPARATUS AND MATERIALS

- Continuous Liquid-Liquid Extractor (Equipped with joints and snapring clips)
- Drying Column (A glass funnel with pyrex glass wool at the neck of the funnel, half filled with dry Na_2SO_4)
- Kuderna-Danish (K-D) Apparatus

- Concentrator tube: 10ml, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

- Evaporator flask: 500ml (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

- Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent)

- Solvent extracted Boiling Chips, approximately 10/40 mesh (silicon carbide or equivalent)

- Heated water Bath, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

- Glass vials, 2ml capacity, with Teflon-lined crimp cap

- pH Indicator Paper covering pH 2 to pH 12

- Rheostat controlled Heating Mantle

- 1.0ml Gas-Tight Luer-Lok Syringe

- One (1) Liter Class A Graduated Cylinder

- Pyrex Glass Wool

- 1g florisil cartridge

- Large disposable glass pipets

5.0 REAGENTS

- Reagent Water (water in which an interferant is not observed at the method detection limit of the compounds of interest).

- Sodium Hydroxide Solution, 10N

  (ACS) Dissolve 40g NaOH in reagent water and dilute to 100ml.

- Sodium Sulfate

  (ACS) Granular, Anhydrous (purified by heating at 400°C for 4 hours in a shallow tray)

- Sulfuric Acid Solution (1:1)
  Slowly add 50ml of H_2SO_4 (sp. gr. 1.84) to 50ml of reagent water.

- Methylene Chloride (B & J GC2 grade or equivalent)

- Hexane (Pesticide grade)
- Acetone (pesticide grade)

6.0 PROCEDURE

6.1 Place a few boiling stones in a 500ml collecting flask and assemble continuous extractor.

6.2 Add 500ml of methylene chloride to the extractor.

6.3 Using a Class A graduated cylinder, measure out 1 liter of sample and transfer it to the continuous extraction. Rinse the sample bottle with 20-30ml methylene chloride and add to the extractor. Add 1.0ml of surrogate spiking solution. Check the pH of the sample using wide range pH paper and adjust the pH to 7.0 using 1:1 H_2SO_4 or 10N NaOH. Use 1.0 liter of deionized water to another extraction for the method blank preparation and analysis.

6.4 For the sample in each analytical batch selected for spiking, measure one additional 1.0 liter aliquots. Add 1.0ml of the matrix spiking standard.

6.5 Add sufficient methylene chloride to the extractor to ensure proper operation and extraction for 18 hours.

6.6 Allow to cool, then detach and label the boiling flask. The extract is then ready to be dried and concentrated.

6.7 Assemble a Kuderna-Danish (K-D) Concentrator by attaching a 10ml concentrator tube to a 500ml evaporation flask.

6.8 Dry the extract by passing it through a drying column containing about 10cm anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30ml of methylene chloride and add to the column to complete the quantitative transfer.

6.9 Add one or two clean boiling chips to the flask and attach a three ball Snyder Column. Pre-wet the Snyder Column by adding approximately 1ml of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (85-95°C) until the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration. When the apparent volume of liquid reaches about 10ml, remove the K-D apparatus from the water bath and perform a solvent exchange by adding 50ml of hexane through the top of Snyder column.

Continue concentration in the water bath until the volume of extract reaches approximately 5ml.

6.10 Take the K-D off the water bath and place on a rack and allow to cool. Disconnect the concentrator tube and adjust the volume to 10.0ml with hexane.

6.11 If florisil cleanup is required, carefully homogenize the 10ml extract and take 1.0ml for cleanup.

6.11.1 Florisil cartridge cleanup

- Attach the vacuum manifold to a vacuum pump with a trap installed betwen the manifold and vacuum source. Place 1 florisil cartridge into vacuum manifold for each sample extract.

- Wash each cartridge with hexane/acetone (90:10) v:v. Pass at least 5ml of hexane/acetone solution through the cartridge while pulling a vacuum, adjust the vacuum so that the flowrate is approximately equal through each cartridge. DO NOT LET THE CARTRIDGES GO DRY AFTER THEY HAVE BEEN WASHED.

- After the cartridges have been washed, release the vacuum, and place a rack containing labeled 20ml vials inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is in the appropriate cartridge as the manifold top is replaced.

- Once the flasks are in place, restore vacuum to the manifold and place 1ml of the sample extract into the cartridge.

- Elute the cartridge with 8ml of hexane/acetone (90:10), then rinse the cartridge with two 1ml portions of hexane.

- Shut off the vacuum, take off the manifold top and remove the 20ml vials and place in the nitrogen blowdown manifold and blow the extract down to 1.0ml.

- Pipet the extract into labeled 1ml vials using a disposable pasteur pipet, taking care to rinse the sides of the 20ml vial with extract to ensure a quantitative transfer of extract. The 1ml vial is then transferred for GC analysis.

7.0 QUALITY CONTROL

7.1 Method Blank

7.1.1 The method blank is a volume of deionized, laboratory water carried through the entire extraction. The method blank volume must be equal to 1.0 liter or the sample volumes being extracted.

7.1.2 Frequency of Method Blanks

Method blank extraction must be performed per each batch of 20 samples or less (counting MS/MSD as samples).

7.2 Matrix Spike/Matrix Spike Duplicate

7.2.1 MS/MSD Frequency of Extraction

Matrix spike and matrix spike duplicate extraction must be performed per each batch of 20 samples or less. If the batch of samples are received periodically, then MS/MSD are extracted every 14 days.

7.3 Matrix Spiking Solutions

7.3.1 Method 8080 matrix spikes

Matrix spike is prepared in methanol and 1.0ml is added to the designated samples. The mixture contains the following compounds at the given concentrations:

g-BHC	0.2ug/ml
Heptachlor	0.2ug/ml
Aldrin	0.2ug/ml
Dieldrin	0.5ug/ml
Endrin	0.5ug/ml
4,4'-DDT	0.5ug/ml

LCS spiking levels are the same as those used to spike samples.

7.4 Surrogate Spike (SS)

Each sample, matrix spike, and blank are spiked with surrogate compounds prior to extraction. The concentration in the following table exhibits the concentration in the spiking solution.

Compounds	Concentration Added
Decachlorobiphenyl	1.0ml of 0.2ug/ml
TCMX	1.0ml of 0.2ug/ml

7.5 Lab Control Spike (LCS)

Blank spikes are extracted at the same frequency as matrix spikes using deionized water as the matrix.

7.6 PCBs Spike

When PCBs are only needed, follow the same extraction procedure as Pest/PCBs. For matrix spike and LCS QC runs use 1.0ml of AR1260 and AR1016 spiking solution of the concentration of 1.0 and 0.5ug/ml, respectively.

8.0 SAFETY

8.1 Safety glasses, lab coat, and gloves should be worn at all times during extraction.

8.2 Label reagents, spikes, surrogate solutions by identifying the solution, concentration, date, chemist's initials, and shelf life.

8.3 Waste Disposal

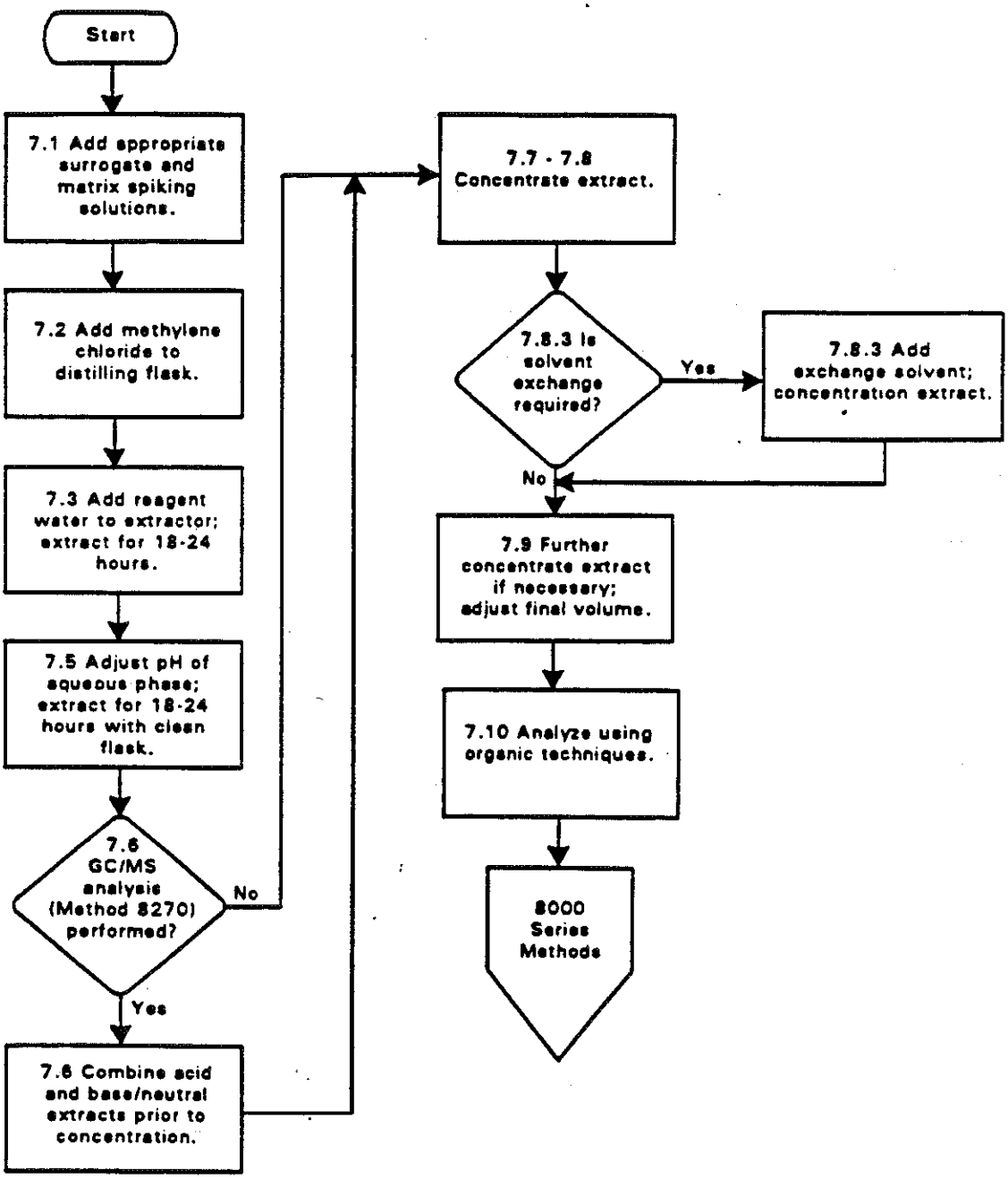
8.3.1 Chlorinated solvent waste should be put into a polyethylene safety can designated for methylene chloride. This will be disposed of by the hazardous waste coordinator.

8.3.2 Water waste can be poured down the drain after neutralizing it using H_2SO_4 or NaOH depending upon the pH of the waste.

9.0 REFERENCES

- Test Methods For Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition.

METHOD 3520b
CONTINUOUS LIQUID-LIQUID EXTRACTION



Effective Date: June 1997
Version Number: 5
Initiated By:
Approved By:

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SOP No: 12.16

Title: Soil Extraction for Pesticides/PCBs Compounds by Method 3550A (Sonication Extraction)

1.0 APPLICATION AND SCOPE

1.1 This method is a procedure for extracting organochlorine pesticide and PCB compounds from solids such as soils, sludges, and wastes. Extracts are suitable for analysis of method 8080.

1.2 Method 3550A describes both high level and low level extraction procedures. This SOP is based on the low level version of method 3550.

2.0 SUMMARY OF METHOD

2.1 A 30g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. Mixture is extracted with solvent three times using sonication. The extract is separated from the sample by filtration. The extract is ready for cleanup following concentration.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. These materials must be demonstrated to be free from interferences under the conditions of the analysis of analyzing method blanks.

4.0 APPARATUS AND MATERIALS

4.1 Mortar Model 155 Grinder, Fisher Scientific Company, or an equivalent brand and model.

4.2 Ultrasonic cell disrupter, Heat Systems - Ultra Sonic, Inc., Model W-385 (475 watt) SOnicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapped Microtip Probe (where applicable).

4.3 Apparatus for Determining Percent Moisture

- Oven: drying
- Desiccator
- Crucibles: Porcelain

4.4 Pasteur Glass Pipets, Disposable, 1ml

4.5 Beakers, 400ml

4.6 Filtration Apparatus

- Conical funnel
- Filter paper: Whatman No. 41 or equivalent

4.7 Kuderna-Danish (K-D) Apparatus

4.7.1 Concentrator tube: 10ml graduated (Kontes K-570050-1025 or equivalent).

4.7.2 Evaporator Flask: 500ml (Kontes K-570001-0500 or equivalent).

4.7.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8 Solvent extracted Boiling Chips, approximately 10/40 mesh (Silicon Carbide or equivalent).

4.9 Heated Water Bath, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.10 Top-loading Analytical Balance, capable of accurately weighing 0.01 grams.

4.11 12ml Vials and Caps

4.12 Glass Funnel

4.13 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C.

4.14 Spatula, Stainless steel or Teflon

4.15 Syringe, 1ml

4.16 Large disposable glass pipets

5.0 REAGENTS

5.1 Sodium Sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Methylene chloride: acetone (1:1, V:V)

5.3 Methylene chloride (B&J GC2 grade or equivalent)

5.4 Hexane (pesticide quality or equivalent).

5.5 Activity III Neutral Alumina (Al_2O_3 - H_2O_x)

5.5.1 Prepared by adding 8% (v/w) deionized water to Super I Woelm neutral alumina in a 150ml E-flask. Shake in a wrist shaker for at least two hours.

6.0 PROCEDURE

6.1 Sample Handling and Storage

6.1.1 Samples must be refrigerated at 4°C upon arrival. Holding time for soil samples is 14 days from the collection date. Samples must be brought to room temp before extraction begins. Spare containers (if provided) should be used for matrix spike and re-extractions (if needed).

6.1.2 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

6.2 Determination of Percent Moisture

In most cases sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed simultaneously with the portion used for the analytical determination.

Immediately after weighing the sample for extraction, weigh 5-10g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\frac{\text{g of Sample - g of dry Sample}}{\text{g of sample}} \times 100 = \text{\% moisture}$$

6.3 Determination of pH

Transfer 50g of sample to a 100ml beaker. Add 50ml of water and stir for 1 hour. Determine the pH of sample with pH paper. Discard this portion of sample. A lesser amount of sample may be used if 50g is not available. In this case, adjust the amount of water proportionally also.

6.4 The following step should be performed to avoid loss of the more volatile extractables. Weigh approximately 30g of sample into a 200ml beaker. Record the weight to be nearest 0.1g. Add 1ml of surrogate standards to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, add 1.0ml of the matrix spiking standard. The surrogates and spiking solutions must be added before any processing of the sample and QC begins. Nonporous or wet samples (gummy or clay type) lacking a free-flowing sandy texture must be mixed with 60g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Then immediately add 100ml of 1:1 methylene-chloride: acetone.

6.5 Place the bottom surface of the tip of the #207 3/4" disrupter horn about 1/2" below the surface of the solvent, but above the sediment layer.

6.6 Sonicate for 3 minutes with the output control knob set at 10 and the mode switch set on pulse and the percent-duty cycle knob set at 8-10. DO <u>NOT</u> use a microtip probe.

6.7 Decant and filter extracts through Whatman No. 41 filter paper using filtration or centrifuge and decant extraction solvent.

6.8 Repeat the extraction two more times with two additional 100ml portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the conical funnel and rinse with extraction solvent.

6.9 Assemble a Kuderna-Danish (K-D) Concentrator by attaching a 10ml concentrator tube to a 500ml evaporative flask.

6.10 Dry the extract by passing it through a drying funnel filled with anhydrous Sodium Sulfate. Collect the dried extract in a K-D Concentrator. Wash the extractor flask and Sodium Sulfate Column with 100-125ml of extraction solvent to complete the quantitative transfer.

6.11 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder Column. Pre-wet the Snyder Column by adding about 1ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-85°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical

position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10ml, remove the K-D apparatus and add 15ml of Hexane through the top of Snyder column and continue concentration until liquid volume reaches about 7ml.

6.12 Remove the Snyder Column and rinse the flask and its lower joints into the concentrator tube with 1-2ml of Hexane. The extract may be further concentrated and adjusted to 1.0ml with the solvent. Add 0.5ml of acetone. Plug a large disposable glass pipet with a small piece of pyrex glass wool. Add about 1.5 inches of deactivated alumina to the column. Tap the column to settle the alumina.

6.13 Transfer the extract to the micro alumina column and collect the eluent in a 12ml vial. Rinse the alumina continuously with about 10ml of Hexane and collect all eluent until 10ml of extract have been collected. Do not allow the alumina to go dry.

7.0 QUALITY CONTROL

7.1 Method Blank

7.1.1 A method blank is purified solid matrix (NA_2SO_4) for soil samples, carried through the entire extraction. The method blank weight must be approximately equal to the sample weights being processed.

Method blank extraction must be performed per each batch of 20 samples or less (counting MS/MSD as samples).

7.2 Matrix Spike/Matrix Spike Duplicate

7.2.1 Matrix Spike/Matrix Spike Duplicate frequency of extraction

Matrix spike and matrix spike duplicate extraction must be performed per each batch of 20 samples or less. If the batch of samples are received periodically, then MS/MSD are extracted every 14 days.

7.3 Matrix Spiking Solution is prepared in methanol and 1.0ml is added to the designated samples. The mixture contains the following compounds at the given concentrations:

Analyte	Conc.	Analyte	Conc.
g-BHC	0.2ppm (µg/ml)	4,4'-DDT	0.5ppm (µg/ml)
Heptachlor	0.2ppm (µg/ml)	Endrin	0.5ppm (µg/ml)
Aldrin	0.2ppm (µg/ml)	Dieldrin	0.5ppm (µg/ml)
AR1260	10 ppm (µg/ml)	AR1016	5ppm (µg/ml)

Aroclors 1016 and 1260 are added when samples are extracted for PCBs only.

7.4 Surrogate Spike

Each sample, matrix spike, matrix spike duplicate and blank is spiked with surrogate compounds prior to extraction. The concentration in the following table exhibits the concentration in the spiking solution.

Compounds	Concentration Added
Decachlorobiphenyl (PCBs only)	1.0ml of 2.0ug/ml
Dibutylchlorendate (Pest/PCBs)	1.0ml of 1.0ug/ml

7.5 Lab Control Spikes (LCS)

Blank spikes are extracted at the same frequency as matrix spikes using Na_2SO_4 as the matrix. LCS spiking levels are the same as matrix spike concentrations. If only PCBs are needed LCS is spiked with AR1260 and AR1016 only. Aroclors LCS level are the same as matrix spike concentrations.

8.0 SAFETY

8.1 Safety glasses, lab coat, and gloves should be worn at all times during extraction.

8.2 Label reagents, spikes, surrogate solutions with solution type, concentration, date, chemist's initials and shelf life.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition.

SOP No: 13.38

Title: SOP for Method 8081
Organochlorine Pesticides and PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentration of various organochlorine pesticides, polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCTs) in various matrices such as aqueous, solids, oils, products and wipes. Table 1 indicates compounds that may be determined by this method. The retention times for the pesticide compounds are also listed in Table 1.

TABLE 1

Retention Time Table

Target Compounds	Primary Column	Confirmation Column
alpha-BHC	5.90	8.77
gamma-BHC (Lindane)	6.88	11.00
Heptachlor	9.81	12.22
Aldrin	11.79	14.15
beta-BHC	6.72	17.09
delta-BHC	7.76	18.05
Heptachlor Epoxide	14.85	18.59
Endosulfan I	17.08	19.99
4,4'-DDE	18.60	21.86
Dieldrin	18.43	22.41
Endrin	19.57	23.93
Endosulfan II	20.18	28.73
4,4'-DDD	21.05	28.95
4,4'-DDT	23.70	29.86
Endrin Aldehyde	21.42	31.04
Endosulfan Sulfate	23.11	32.30
Methoxychlor	29.30	32.41
Endrin Ketone	26.96	33.36
Alpha-Chlordane	10.28	16.70
Gamma-Chloridane	9.49	16.20
Hexachlorobenzene	4.05	4.93
Hexachlorocyclopentadiene	3.49	3.78
Chlorobenryilate	29.92	34.42
DBCP	2.14	2.84

Diallate	12.79	14.58
Isodrin	22.08	25.29
Kepone	30.85	31.49

	RTX-5	RTX-1701
Aroclor 1016	1. 6.52	1. 8.19
	2. 8.76	2. 10.15
	3. 10.08	3. 11.64
	4. 10.63	4. 13.11
	5. 12.15	5. 14.20
Aroclor 1260	1. 24.22	1. 25.24
	2. 27.05	2. 27.42
	3. 29.17	3. 30.07
	4. 30.67	4. 31.61
	5. 31.77	5. 32.57
Aroclor 1221	1. 5.66	1. 6.82
	2. 5.94	2. 7.42
	3. 6.11	3. 7.64
Aroclor 1232	1. 6.08	1. 7.64
	2. 8.21	2. 9.50
	3. 9.45	3. 12.27
	4. 9.98	4. 16.74
	5. 17.06	5. 17.28
Aroclor 1242	1. 6.07	1. 7.60
	2. 8.19	2. 9.45
	3. 9.43	3. 12.21
	4. 9.95	4. 13.24
	5. 17.04	5. 16.69
Aroclor 1248	1. 9.13	1. 9.13
	2. 12.41	2. 11.78
	3. 15.47	3. 16.31
	4. 15.71	4. 16.88
	5. 19.00	5. 22.48
Aroclor 1254	1. 16.15	1. 18.91
	2. 17.48	2. 19.96
	3. 18.83	3. 23.03
	4. 19.37	4. 25.01
	5. 24.65	5. 29.46
Toxaphene	1. 20.16	1. 29.80
	2. 22.53	2. 31.00
	3. 24.30	3. 31.38
	4. 25.01	4. 32.08
	5. 27.52	5. 32.34

Tetrachloro-m-xylene(Sur)	30.86	32.69
Decachlorobiphenyl (Sur)	36.54	38.30

1.2 The following compounds may also be determined using this method:

Compound Name	CAS Registry No.
Alachlor	15972-60-8
Captafol	2425-06-1
Captan	133-06-2
Chloroneb	2675-77-6
Chloropropylate	99516-95-7
Chlorothalonil	1897-45-6
DCPA	1861-32-1
Dichlone	117-80-6
Dicofol	115-32-2
Etridiazole	2593-15-9
Halowax-1000	58718-66-4
Halowax-1001	58718-67-5
Halowax-1013	12616-35-2
Halowax-1014	12616-36-3
Halowax-1051	2234-13-1
Halowax-1099	39450-05-0
Mirex	2385-85-5
Nitrofen	1836-75-5
PCNB	82-68-8
Perthane	72-56-0
Propachlor	1918-16-17
Strobane	8001-50-1
trans-Nonachlor	39765-80-5
trans-Permethrin	51877-74-8
Trifluralin	1582-09-8

2.0 SUMMARY OF METHOD

2.1 Method 8081 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides,

polychlorinated biphenyls and terphenyls. Prior to the use of this method, appropriate sample extraction techniques must be used.

3.0 INTERFERENCES

3.1 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large-eluting peaks, especially in the 15% and 50% fraction from cleanups. Interferences from pthalates can best be minimized by avoiding contact with any plastic materials.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett Packard GC Systems 5890 equipped with autosampler is used. EnviroQuant software systems for data recording and processing is interfaced with the GC system.

4.2 Columns

4.2.1 Dual column connected with a "Y" connector to a single injection port is used. In this mode, material injected is split between the columns and detected by 2 separate ECD detectors.

4.2.2 Column 1: 30 meter, 0.53 I.D., 0.5 micron film thickness, Restek RTX-1701, fused silica column is used.

4.2.3 Column 2: 30 meter, 0.53 I.D., 0.5 micron film thickness, Restek RTX-5, fused silica column is used.

4.2.4 5 meter guard column (inert) is used at the "Y" connector.

4.3 GC Condition

4.3.1 The following GC parameters are implemented when Pest/PCBs are analyzed:

- Injection port temperature 265°C
- Detectors temperature 300°C
- A tri-ramp temperature program is used

1st Ramp:	
Initial temperature	150°C
Initial time	0.5 min
Rate	8°C/min
Final temperature	180°C
Final time	10 min
2nd Ramp:	
Initial temperature	180°C
Rate	8°C /min
Final temperature	210°^C
Final time	10 min
3rd Ramp:	
Initial temperature	210°C
Rate	15° /min
Final temperature	270°C
Final time	8 min

- Equilibrium time 0.75 min
- Septum purge on at 0.75 min at about 2ml/min
- Attenuation 0
- Signal rages 0

- Splitless purge 50ml/min
- Makeup gas 80ml/min

4.4 Gases

4.4.1 Helium ultrapure grade is used as a gas carrier at about 5ml per min at 50° measured at the column end.

4.4.2 Make up gas is Argon/Methane (5% methane) and the flow rate is about 80 ± 5ml per min for each detector.

5.0 CALIBRATION

5.1 Calibration standards are prepared at five concentration levels through dilution of the stock standards with hexane (refer to standard logbook). Five ul of each level is injected. Concentrations of the compounds are listed on Table 3.

TABLE 3

	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
4,4'-DDD	10	25	50	75	100
4,4'-DDE	10	25	50	75	100
4,4'-DDT	10	25	50	75	100
Aldrin	10	25	50	75	100
alpha-BHC	10	25	50	75	100
beta-BHC	10	25	50	75	100
Chlordane	100	250	500	1000	2000
Decachlorobiphenyl (CB Surr)	5	12.5	25	37.5	50
delta-BHC	10	25	50	75	100
Tetrachloro-m-xylene(Surr)	5	12.5	25	37.5	50
Dieldrin	10	25	50	75	100
Endosulfan I	10	25	50	75	100
Endosulfan II	10	25	50	75	100
Endosulfan Sulfate	10	25	50	75	100
Endrin	10	25	50	75	100
Endrin aldehyde	10	25	50	75	100
Endrin ketone	10	25	50	75	100
gamma-BHC (Lindane)	10	25	50	75	100
Heptachlor	10	25	50	75	100
Heptachlor epoxide	10	25	50	75	100
Methoxychlor	10	25	50	75	100
Toxaphene	100	250	500	1000	2000
AR1016	100	250	500	750	1000
AR1221	100	250	500	750	1000
AR1232	100	250	500	750	1000
AR1242	100	250	500	750	1000
AR1248	100	250	500	750	1000
AR1254	100	250	500	750	1000
AR1260	200	500	1000	1500	2000

5.2 Surrogate standard Tetrachloro-m-xylene and Decachlorobiphenyl is used in PCB analyses. It is calibrated at levels indicated on Table 3.

6.0 GC ANALYSIS

6.1 Retention time windows

6.1.1 Make 3 injections of all single component standard mixtures and multipeaks throughout the course of a 72-hour period. Calculate standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the cluster and calculate the standard deviation of the three retention times for that peak.

6.1.1.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define retention time window. For multipeak products, primarily combination of chromatography pattern and retention times are used.

6.1.1.2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

6.1.1.3 When a new GC column is installed retention time window must be established. Typical retention times for 8081 target analytes under the parameters listed in Section 6.1 is provided on Table 1.

6.2 Degradation of DDT and Endrin

6.2.1 Check for degradation problems by injecting a EVAL MIX containing 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). Degradation must be less than 15% before any sample analyzed.

$$\text{\% Breakdown for Endrin} = \frac{\text{Total DDT degradation peak area (DDE + DDD)} \times 100}{\text{Total DDT peak area (DDT + DDE + DDD)}}$$

$$\text{\% Breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area (endrin aldehyde+endrin ketone)} \times 100}{\text{Total Endrin peak area (endrin+endrin ketone+endrin aldehyde)}}$$

6.3 Calibration

6.3.1 Five level calibration of Pesticide, Arochlors and Toxaphene is initially analyzed. Percent RSD (relative standard deviation) must be below 20% for all compounds except surrogate and any two analytes which have %RSD more than 20 but less than 30 percent.

6.3.2 Daily working calibration consists of EVAL MIX, mid level pesticide, Arochlor 1660, Toxaphene, and Chlordane are analyzed at the beginning of each shift. Percent difference should be kept at less than 15% for all compounds except for surrogates and any two analytes which may have % RSD more than 15 but less than 25 percent.

6.3.3 A continuing calibration of EVAL (check for degradation), mid-level Pesticide and Arochlor 1660 must be injected between every 10 injections of samples and/or QC and at the end of every 12 hours whichever is more frequent. All samples that were injected after the standard exceeding the criteria of degradation and/or linearity must be reinjected if the initial analysis indicate the presence of a specific target analyte that exceeded the criteria. However, if % difference for any analyte exceeds 30 percent due to loss of sensitivity, reanalysis should be performed for those parameter that fail to meet the criteria.

6.3.4 Daily calibration sequence for Pesticide analyses consists of EVAL, mid level pesticide standard. AR1660 (combined AR1016 and AR1260), mid-level Toxaphene and Chlordane. If only PCB's were to be analyzed, mid-level AR1660 standard is required. Reinjection of all Aroclors is necessary when retention time and/or sensitivity shifts are experienced. Experience of the chromatographer is an influential factor in determination of instrument drift and the necessity of injecting the entire Aroclor standards. Mid-sequence and closing standards include EVAL, mid-level pesticide and AR1660 standards. Other mid-sequence and closing multiple peak standard compounds are injected only when those analytes are exclusively required.

6.4 Sample Analysis

6.4.1 When all degradation and calibration requirements are met sample analysis may begin. After each batch of 10 runs degradation and linearity should be checked before any more samples analyzed. All samples that were injected after the standard exceeding the criteria of degradation and linearity must be reinjected, if the initial analysis indicates the presence of a specific target analyte that exceeded the criteria.

6.4.2 Dilution must be made if the response exceed the linear range of the compounds.

6.4.3 Peak identification is based on detection on both columns. A daily retention time window is established for each analyte from section 5.1 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± 3 times the standard deviation determined in section 6.1.

6.4.4 GCMS Confirmation may be implemented if the concentration permits.

6.4.5 Wipe samples are treated like a solid sample and results are reported as ug per wipe. All QC parameters used for soil samples are applicable to wipes except for MS/MSD analysis. An actual MS/MSD analysis is impractical since only one wipe is sampled at a location and it can not be splitted.

6.5 PCBs (Polychlorinated biphenyls)

6.5.1 Initially 5 levels of standards for each Aroclor are analyzed and calibration curves are established. When PCBs analysis is required, a continuing calibration is analyzed for Ar-1660. If PCBs are detected in the sample, patterns are compared with initial standards and corresponding PCBs are analyzed for fingerprint match and retention time comparison. Calculation is based on average area or peak height quantification of 5 representative peaks. The representative peaks for PCBs are selected based on peak heights and shape. Each peak should have well defined baseline and peak height. The selected peak should be free of any interferences. As a reference, the selected PCB elution retention time is listed in Table 1. When interferences are present, those peaks with less interferences may be chosen for quantification. Also fewer peaks (minimum of 3) may be used for quantification if there are considerable interferences. Surrogate Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used when only PCB analysis is required. However, only one need to be calculated for recovery.

6.6 Cleanup

6.6.1 If peak detection and identification of pesticides are prevented due to interferences of steroids, esters, ketones, glycerides and some hydrocarbons, the extract may need to undergo florisil cleanup using Method 3620A. If peak detection of pesticides are prevented by sulfur interferences which appear as huge hamp at the beginning of the chromotogram, the extract may need to undergo sulfur cleanup (Method 3660A). For PCBs, if peak detection and

pattern identification are prevented by interferences, the extract should undergo acid cleanup using Method 3665. The experience of the analyst may prove invaluable in determining which cleanup method is appropriate for particular samples.

6.7 Toxaphene and Chlordane

Approach similar to 6.5

6.8 Low Concentration Method

This method is applicable to soil and water samples containing low level contaminants with minimal matrix interferences. To achieve low detection limits, the final volumes of sample extracts are brought to 2.0ml. Concentrations of surrogate and matrix spike standards should be adjusted before extraction in order to produce levels comparable to low level procedure. Quality control and recovery ranges are not expected to be affected by final volume reduction and low level quality control criteria should be applicable to this modified method.

6.9 Calculation

6.9.1 All quantifications are based on external standard calculations.

6.9.1.1 Calculation for calibration factor

$$\text{Calibration factor} = \frac{\text{Total Area of Peak*}}{\text{Mass injected (nonograms)}}$$

* for multipeak analytes use total areas of all designated peaks for quantitation

6.9.1.2 Percent Difference

$$\text{Percent difference} = \frac{R_1 - R_2}{R_1} \times 100$$

R_1 = Calibration factor from first analysis
R_2 = Calibration factor from succeeding analyses

6.9.1.3 The concentration of each analyte in the sample may be determined by calculating the amount of standard injected from the peak response, using the calibration curve or factor determined from 6.7.1.1.

Aqueous Concentration (ug/L) = $[(A_x)(A)(Vt)(D)]/[(As)(Vi)(Vs)]$

Solid Concentration (ug/kg) = $[(A_x)(D)(A)(V_t)]/[(As)(Ws)(Vi)]$

where:

A_x = Response for the analyte in the sample, (area or peak height
A = Amount of standard injected in ng
As = Response for the external standard
Vi = Volume of extract injected
D = Dilution factor, if any
Vt = Volume of total extract
Vs = Volume of sample extracted
Ws = Weight of sample extracted

For non-aqueous samples, the unit is µg/kg and dry weight of sample is used for Ws.

7.0 QUALITY CONTROL

7.1 Required Instrument QC

7.1.1 It is required that the % RSD vary by <20% when 5 point calibration factors are compared. Surrogates and 2 analytes may have RSDs above 20 but less than 30 percent.

7.1.2 It is required that difference of daily response of a given analyte vary ± 15% when compared to initial responses.

7.1.3 All succeeding standards in an analysis sequence must fall within daily retention time window established by the first standard of the sequence. If retention time shift is observed regular maintenance of the instrument should be performed and re-run the standard. If the system still out of control, the problem should be corrected before any sample could be analyzed.

7.2 Matrix Spikes

7.2.1 For each analytical batch of up to 20 samples MS and MSD must be analyzed. If less than twenty samples are analyzed per month, MS/MSD must be analyzed on per month basis. Percent recoveries and Relative Percent Difference (RPD) should be calculated as follows:

$$\text{Matrix Spike Recovery \%} = \frac{SSR-SR}{SA} \times 100$$

where:

SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added from Spiking Mix
RPD = $\frac{D1 - D2}{(D1 + D2)/2} \times 100$
D1 = First Sample Value
D2 = Second Sample Value

Tables 4 and 5 lists the matrix compounds, amounts added and recovery ranges for soil and water matrices. If samples are analyzed for PCBs only, then matrix spikes must be analyzed for AR1016 and AR1260. Concentrations of these Aroclors are listed on Tables 4 and 5.

7.3 Lab Control Sample (LCS)

7.3.1 A control check sample is extracted and analyzed at frequency similar to MS/MSD with each extracted batch. Lab Control Spikes (LCS) are analyzed per batch or every 20 samples, whichever comes first. LCS compounds and their concentrations are listed on Table 7. LCS compound must be within the in-house established control limit. Statistical control limit are based on 20 data points. Data points used in the data set must not be selectively included or excluded. If recovery of LCS compound falls outside the established limit, corrective action must be taken. After corrective action, if LCS analyte recovery is still outside QC acceptance limits, all the associated samples batch must be reextracted if holding times have not elapsed. When PCB analysis is needed the control check sample should be spiked with AR1016 and 1260 at the same levels as matrix spikes. For all Navy pprogram samples, all LCS results must be inside the laboratory established LCS ranges. Should any LCS be out of control, the lab must reextract and reanalyze for all compounds that had criteria failed. The LCS samples will be updated on an annual basis. For specific clients and US Army Corps programs, LCS should contain all target analytes. In-house established recovery limits for LCS should not be greater than ± 20%.

Table 7 lists the LCS compounds used for soil and water matrices and their associated recovery ranges.

7.4 Blanks

7.4.1 Blank is extracted and analyzed with each analytical batch. Blanks must be contaminant free. Concentration of any confirmed peak should be less than MDL.

7.5 Surrogates

7.5.1 Percent recoveries for the surrogates are periodically (minimum of once a year) determined by plotting percent recoveries of surrogates measured in 20 consecutive blanks. Control limits for each surrogate compound is measured using the following formula:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

where p is the mean recovery and s is the standard deviation. Table 6 lists the recoveries of surrogates for different matrices.

7.5.2 Two surrogate (TCMX and DCB) are added to each sample, however, only one need to be calculated for recovery. Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if the recovery is within limits. If recovery is not within limit, re-extract and reanalyze the sample.

8.0 SAFETY

8.1 Safety glasses for eye protection, laboratory coasts for body protection, latex gloves for hand protection.

8.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

8.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the company library.

8.4 Preparation of the standard should be handled under a hood.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition

Table 4

Aqueous Pesticide Matrix Spike/Matrix Spike Duplicate Recovery

Compound	Spike Added (ug/L)	QC Limits RPD	QC Limits REC.
gamma-BHC (Lindane)	0.20	15	56-123
Heptachlor	0.20	20	40-131
Aldrin	0.20	22	40-120
Dieldrin	0.50	18	52-126
Endrin	0.50	21	56-121
4,4'-DDT	0.50	27	38-127
AR1016	5.0	30	31-149
AR1260	10	30	27-137
AR5460	20	30	20-125

Table 5

Non-Aqueous Pesticide Matrix Spike/Matrix Spike Duplicate Recovery

Compound	Spike Added (ug/kg)	QC Limits RPD	QC Limits REC.
gamma-BHC (Lindane)	6.7	50	46-127
Heptachlor	6.7	31	35-130
Aldrin	6.7	43	34-132
Dieldrin	16.7	38	31-134
Endrin	16.7	45	42-139
4,4'-DDT	16.7	50	23-134

PCBs	Spike Added (ug)	QC Limits RPD	QC Limits REC.
AR1016	5.0	50	15-194
AR1260	10.0	50	37-187
AR5460	20.0	50	20-125

Table 6

Surrogate Recovery For Soil and Water

Surrogate Compound	Amount Added (ug)	Water % Recoveries	Soil % Recoveries
Telrachloro-m-xylene (TCMX)	1.0	62 - 122	8 - 205
Decachlorobiphenyl (DCB)	2.5	20 - 116	11 - 212

Table 7

Water and Soil Lab Control Spike

Water

Compound	Spike Added (ug/L)	QC Limits Recovery Range
gamma-BHC (Lindane)	0.20	55 - 132
Heptachlor	0.20	65 - 144
Aldrin	0.20	54 - 138
Dieldrin	0.50	51 - 136
Endrin	0.50	44 - 133
4,4'-DDT	0.50	47 - 168
AR1016	5.0	31 - 149
AR1260	10.0	27 - 137
AR5460	20.0	45 - 125

Soil

Compound	Spike Added (ug/kg)	QC Limits Recovery Range
gamma-BHC (Lindane)	6.7	38 - 130
Heptachlor	6.7	63 - 123
Aldrin	6.7	55 - 118
Dieldrin	16.7	58 - 119
Endrin	16.7	50 - 115
4,4'-DDT	16.7	55 - 136

PCBs	Spike Added (ug)	QC Limits Recovery Range
AR1016	5.0	15 - 194
AR1260	10.0	37 - 187
AR5460	20.0	40 - 130

Effective Date: August 1, 1995
Version No.: 1.0
Initiated By:
Approved By:

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SOP No: 13.36

Title: Organophosphorus Pesticides by Method 8141A

1.0 APPLICATION AND SCOPE

1.1 This method applicable to the determination of certain organophosphorus (OP) pesticides. Specifically, it may be used to detect the following substances:

1.2 Tetraethylpyrophosphate
Thionazin (Zinophos)
Phorate
Disulfoton
Dimethoate
Methyl Parathion
Parathion
Carbophenothion
Famphur
Sulfotepp

Additional organophosphorus compounds may be determined by this method. Extended list of Organophosphorus compounds tabulated by Method 8141A plus the OP compounds listed as Appendix IX are applicable to this method.

2.0 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of ppb levels of certain organophosphoric pesticides. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and dilute organic liquids may be analyzed by direct injection. A 2-μL of the extract is injected into a gas chromatograph using a flush solvent technique. The compounds are then detected with a flame photometric detection (FPD).

2.2 The sensitivity of this method usually depends on the level of interferences rather than on instrumental limitations.

2.3 This method is based on Method 8141A Organophosphorus Pesticides, which is found in USEPA SW-846, September 1994 Edition.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must, therefore, be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone, and finally pesticide-quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes.

3.4 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus.

3.5 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of a solvent blank to check for cross contamination.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, with chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

4.2 All the analytes covered by this method have been tentatively classified as known or suspected, human or mammalian poisons.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

5.1 Sample extracts are preserved by keeping them cooled to 4°C.

5.2 The holding time for extraction of the sample is within 7 days of sampling.

5.3 Samples must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph

Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases and syringes. A data system for measuring peak heights or areas.

6.1.2 Columns

6.1.2.1 Column 1

RTx-5, 30 m x 0.53 mm ID, 0.5um film thickness bonded silicone coated fused silica capillary column or equivalent.

6.1.3 Detectors - flamephotometric (FPD)

6.2 Microsyringe - 10 μL

6.3 Syringe - 5 mL

6.4 Vials - Glass, 2-, 10- and 20mL capacity with Teflon-lined screw cap.

7.0 REAGENTS AND STANDARD PREPARATION

7.1 Solvents - hexane, acetone (pesticide quality or equivalent).

7.2 Stock Standard Solutions

7.2.1 Stock standard solutions are made at volumes and concentrations useful for making working calibration standards, usually at 10,000 or 5,000 ppm depending on what stock is being prepared. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

7.2.2 Transfer the stock standard solutions into Teflon-sealed screw-up bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.2.3 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.

7.3 Calibration Standards

Calibration standards at a minimum of five concentration levels (Table 2) for each parameter of interest are prepared through dilution of the stock standards with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem. See Table 1 for actual calibration levels.

7.4 Surrogate Standards

The extraction and analytical system performance is monitored by spiking pesticide surrogate into each standard, sample and reagent water blank. Ethyl p-nitrophenylbenzenthiophosphonate (EPN) is the primary surrogate standard and should be used whenever possible. See Table 1 for surrogate concentration levels. See section 12 for surrogate acceptance limits and corrective action. A surrogate standard is also prepared containing Tetrapropylphosphate (TPP). The levels can be found on Table 1.

8.0 CALIBRATION

8.1 The working calibration range of this method can be found for each compound by looking at Table 1. The calibration range is that range which is inclusive of the 5 standards run for each compound.

8.2 External standard calibration procedure

8.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

8.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 2 μL injections). Tabulate peak height responses against the concentration injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas

chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of the calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Height of Peak}}{\text{conc. of std (in } \mu\text{g/ml)}}$$

8.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent of the detector. A mid-level continuing calibration standard must be analyzed every working day (at a minimum) and every 10 samples. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{|R_1 - R_2| \times 100}{R_1}$$

Where:

R_1 = Calibration Factor from first analysis.
R_2 = Calibration Factor from succeeding analyses.

8.3 Retention Time Windows

8.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

8.3.2 Calculate the standard deviation of the three absolute retention times for each single component standard. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

8.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

8.3.4 In those cases where the standard deviation for particular standard is zero, the analyst must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

8.3.5 The retention time windows will be updated at least weekly.

8.3.6 The analyst must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the analyst in each batch carcass.

9.0 QUALITY CONTROL

9.1 Method detection limits are calculated according to 40CFR Part 136, Appendix B of the Federal Register.

9.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

Required Instrument QC:

9.3.1 Section 8.2 requires that a %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

9.3.2 Section 8.2 sets a limit of ±15% difference when comparing the initial response of a give analyte versus any succeeding standards analyzed during an analysis sequence.

9.4 The laboratory must, on an ongoing basis, perform at least one MS/MSD per analytical batch (maximum of 20 samples per batch) to assess accuracy. If ten or less samples are analyzed within a given month, at least one spiked sample per month is required.

9.5 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the sample matrix type), calculate the average percent recovery (p) and the standard deviation of the percent recovery (sp).

9.6 To determine acceptable accuracy and precision limits for surrogate standards, the following procedure should be performed:

9.6.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

9.6.2 Once a minimum of 20 blanks of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

9.6.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

9.6.4 If recovery is not within limits, the following is required:

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

9.6.5 At a minimum, surrogate recovery limits are reviewed on a matrix-by-matrix basis, annually.

9.7 Summary of QC

Surrogates	Every sample and standard
Calibration check standard	Every working day After every 10th injection
Method blank	One per batch, per matrix, per concentration level
Matrix spike	One per batch, per matrix, per concentration level

Matrix spike duplicate	One per batch, per matrix, per concentration level
QC blank spike sample (Laboratory Control Sample)	One per batch, per matrix, per concentration level

10.0 INSTRUMENTAL PROCEDURES

10.1 Gas Chromatography Conditions

10.1.1 Column - A 30um, 0.53 ID, 0.5um RTX5 column used. GC parameters are as follows:

- Splitless mode
- Purge flow 2ml/min
- Splitless flow 50ml/min
- Carrier gas He at about 10ml/min
- Oven heating parameters
  - Inj part 200°
  - Initial temp 45°
  - Initial time 2 min
  - Ramp Rate 25°/min
  - Final temp 250°
  - Final time 2 min
- Detector Parameters
  - Detector in phosphorous mode
  - Temp 250°
  - Nitrogen flow 8ml/min
  - Air flow 100ml/min
  - Hydrogen flow 80ml/min

10.2 Suggested chromatography system maintenance:
Corrective action may require one or more of the following remedial actions.

10.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned deactivated insert. Carefully cut off the first few inches (up to one foot) of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If problems persist, replace the column.

10.3 A compound is qualitatively identified as being present if the peak is detected within the established retention time window for that specific compound. To confirm that an analyte is present, the extract must be run on a secondary column. Again, the peak must be detected within the established retention time window.

10.4 If both columns confirm the presence of an analyte, the analyte is quantitated using the peak area of the primary column. The concentration of the analyte is then computed using the calculation from Section 11.1.

10.5 The target analyte concentration must be within the calibration range for quantitation. If the sample requires dilution, the dilution must also be acquired on a secondary column for confirmation.

11.0 CALCULATIONS

11.1 External Standard Calibration

Aqueous Samples:

Concentration (μg/L) = $[(A_x)\ (V_t)\ (D)]/[(CF)\ (V_i)\ (V_s)]$

Where:

A_x = Response for the analyte in the sample, units are peak heights counts.

CF = Calibration Factor (see Section 8.2.2)

V_i = Volume of extract injected, μL.

D = Dilution factor - if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, μL.

V_s = Volume of sample extracted, mL.

Nonaqueous Samples:

Concentration (μg/kg) = $[(A_x\ (D)\ (V_t)]/[(CF)\ (W_s)\ (V_i)]$

Where:

A_x = Response for one analyte in the sample, units are peak heights counts.

CF = Calibration Factor (see Section 8.2.2.)

V_i = Volume of extract injected, μl.

D = Dilution Factor - if dilution was made on the sample prior to analysis. If no dilution was made D=1, dimensionless.

V_t = Volume of total extract, μl.

W_s = Weight of sample extracted, either dry weight or wet weight may be used, depending upon the specific application. All concentrations are to be reported on a dry weight basis otherwise specified.

11.2 Percent Recovery (%R)

$$\%R = \frac{\text{(Observed - Sample) Concentration}}{\text{Expected Concentration}} \times 100$$

11.3 Relative Percent Difference (RPD)

$$RPD = \frac{\text{(Measurement 1 - Measurement 2)}}{\text{Average of Measurement 1 and 2}} \times 100$$

12.0 ACCEPTANCE OF DATA

12.1 If the method blank contains any analytes of interest above the method detection limit as determined by GC analysis, the batch is rejected and the samples are re-extracted.

12.2 The advisory limits for the surrogate recovery are:

TPP	25-125 (Aqueous)	20-150 (Non-aqueous)

12.2.1 If the percent recovery is outside of the control limits, the sample must be reanalyzed. If the surrogate recoveries for method blank are outside the advisory limit reanalysis and/or re-extraction of the blank and associated samples is required.

13.0 REPORTING OF RESULTS

13.1 Aqueous results are routinely reported as μg/L and nonaqueous results as μg/kg.

13.2 If the analyte is detected above the minimum reporting limits, the value will be reported.

13.3 If there is no evidence of the presence of the analyte, the analyte is reported as ND.

13.4 If the analyte is detected below the practical quantitation limit, the analyte is reported as BQL.

14.0 SUPPLEMENTAL DOCUMENTS

14.1 GP Sops for sample preparations.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, United States Environmental Protection Agency, SW-846, Volume 1-B Laboratory Manual, Third Edition, November 1986, "Method 8000 Gas Chromatography" and "Method 8140 Organophosphorous Pesticides".

Table 1

Standards

L E V E LS

Calibration Levels for Individual Mix A:

Compound	I	II	III	IV	V
Tetraethylpyrophosphate	0.25	0.50	1.00	2.00	4.00
Thionazin (Zinophos)	0.10	0.20	0.40	0.80	1.60
Disulfoton	0.05	0.10	0.20	0.40	0.80
Dimethoate	0.25	0.50	1.00	2.00	4.00
Methyl Parathion	0.10	0.20	0.40	0.80	1.60
Parathion	0.10	0.20	0.40	0.80	1.60
Famphur	1.00	2.00	4.00	8.00	16.00
TPP	0.20	0.50	1.00	2.00	4.00
Sulfotep	0.20	0.50	1.00	2.00	4.00

Calibration Levels for Individual Mix B:

Compound	I	II	III	IV	V
Phorate	0.25	0.50	1.50	2.00	4.00
Carbophenothion	1.00	2.00	4.00	8.00	16.00

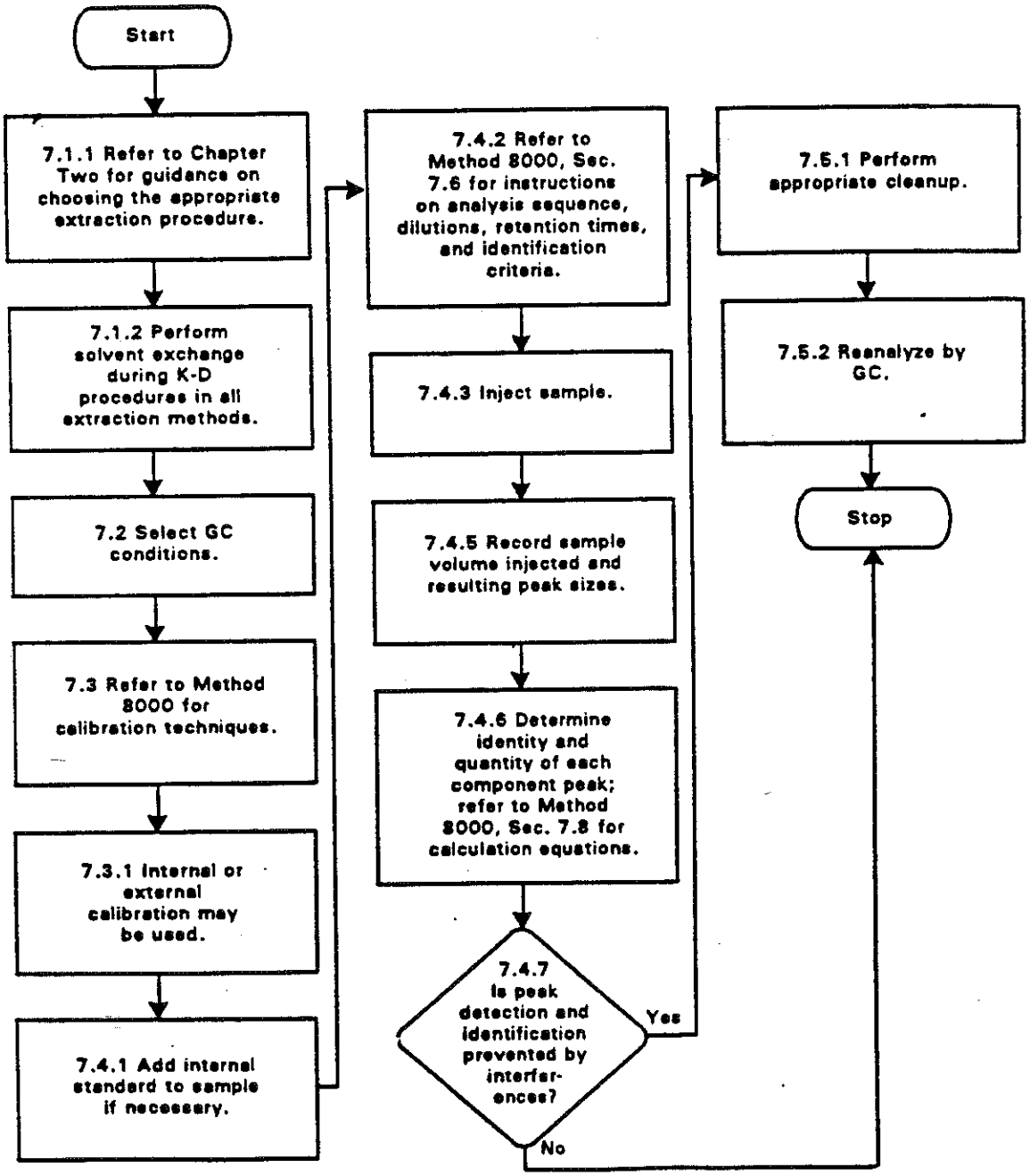
Calibration standards units are μg/ml. Application of the sample extraction concentration step (1000 ml to 10 ml) decreases the equivalent concentration by a fraction of 100x.

CORRECTIVE ACTION TABLE
ORGANOPHOSPHORUS PESTICIDES BY GC/FPD

QC PARAMETER	FREQUENCY	CRITERIA	ACTION
Retention Time Window (RT)	Every Calibration standard; sample surrogate	+3 standard deviation of absolute RT	Verify calibration standard Check instrument performance Evaluate matrix interference Re-establish RT windows
Initial 5 PT Calibration Average Response CF: %RSD	Prior to Sample analysis	<20%	Verify calibration standard Check regression criteria
Linear Regression: Corr. Coefficient [1yr intercept value]		>0.995 <Reporting Limit	Verify calibration standards Calibrate check standard for possible contamination Recalibrate instrument for that analyte
Continuing Calibration: (Mid Level Standard) %D	Every working day: every 10 samples.	<15%	Verify calibration standard Check instrument performance Recalibrate instrument for that analyte Reanalyze any samples acquired after failed continuing calibration standard
Method Blank	1 per every batch per matrix per concentration	All analytes detected below the reporting limit.	Check Instrument performance Recalibrate/re-analyze Contact QA if reoccurs

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	1 per batch per matrix per concentration	All analytes detected below the reporting limit	Check instrument performance Recalibrate/re-analyze Contact QA if reoccurs
QC Blank Spike (QC Check Sample)	1 per batch per matrix per Concentration level	See Table 3	Verify standards and calculation Check instrument performance Recalculate/reanalyze sample
Matrix Spike / Matrix Spike Duplicate	1 per batch (maximum of 20 samples) per matrix per concentration level	See Table 3	Verify standards and calibration Check instrument performance Evaluate for possible matrix interference
Surrogates	All standards, blanks, samples	TPP: Aqueous: 25-125% Nonaqueous: 20-150%	Verify calculation and instrument performance Confirm on a secondary column Reanalyze sample. If surrogate out of control in Blank, Confirm on a secondary column Re-extract/re-analyze batch.

METHOD 8141A
ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE



Effective Date: May 1997
Version Number: 3
Initiated By:
Approved By:

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SOP No: 13.35

Title: Analysis of Herbicides by Method 8150B

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of certain chlorophenoxy acid herbicides by GC/ECD.

1.2 The following compounds can be determined using this method:

2,4-D	2,4,5-T	2,4,5-TP
2,4-DB	Dichlorprop	MCPP
Dalapon	Dinoseb	
Dicamba	MCPA	

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated phenoxy acid herbicides. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector. The results are reported as the acid equivalents. Table 1 lists method detection limits determined for aqueous samples using deionized water.

3.0 INTERFERENCES

3.1 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.2 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis.

3.3 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must, therefore, be demonstrated to be free from interferences under the

conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

3.5 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone, and finally pesticide-quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

5.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

5.1 Samples are preserved by keeping them cooled to 4°C.

5.2 The holding time for extraction of the sample is within 7 days of sampling. Sample extracts must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph

Analytical system complete with gas chromatograph suitable for splitless mode capillary column injections and all required accessories, including detector, column supplies, recorder, gases and syringes. A data system for measuring peak heights. The gas chromatograph is a Hewlett Packard 5890 Series II.

6.1.2 Columns - Dual column connected with a "Y" connector to a guard column is used. In this mode, material injected is split between the columns and detected by 2 separate ECD detectors.

6.2 Vials: Amber glass, 10 to 15mL capacity with Teflon-lined screw cap

6.3 Microsyringe: 10uL

6.4 Syringe: 5mL

7.0 REAGENTS AND STANDARD PREPARATION

- Solvents: Acetone, methanol, ether, methylene chloride, hexane (pesticide quality or equivalent).

- Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

  - Prepare stock standard solutions by accurately weighing about 0.0100g of pure methylesters. Dissolve the material in hexane (pesticide quality) solvent and dilute to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

  - Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

  - Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

7.3 Calibration Standards

7.3.1 Calibration standards at a minimum of five concentration levels (listed below) for each parameter of interest are prepared through dilution of the stock standards with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels correspond to the expected range of concentrations found in the real samples

or define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

Concentrations in µg/L

Compound	I	II	III	IV	V
2,4-DCAA (Sur)	250	500	1000	1500	2000
Dalapon	250	500	1000	1500	2000
Dicamba	10	20	40	60	80
Dichloroprob	100	100	450	650	800
2,4-D	100	200	400	600	800
2,4,5-TP (Silvex)	10	20	40	60	80
2,4-DB	100	200	400	600	800
2,4,5-T	10	20	40	60	80
Dinoseb	50	100	200	300	400
MCPA*	10	25	50	75	100
MCPP*	10	25	50	75	100

*Conc µg/mL

7.4 Surrogate Standards

Compound 2,4-dichlorophenyl acetic acid has been chosen to be the surrogate for this analysis. See above calibration table for actual calibration ranges. Methyl ester of this compound is used in calibration, where 1.0ml of 10ug/ml of the acid form of this compound is added to sample and QC. Surrogate recovery ranges for soil and water are listed on Table 2.

8.0 CALIBRATION

8.1 Inject 2.5 microliter of each calibration standard using the splitless mode. Tabulate peak height or area responses against the mass injected. The results are used to prepare a calibration curve for each analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of the calibration curve.

$$\text{Calibration factor} = \frac{\text{Height of Peaks}}{\text{mass injected (nanograms)}}$$

8.2 The working calibration curve or calibration factor must be verified on each working day by the injection of one calibration standards. A mid-level continuing calibration standard must be analyzed every 12 hours. If the response for any analyte varies from the predicted response by more than ±15%, corrective action is required. After corrective action if criterias are not met a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{[R_1 - R_2] \times 100}{R_1}$$

where:

R_1 = Average Calibration Factor
R_2 = Calibration Factor from succeeding analyses

8.3 Retention Time Windows

8.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all calibration standard mixtures.

8.3.2 Calculate the standard deviation of the three absolute retention times for each component.

8.3.3 The mean retention time plus or minus three times the standard deviation of the mean retention time for each component will define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

8.3.4 In those cases where the standard deviation for particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

8.3.5 The retention time windows are updated at least weekly or upon sample analysis if the method is performed less frequently.

8.3.6 The laboratory must calculate retention time windows for each component on each GC column and whenever a new GC column is installed. Table 3 lists typical retention times for target herbicides for primary and confirmation columns.

9.0 QUALITY CONTROL

9.1 Method detection limits are calculated according to 40CFR Part 136, Appendix B of the Federal Register.

9.2 Minimum Reporting Levels for all compounds are the method detection limits and can be found on Table 1.

9.3 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.4 For each analytical batch (up to 20 samples), a reagent blank, a spiked blank, matrix spike and matrix spike duplicate must be analyzed. The blank, spiked blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

Required Instrument QC:

9.4.1 Section 8.1 requires that a %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

9.4.2 Section 8.2 sets a limit of ±15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

9.4.3 Paragraph 8.2 sets a limit of ±15% difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

9.5 The laboratory must, on an ongoing basis, perform at least one Matrix Spike/Matrix Spike Duplicate per analytical batch (maximum of 20 samples per batch) to assess accuracy. If ten or less samples are analyzed within a given month, at least one MS/MSD sample per 14 days is required. At least one matrix spike (no duplicate) is extracted and analyzed per each TCLP batch. Compounds 2,4-D, Silvex and 2,4,5T are used for matrix spike. Table 4 lists spike compounds, amount added and their recovery ranges for water samples.

9.6 To determine acceptable accuracy and precision limits for surrogate standards, the following procedure should be performed:

9.6.1 For each blank analyzed, calculate the percent recovery of each surrogate in the blank.

9.6.2 Once a minimum of 20 blanks of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

9.6.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

where p is the mean and s is standard deviation

9.6.4 If recovery is not within limits, the following is required:

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

9.6.5 At a minimum, surrogate recovery limits are reviewed on a matrix-by-matrix basis, annually.

9.7 The laboratory performs, on an ongoing basis, one blank spike (LCS) per analytical batch (maximum of 20 samples per batch). If fewer samples are analyzed within a given month, at least one LCS per 14 days is required.

9.8 Summary of QC

Surrogates	Every sample and standard
Calibration check standard	After every 10th sample injection
Method blank	One per batch, per matrix, per concentration level
Matrix spike	One per batch, per matrix, per concentration level
Matrix spike duplicate	One per batch, per matrix, per concentration level
QC blank spike sample (Laboratory Control Sample)	One per batch, per matrix, per concentration level

10.0 INSTRUMENTAL PROCEDURES

10.1 Gas Chromatography

10.1.1 Gas Chromatography Conditions

Column 1: DB1701

Carrier Gas	Helium
Split Flow	60ml/min
Purge Flow	3ml/min
Column Flow	4ml/min @ 180°C
Make-Up Flow	60ml/min (95:5 Argon/Methane)
Injector Port	245°C
Column Temp	150°C Isothermal
Final Temp	270°C
Final Time	5 min.
Ramp Rate	8°/min.
Split Valve On	1.0 min.
Split Valve Off	0.0 min.

Column 2: RTX-5

Carrier Gas	He
Split Flow	60ml/min
Purge Flow	3ml/min
Column Flow	4ml/min @ 180°C
Make-Up Flow	60ml/min (95:5 Argon/Methane)
Injector Port	245°C
Column Temp	150°C Isothermal
Final Temp	270°C
Final Time	5 min.
Ramp Rate	8°/min.
Split Valve On	1 min.
Split Valve Off	0 min.

10.2 Suggested chromatography system maintenance: corrective action may require the following remedial action.

10.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned deactivated insert. Carefully cut off the first few inches (up to one foot) of the injection port side of the column. Remove the column and solvent backflush according to the manufacture's instructions. If degradation problems persist, replace the column.

10.3 A compound is qualitatively identified as being present if the peak is detected within the established retention time window for that specific compound. To confirm that an analyte is present, the extract must be run on a secondary column. Again, the peak must be detected within the established retention time window.

10.4 If both columns confirm the presence of an analyte, the analyte is quantitated using the peak area of the primary column. The concentration of the analyte is then computed using the calculation from Section 11.1.

10.5 The target analytes concentration must be within the calibration range for quantitation. If the sample requires dilution, the dilution must also be acquired on a secondary column for confirmation.

11.0 CALCULATIONS

11.1 External Standard Calibration

Aqueous Samples:

Concentration (ug/L) = $[(A_x)(V_t)(D)]/[(CF)(V_f)(V_8)]$

Where:

A_x = Response for the analyte in the sample, units are peak heights counts

CF = Calibration Factor (See Section 8.2.2)

V_i = Volume of extract injected, uL

D = Dilution factor - if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless

V_t = Volume of total extract, uL

V_s = Volume of sample extracted, ml

Nonaqueous Samples:

Concentration (ug/kg) = $[(A_x)(D)(V_t)]/[(CF)(W_s)(V_i)]$

Where:

A_x = Response for the analyte in the sample, units are peak heights counts

CF = Calibration Factor (See Section 8.2.2)

V_i = Volume of extract injected, uL

D = Dilution factor - if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless

V_t = Volume of total extract, uL

W_s = Weight of sample extracted. Either dry weight or wet weight may be used, depending upon the specific application. All concentrations are to be reported on a dry weight basis otherwise specified.

11.2 Percent Recovery (%R)

$$\%R = \frac{\text{(Observed - Sample) Concentration}}{\text{Expected Concentration}} \times 100$$

11.3 Relative Percent Difference (RPD)

$$RPD = \frac{\text{(Measurement 1 - Measurement 2)}}{\text{Average of Measurement 1 and 2}} \times 100$$

12.0 ACCEPTANCE OF DATA

12.1 If the method blank contains any analytes of interest above the method detection limit as determined by GC analysis, the batch is rejected and the samples are re-extracted.

12.2 The percent recovery for the entire surrogate is periodically (annually) determined using 20 cause blanks. Control limits surrogate compound is measured using the following formula:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

where p is the mean and s is standard deviation.

13.0 REPORTING OF RESULTS

13.1 The minimum reporting limits for all compounds are the method detection limits and can be found in Table 1.

13.2 Aqueous results are routinely reported as ug/L and nonaqueous results are ug/kg.

13.3 TCLP results are to be reported as μg/L.

13.4 The number of significant figures to be reported is

13.5 If the analyte is detected above the minimum reporting limits, the value will be reported.

13.6 If there is no evidence of the presence of the analyte, the analyte is reported as ND.

13.7 If the analyte is detected below the practical quantitation detection limit, the analyte is reported as BQL.

14.0 SUPPLEMENTAL DOCUMENTS

14.1 Method 8150 SOP for sample preparation.

15.0 REFERENCES

- U.S. EPA 40 CFR Part 136: Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act. October 1984.

- Test Methods for Evaluating Solid Waste, United States Environmental Protection Agency, SW-846, Volume 1-B Laboratory Manual, Third Edition, November 1986, "Method 8000 Gas Chromatography" and "Method 8150 Chlorinated Herbicides".

Table 1

Method Detection Limit Study

Compound	Water MDL ug/L)
Dalapon	0.063
Dicamba	0.025
Dichloroprob	0.038
MCPP	29.8
MCPA	33.4
2,4-D	0.060
2,4,5-TP(Silvex)	0.005
2,4,5-T	0.007
2,4-DB	0.054
Dinoseb	0.044

Matrices	Factor
Ground water	10
Soil/sediment and other solids	200
Waste samples	10000

Estimated Quantitation Limit (EQL) = MDL X Factor (matrix dependent)

Table 2

Surrogate	Amount Added Water	Percent Recovery Range	Amount Added Soil	Percent Recovery Range
2,4-DCAA	10ug	7 - 170	10ug	D - 175

Table 3

Compound	Retention Time Rtx-5	Rtx-1701
Dalapon	3.44	4.40
Dicamba	15.29	17.17
Dichloroprob	16.78	18.70
2,4-D	17.17	19.42
2,4,5-TP(Silvex)	18.91	20.73
2,4,5-T	19.39	21.55
2,4-DB	20.28	22.25
Dinoseb	20.28	23.25
2,4-DCAA(Surrogate)	15.07	16.77
MCPP	16.86	18.55
MCPA	16.50	18.90

Table 4

Water Matrix Spike Recovery

Compound	Spike Added (ug/L)	Recovery Range Percent
2,4-D	10.0	10 - 150
2,4,5-TP(Silvex)	2.0	10 - 150
2,4,5-T	2.0	10 - 150

Table 5

Water Lab Control Spike Recovery

Compound	Spike Added (ug/L)	Recovery Range Percent
2,4-D	10.0	25 - 140
2,4,5-TP(Silvex)	2.0	25 - 140
2,4,5-T	2.0	25 - 140

GP ENVIRONMENTAL SERVICES

Effective Date: May 1997
Version Number: 2
Initiated By :
Approved By :

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SOP No: 11.36

Title: Acid Digestion of Surface and Ground Water Samples for Flame/ICP Analyses and Furnace Analysis of Antimony in Accordance With SW846 Method 3005A.

Scope: The method detailed in this procedure is performed to prepare aqueous samples for quantitation of certain metallic analytes using Inductively Coupled Plasma (ICP) or Flame Atomic Absorption (FLAA) or Graphite Furnace Atomic Absorption for antimony (GFAA) spectroscopy in accordance with SW846 method 3005A.

1.0 PURPOSE

1.1 The method detailed in this procedure is used to prepare aqueous samples for analysis using an Inductively Coupled Plasma (ICP) spectrophotometer or a Flame Atomic Absorption (FLAA) spectrophotometer or Graphite Furnace Atomic Absorption for antimony (GFAA). The sample holding time before digestion is 180 days. This method is applicable to the following analytes: Ag, Al, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Rc, K, Mg, Mn, Na, Ni, Pb, Se, Sb, Tl, V, 2n, B, Mo< Sr, Ti, Sn and Si.

2.0 REFERENCES

- SW846 method 3005A revision 1

3.0 EQUIPMENT AND SUPPLIES

- 250ml teflon beakers
- 100ml volumetric flasks
- Hot plate
- Whatman No. 41 filter paper
- 250ml sample bottle (plastic)
- Watch glass
- Plastic disposable funnels
- Thermometer, calibrated, NBS traceable
- Fume hood
- Eppendorf and Oxford pipettors (calibrated)
- 100ml graduated cylinders

4.0 REAGENTS

- Concentrated Nitric Acid - trace metals grade
- Concentrated Hydrochloric Acid - trace metals grade
- Metals Standards - (ICP spk 1,2,3) commercially prepared NIST traceable metals standards with documented concentrations, including impurities and expiration dates (Vendor: High Purity Standards, Charleston, SC).
- Diluent for ICP & FLAA standards. = Flame Water. Flame water is prepared by adding 100ml concentrated nitric acid and 500ml concentrated hydrochloric acid to 10 liters deionized water.
- Grade and quality of water required is ASTM Type II water (ASTM D1193): Water must be monitored for changes in conductivity by laboratory staff and is currently provided by a laboratory pure water system.

5.0 PROCEDURE (see Figure 2 for flow chart)

5.1 Sample Digestion Procedure

5.2.1 Mix the sample thoroughly to achieve homogeneity. Transfer 100ml of sample using a graduated cylinder to a beaker. Transfer 100ml of sample each for duplicate and matrix spike analysis and label as duplicate and matrix spike.

5.2.2 To the matrix spike beaker, add 0.1ml of matrix spike solution ICP spk 1,2 and 3).

5.2.3 Label one empty beaker "LSCW" for the laboratory control sample. Add 100ml ASTM type II water and 1ml of ICV part 1 & 2 solution.

5.2.4 Label one empty beaker "PBW" for the preparation blank. Add 100ml ASTM type II water.

5.2.5 To all beakers, add 2ml of concentrated nitric acid (HNO_3) and 5ml of concentrated hydrochloric acid. Cover the samples with watch glasses and heat on a hot plate in the fume hood to 95°C (± 4°C) until volume has been reduced to 15-20ml or 2 hours. Do not boil. Remove beaker from hot plate and allow to cool.

5.2.6 After cooling, filter sample if necessary through Whatman No. 41 filter paper (or equivalent) using disposable funnel. Dilute to 100ml in volumetric flask with Type II water. NOTE: In place of filtering, the sample may be centrifuged or allowed to settle by gravity overnight to remove

insoluble material. Filter or centrifuge the sample only when sample contains insoluble materials that may clog the nebulizer. The diluted digestate solution contains approximately 5% (v/v) HCL and 2% HNO3. Transfer to 250ml plastic sample bottle and label with GP work order, fraction, WFL (for water matrix, flame/ICP digestion) and date of digestion. Date of digestion may be put on the box of digestates instead of on each bottle. For analysis, withdraw aliquots of approximate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

6.0 QUALITY CONTROL

6.1 Troubleshooting and corrective action.

The furnace, ICP and flame AA operators should report to his/her supervisor and lab manager any recoveries outside warning limits for LCS samples for analytes being determined. Sample recoveries for any element which are outside of the control established limits for the laboratory control sample, are deemed unacceptable. The digestion batch must be redigested for those analytes. Document the incident on a redigestion form and submit to supervisor.

Other items pertaining to quality control are addressed in Section V.

7.0 SAFETY

7.1 Safety equipment required

- Fume hood - minimum flow of 100 linear feet/minute
- Safety glasses
- Safety gloves (unpowdered)
- Lab apron
- Face shield, if necessary

7.2 Potential hazards

The most hazardous chemical acids that laboratory personnel are likely to encounter are strong acids such as Hydrochloric Acid and Nitric Acid (HNO_3).

7.3 Special handling requirements

Analysts should always read the label on the bottle. Chemicals require handling with care to include wearing adequate garments for skin protection. Also, acid use should be performed under a ventilated hood.

8.0 DISPOSAL REQUIREMENTS

8.1 Acid wastes should be placed into the acid waste bottle which is located under the sink in the metals digestion lab. Any remaining samples should be returned to sample control. More details concerning disposal characteristics and procedures can be located in the SOP 9.1 "Analytical Division Laboratory Waste Handling and Disposal Procedure".

9.0 REPORTING REQUIREMENTS

9.1 Documentation to include Work Orders and Work Sheets (see SOP 7.3, Sample Logging and Record Keeping), Sample Description Forms and the Metal Digestion Log Forms (Figure 1) must be submitted to the Metals Supervisor with the Digestion Technician's initials and the preparation date documented on each form for each case.

9.2 Sample Description Forms must be filled out for any work order of type VI or VII (see comment section on work order) and should contain the following information for aqueous digestates. The fields for color and clarity, before and after digestion, must be completed. The following descriptive terms are recommended:

Color - red, blue, yellow, green, orange, violet, white, colorless, brown, grey, black

Clarity - clear, cloudy, opaque

Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the Comments section. Enter any sample-specific comments concerning the analyte results in the comments section.

9.3 Metal Digestion Log Forms must be documented completely by the Digestion Technician during digestion include the date of digestion, work order number, client name, digestion technician signature, digestion supervisor approval, identification of method or SOP used, client ID, GP fraction ID, sample matrix (soil/water), amount of sample used in digestion and final volume of sample, identification of the matrix spiking solution used and the amount used.

9.4 QC records are maintained in the form of control charts to document percent recovery of analytes from EPA ICV and independent laboratory control samples subjected to the digestion procedure. See SOP 3.12, Quality Control Charts for more information.

Figure 1

Metals Digestion Form

GP Environmental Services Metals Preparation & Sample Description Log

Date: SOP No.: Method: Document Control No. GP310 Batch No.: 595

Analyst: Comments:

Reviewed: Comments:

	GP Work Order No.	Frac	SIZE mL or g	Final Vol. (mL)	Matrix S, W Other	Reported Client ID (Six characters)	Color Before Red, Blue, Yellow, Green, Violet, Grey, White, Colorless, Cloudy, Brown, Black	Color After	Clarity Before or Soil Texture	Clarity After Clear, Cloudy, Opaque	Soil Artifacts or water pH
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
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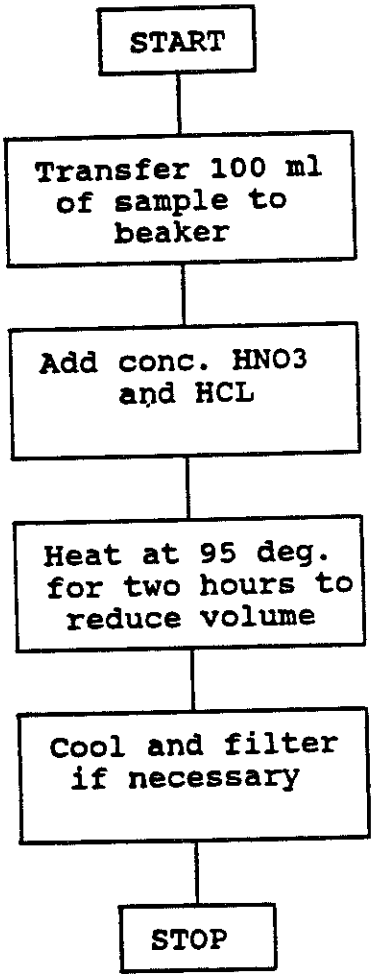
22											
23											
24											
25											
26											

Standards Traceability: List LCS and Spiking solutions & Amount Below:	List Reagent Manufacturer & Lot# Below
LCS Source:	HNO3
Spiking Source & Amount (ml):	HCl
	Peroxide:
Temp(C):	_____:

[illegible]

Figure 2

ACID DIGESTION OF SURFACE AND GROUND WATER SAMPLES
FOR FLAME/ICP ANALYSIS AND FURNACE ANALYSIS OF SB



Effective Date: May 1997
Version Number: 3.0
Initiated By :
Approved By :

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SOP No: 11.35

Title: Acid Digestion of Soil, Sludge, Sediment, and Other Solid Waste Samples for Flame/ICP and Furnace Analyses in Accordance with SW 846 Method 3050A.

Scope: The method detailed in this procedure is performed to prepare soil, sediment, sludge and other solid samples for quantitation of certain metallic analytes using Inductively Coupled Plasma (ICP), Flame Atomic Absorption (FLAA), or Graphite Furnace Atomic Absorption spectroscopy in accordance with SW846 method 3050A.

1.0 PURPOSE

1.1 The method detailed in this procedure is used to prepare solid waste samples for analysis using an Inductively Coupled Plasma (ICP) spectrophotometer, a Flame Atomic Absorption (FLAA) spectrophotometer, or a Graphite Furnace Atomic Absorption (GFAA) spectrophotometer. The sample holding time before extraction is 180 days. Samples must be stored in refrigerator at 4°C until time of preparation. The elements to be analyzed using this procedure are:

ICP Elements	FLAA Elements	GFAA Elements
Al	K	As
Ba	Na	Se
Be		Tl
Cd		Pb
Ca		Sb
Cr		Ag
Co, Ag		
Cu, As		
Fe, K		
Mg, Na		
Mn, Pb		
Ni, Sb		
V, Se		
Zn, Tl		

This method is also applicable to other metals.

2.0 REFERENCES

- SW846 method 3050A revision 1

3.0 EQUIPMENT AND SUPPLIES

- 250ml teflon beakers
- Analytical balance accurate to 0.001 grams
- 100ml volumetric flasks
- Hot plate, capable of maintaining temp. of 90-95 degrees C.
- Whatman No. 41 filter paper
- 250ml sample bottle (plastic)
- Watch glass, ribbed and non-ribbed
- Plastic disposable funnels
- Thermometer, calibrated, NBS traceable
- Fume hood
- Eppendorf and Oxford pipettors (calibrated)
- Teflon coated spatulas

4.0 REAGENTS

- Concentrated Nitric Acid - trace metals grade
- 8M Nitric Acid - trace metals grade
- Concentrated Hydrochloric Acid - trace metals grade
- Metals Standards - commercially prepared NBS traceable metals standards with documented concentrations, including impurities and expiration dates (Vendor: High Purity Standards, Charleston, SC).
- 30% Hydrogen Peroxide
- Diluent for furnace standards. = Furnace Water. Furnace water is prepared by adding 125ml of concentrated nitric acid to 60ml hydrogen peroxide (30%) to 5 liters of distilled water, then to a final volume of 10 liters.
- Diluent for ICP & FLAA standards. = Flame Water. Flame water is prepared by adding 100ml concentrated nitric acid and 500ml concentrated hydrochloric acid to 10 liters deionized water.
- Grade and quality of water required is ASTM Type II water (ASTM D1193): Water must be monitored for changes in conductivity by laboratory staff and is currently provided by a laboratory pure water system.
- Solid laboratory control sample (Vendor: Environmental Resources Associates, Arvada, CO).

5.0 PROCEDURE

5.1 Sample Digestion Procedure

5.1.1 Mix the sample thoroughly to achieve homogeneity using a teflon coated spatula. For each digestion procedure, weigh (to the nearest .01g) a 1.0g portion of sample and transfer to a beaker. (three beakers for flame/ICP analysis) soil; (three beakers for furnace analyses) soil; (four empty beakers for LCSS samples and preparation blanks).

Note: A separate sample shall be dried for percent solids determination. See SOP 11.24, Percent Solids Determination Procedure.

5.1.2 Label two soil beakers, one as a duplicate and the second as a sample for ICP/flame analyses.

5.1.3 Label two soil beakers, one as a duplicate and the second as a sample for furnace analysis.

5.1.4 Label two remaining soil beakers as matrix spike furnace and matrix spike flame. To each matrix spike beaker add 0.1ml each of spiking solution (ICP SPK1,2,3).

5.1.5 Take two empty beakers and add 1.0ml each of deionized water and label as prep blank furnace and prep blank ICP.

5.1.6 Take the two remaining empty beakers and weigh out 1.0 gram (± .01g) of ERA laboratory control solid (record GP-ID) and label these as LCSS-ICP/FLAA and as LCSS-Furnace.

5.1.7 To all beakers, add 10ml of 8M nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample on a hot plate in the fume hood to 95°C (± 4°C) and reflux for 10 minutes without boiling. Allow the sample to cool, add 5ml of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Repeat this step. Do not allow the volume to be reduced to less than 5ml while maintaining a covering of solution over the bottom of the beaker. Check the temperature achieved during the digestion with a beaker containing 50ml ASTM type II water. Record temperature in digestion log.

5.1.8 After the second reflux step has been completed and the sample has cooled, add 2ml of Type II water and 3ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate to warm to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

5.1.9 Continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10ml 30% H_2O_2.)

5.1.10 Final reflux, cooling and transfer.

5.1.10.1 Furnace Analyses [1]

When the sample is being prepared for furnace analyses of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, Sb, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5ml, add 10ml of Type II water, and warm the mixture. After cooling, filter sample through Whatman No. 41 filter paper (or equivalent) using disposable funnel and dilute to 100ml with Type II water (or centrifuge the sample). NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO_3. Transfer to 250ml plastic sample bottle and label with GP work order, fraction, SFN (for soil matrix, furnace digestion) and date of digestion. Date of digestion may be put on the box of digestates instead of on each bottle. For analysis, withdraw aliquots of approximate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

5.1.10.2 Flame Analyses [1]

When the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl,

---

[1] - As in the acid digestion for aqueous samples procedures, remember to pre-wet filter with 1% nitric acid and to mix samples completely between volumetric flasks and sample bottle containers (See comment concerning this in SOP 11.1 and 11.2). See Standard Operating Procedure for Acid digestion of aqueous samples for furnace or ICP/flame analysis.

V, and Zn, add 5ml of concentrated HCl and 10ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 15 minutes. After cooling, filter through Whatman No. 41 filter paper (or equivalent) using disposable funnel and dilute to 100ml with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Transfer the sample diluted sample to a 250ml plastic sample bottle labeled with the GP work order, fraction, SFL (for soil matrix and flame/ICP digestion) and date of digestion. Date of digestion may by put on the box of digestates instead of on each bottle. The sample is now ready for analysis.

6.0 QUALITY CONTROL

6.1 Troubleshooting and corrective action.

6.1.1 The furnace, ICP and flame AA operators should report to his/her supervisor and lab manager any recoveries outside warning limits for LCS samples for analytes being determined. Sample recoveries for any element which are outside of the control established limits for the laboratory control sample, are deemed unacceptable. The digestion batch must be redigested for those analytes. Document the incident on a redigestion form and submit to supervisor.

Other items pertaining to quality control are addressed in Section V.

7.0 SAFETY

7.1 Safety equipment required

- Fume hood - minimum flow of 100 linear feet/minute
- Safety glasses
- Safety gloves (unpowdered)
- Lab apron
- Face shield if necessary

7.2 Potential hazards

The most hazardous chemical acids that laboratory personnel are likely to encounter are strong acids such as Hydrochloric Acid and Nitric Acid (HNO_3).

7.3 Special handling requirements

Analysts should always read the label on the bottle. Chemicals require handling with care to include wearing adequate garments for skin protection. Also, acid use should be performed under a ventilated hood.

8.0 DISPOSAL REQUIREMENTS

8.1 Acid wastes should be placed into the acid waste bottle which is located under the sink in the metals digestion lab. Any remaining samples should be returned to sample control. More details concerning disposal characteristics and procedures can be located in the SOP 9.1 "Analytical Division Laboratory Waste Handling and Disposal Procedure".

9.0 REPORTING REQUIREMENTS

9.1 Documentation to include Work Orders and Work Sheets (see SOP 7.3, Sample Logging and Record Keeping), Sample Description Forms/Digestion Log Forms (Figure 1), must be submitted to the Metals Supervisor with the Digestion Technician's initials and the preparation date documented on each form for each case.

9.2 Sample Description Forms must be filled out for any work order of type VI or VII (see comment section on work order) and should contain the following information for aqueous digestates. The fields for color and clarity, before and after digestion, must be completed. The following descriptive terms are recommended:

Color - red, blue, yellow, green, orange, violet, white, colorless, brown, grey, black

Clarity - clear, cloudy, opaque

Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the Comments section. Enter any sample-specific comments concerning the analyte results in the comments section.

9.3 Metal Digestion Log Forms must be documented completely by the Digestion Technician during digestion include the date of digestion, work order number, client name, digestion technician signature, digestion supervisor approval, identification of method or SOP used, client ID, GP fraction ID, sample matrix

(soil/water), amount of sample used in digestion and final volume of sample, identification of the matrix spiking solution used and the amount used.

A copy of this log is filed in the metals laboratory for the metals analyst access.

9.4 QC records are maintained in the form of control charts to document percent recovery of analytes from EPA ICV and independent laboratory control samples subjected to the digestion procedure. See SOP 3.12, Quality Control Charts for more information.

Figure 1

Metals Digestion Form

GP Environmental Services Metals Preparation & Sample Description Log

Date: SOP No.: Method: Document Control No. GP310 Batch No.: 535

Analyst: Comments:

Reviewed: Comments:

	GP Work Order No.	Frac	SIZE mL or g	Final Vol. (mL)	Matrix S, W Other	Reported Client ID (Six characters)	Color Before Red, Blue, Yellow, Green, Violet, Grey, White, Colorless, Cloudy, Brown, Black	Color After	Clarity Before or Soil Texture	Clarity After Clear, Cloudy, Opaque	Soil Artifacts or water pH
1											
2											
3											
4											
5											
6											
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26											

Standards Traceability: List LCS and Spiking solutions & Amount Below:

LCS Source:

Spiking Source & Amount (ml):

Temp(C):

List Reagent Manufacturer & Lot# Below:

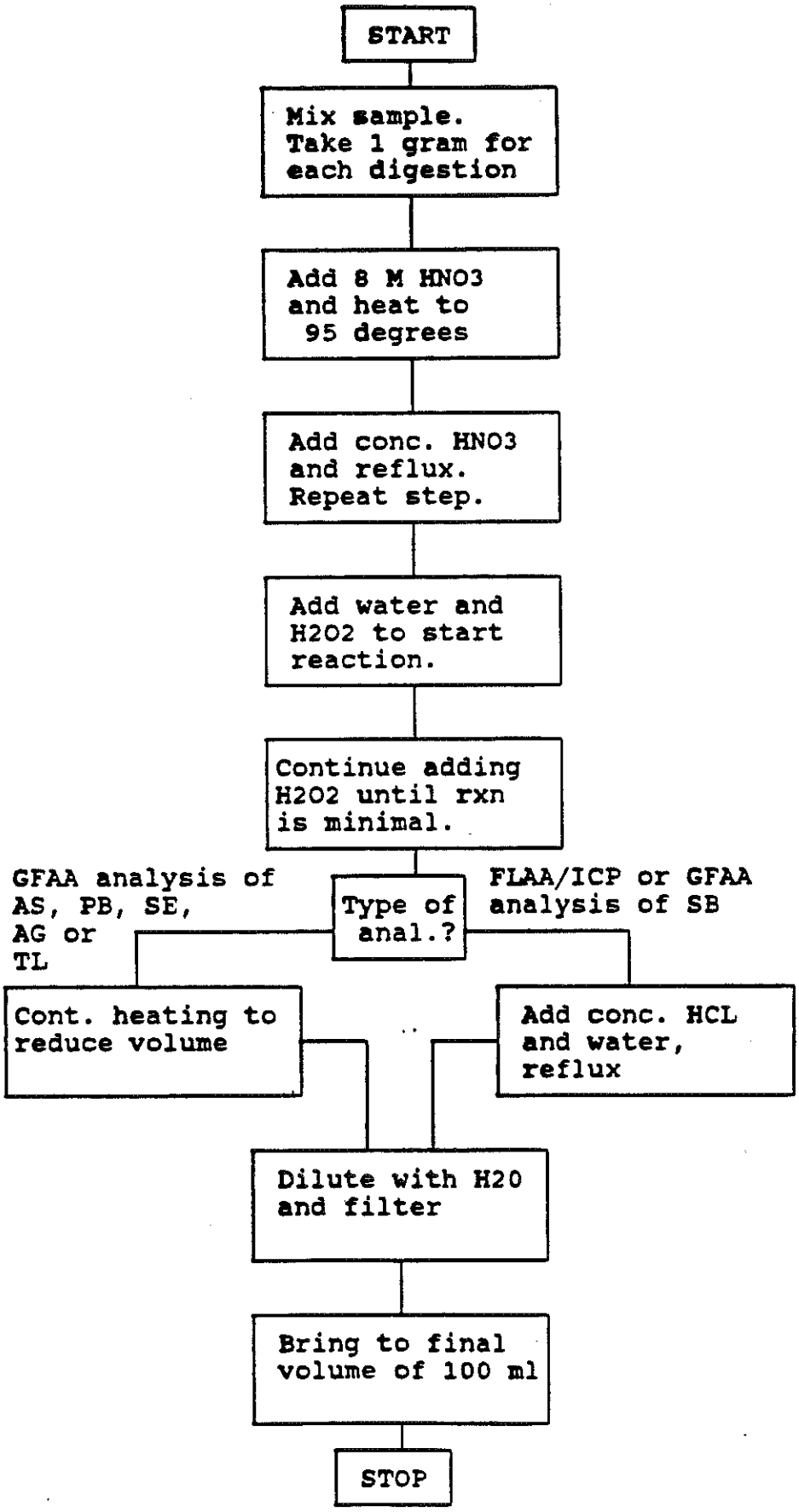
HNO3:

HCl:

Peroxide:

_____:

Figure 2


START
Mix sample. Take 1 gram for each digestion
Add 8 M HNO3 and heat to 95 degrees
Add conc. HNO3 and reflux. Repeat step.
Add water and H2O2 to start reaction.
Continue adding H2O2 until rxn is minimal.
Type of anal.?
GFAA analysis of AS, PB, SE, AG or TL
FLAA/ICP or GFAA analysis of SB
Cont. heating to reduce volume
Add conc. HCL and water, reflux
Dilute with H20 and filter
Bring to final volume of 100 ml
STOP

SOP No: 11.39

Title: Cold Vapor Analysis for Mercury in Accordance with SW846 Methods 7470A and 7471A.

Scope: The method detailed in this procedure explains the analysis of mercury in water, soil, sediment and TCLP extracts, by the Manual Cold Vapor Technique in accordance with SW 846 methods 7470A and 7471A.

1.0 PURPOSE

1.1 To quantify both organic and inorganic forms of mercury in water, TCLP extracts, soil and sediment. The sample holding time is 28 days from sample collection. Sample digests containing mercury concentrations greater than the highest calibration standard will be diluted.

2.0 REFERENCES

- SW846 method 7470A and 7471A.
- Leeman Labs PS200 Manual, Leeman Labs, Inc., Lowell, MA, Part No. 150-00018.

3.0 EQUIPMENT AND SUPPLIES

3.1 Mercury Digestion Equipment

- 300mL BOD bottles with glass stoppers
- hot plates
- hot water bath trays
- 5000μL pipet with tips (Oxford)
- 1000μL pipet with tips (Eppendorf)
- 100μL pipet with tips (Eppendorf)
- 5mL disposable cups (plastic)
- 100mL graduated cylinders, class A
- balance capable of accurately measuring 0.200 grams (± .001g)
- squirt bottle filled with deionized water
- squirt bottle filled with 2% nitric acid
- squirt bottle filled with 10% hydrochloric acid
- Parafilm squares for mixing standards in volumetric flasks
- thermometer traceable to NIST, alcohol based.

3.2 Leeman Labs Automated Mercury Analyzer, Model PS200

3.3 Air source capable of delivering 1 liter of air per minute, argon source.

4.0 REAGENTS

- Concentrated Nitric Acid, Trace Metals Grade.
- Concentrated Sulfuric Acid, Trace Metals Grade.
- Concentrated Hydrochloric Acid, Trace metals Grade.
- Potassium Permanganate solution, 5% w/v. Dissolve 50g Potassium Permanganate to a final volume of 1 liter of distilled water.
- Potassium Persulfate solution, 5% w/v. Dissolve 50g Potassium Persulfate to a final volume of 1 liter of distilled water.
- Stock Mercury solution, 1μg/mL, traceable to NBS standard reference materials. (Source: High Purity Standards, Charleston, SC).
- Stannous chloride (10%). Dissolve 100g of Stannous chloride to 1 liter of 10% HCl. [Leeman requires the use of 10% Stannous chloride in 10% HCl, DO NOT SUBSTITUTE stannous sulfate or sulfuric acid as described in the EPA method.]
- 10% Hydrochloric acid. To a 20L HDPE carboy, add 10L deionized water, then add 2000mL of concentrated hydrochloric acid. Add deionized water to 20L final volume, cap container and mix. Record initials, date of preparation, and lot number of acid on side of carboy.
- Deionized water ASTM Type II or equivalent.
- Sodium chloride - Hydroxylamine sulfate solution - Dissolve 12g of sodium chloride and 12g of hydroxylamine sulfate in deionized water and dilute to 100ml (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate).
- Mercury scrubber solution - 0.1N Potassium Permanganate in 10% Sulfuric Acid, or 0.25% Iodine in a 3% Potassium Iodide solution.
- ICV Solution, Laboratory Control Sample Solid.(ICVE from High Purity Standards, Charleston, SC; LCSS from Environmental Resource Associates, Arvada, CO.)

5.0 PROCEDURE (See Figure 5 for flow chart)

5.1 Preliminary Preparations.

5.1.1 Read workorders and test sheets for assigned samples, noting which samples are selected for duplicate and spike analysis. Review special instructions and submit sample request form to sample receiving for assigned samples.

5.1.2 Obtain samples from sample receiving and verify the identity of each sample. Record in the Mercury Digestion Log Form the date of digestion, analyst initials, and make an entry for each sample assigned (workorder-sample-fraction, and client ID) using one line for each sample, standard, quality control check standard, blank, duplicate, spiked sample, and laboratory control sample.

5.1.3 Prepare BOD bottles for each entry by writing with permanent ink on the outside of the bottle the workorder number, the sample number, and fraction--for duplicate of spikes, using "DUP" and "SPK".

5.2 Sample Digestion for Waters/TCLP Extracts

5.2.1 In the metals digestion lab measure 100.0mL of water or leachate sample into a clean, 100mL graduated cylinder and transfer sample into a clean, labelled 300mL BOD bottle. Stopper the BOD bottle, replace onto spill cart.

5.2.2 In the hood, to each bottle, add 5.0mL of concentrated sulfuric acid, 2.5mL of concentrated nitric acid, and 15mL of 5% potassium permanganate solution. Mix sample after each addition. After the first 3 reagents have been added let the samples sit for 15 minutes. If a sample does not retain a purple color after sitting for 15 minutes, add additional potassium permanganate in 8mL increments until the sample is able to sit for 15 minutes without losing color. Do not add more than 32mL of potassium permanganate to any sample. Record the amount of permanganate added, if additional permanganate was required into the digestion log.

Note: If additional permanganate is added, the final volume must be changed accordingly on the bench sheet for correct final calculation of results.

5.2.3 Add 8mL of 5% potassium persulfate solution to each sample.

5.2.4 Set up water bath and pre-heat to 95°C using a NBS traceable thermometer to check temperature. Cover the pan with the heat retention plastic balls. When water bath has reached the correct temperature, record temperature in digestion log, and place bottles in water for 2 hours.

5.2.5 Remove samples from water bath and allow samples to cool to room temperature. Add 6mL of Sodium Chloride Hydroxylamine Hydrochloride solution and swirl bottle to mix so that all traces of permanganate will be reduced. [Caution: the addition of this solution produces an effervescence which could cause back-pressure build up and force out the glass stopper. After adding the hydroxylamine to the sample, let the pressure vent off by removing the glass stopper periodically.]

5.2.6 Samples are ready for analysis.

5.3 Sample Digestion for Soils and Sediments

5.3.1 Use an analytical balance to measure a representative 0.500-1.00g soil, or sludge, Laboratory Control Sample - Solid or sediment sample into a small weigh boat. Wash the sample into a clean, labelled 300mL BOD bottle using a minimum of distilled water dispensed from a squirt bottle. Stopper the BOD bottle. When all samples have been measured, return the unused portion of sample to sample receiving, then transport the measured portion of sample to the high concentration lab.

5.3.2 Add 5mLs of concentrated sulfuric acid, and 2.5mL of concentrated nitric acid to the sample, mixing after each addition. Heat sample for 2 minutes at 95°C.

5.3.3 Allow bottles to cool. Add 55mL of distilled water, 15mL of potassium permanganate, and 8mL of potassium persulfate to each bottle. If a bottle turns clear or yellow within 15 minutes, add 8mL of potassium permanganate. Add potassium permanganate in 8mL aliquots until purple color persists for 15 minutes. Heat samples in water bath in hood in the high concentration room for 30 minutes.

5.3.4 Allow samples to cool to room temperature. Add 6mL of Sodium Chloride Hydroxylamine Hydrochloride solution to reduce the excess permanganate.

5.4 Standards and QC Preparation

5.4.1 10ppm Hg intermediate stock in 2% HNO_3. Pipet 0.5000ml of 1000ppm Hg stock standard into a 50ml volumetric flask. Add 2% HNO_3 to a final volume of 50ml.

5.4.2 0.1ppm (100ppb) Hg working solution. Pipet 1ml of 10ppm Hg intermediate stock standard into a 100ml volumetric flask. Add 2% HNO_3 to final volume of 100ml.

Standards for Water Samples.

5.4.3 5.0ppb Calibration standard. Pipet 5.0ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.4 2.0ppb Calibration standard. Pipet 2.0ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.5 1.0ppb Calibration standard. Pipet 1.0ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.6 0.5ppb Calibration standard. Pipet 0.5ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.7 0.1ppb Calibration standard. Pipet 0.1ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.8 0.2ppb CRA standard. Pipet 0.2ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

5.4.9 Calibration blank. Add 100ml 2% HNO_3 using a graduated cylinder into BOD bottle.

5.4.10 ICV working solution (0.1ppm) Pipet 0.100ml of ICV solution (100ppm) into a 100ml volumetric flask. Dilute to volume with 2% HNO_3.

5.4.11 ICV check solution (2.5ppb) Pipet 2.500ml of working solution (0.1ppm) into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Final concentration is 2.5ppb. Transfer into BOD bottle.

5.4.12 ICB check solution. Add 100ml 2% HNO_3 using a graduated cylinder. Transfer into BOD bottle.

5.4.13 Preparation Blank for Water. (PBW) Add 100mL deionized water using graduated cylinder into BOD bottle.

5.4.14 Laboratory Control Sample (LCSW) Add 100mL deionized water using graduated cylinder to BOD bottle. Spike with 1.0mL of 0.1ppm Working standard.

Standards for Soil Digestion.

5.4.15 Pipet 0, 0.1, 0.5, 1.0, 2.0, and 5.0mL aliquots of 0.1ppm Working standard directly into BOD bottle. Add 5.0, 4.9, 4.5, 4.0, and 3.0ml compensating volumes of 2% HNO_3. Additional, pipet 0.2 mL of 0.1ppm Working standard for CRA and 4.8mL 2% HNO3.

5.4.16 ICV for soils: Pipet 2.5mL of 0.1ppm working solution and 2.5mL of 2% HNO_3.

5.4.17 Preparation Blank. Pipet 5.0mL of DI water.

(note: during the digestion, use only 50ml of ASTM type II water during step C.3 for the standards to compensate for the volume of water added in the beginning.

5.5 Tuning and Calibration of Instrument PS200.

5.5.1 Maintenance: change wash bath (daily), change drying tube filled with coarse magnesium perchlorate (daily), check pump tubing (replace weekly), reductant level, and waste vessel.

5.5.2 Change Wash bath: Press F10 to interrupt overnight macro. Press Utilities, Diagnostics, then select "tip home" with cursor keys and press enter (autosampler tip will move up allowing water bath to be removed). Pour off old wash acid into disposal container, rinse with tap water, clean with soap, fill with 1:1 nitric acid for leaching for 1 hour, rinse with DI water, and refill with 10% HCl acid. Replace water bath and press F1, Instrument, Tip to rinse.

5.5.3 Replace Drying tube: Remove wash bath (see above), Pull off end caps, and remove drying tube. Immerse tube in water to remove unused magnesium perchlorate, discard old quartz wool. Clean tube thoroughly, dry, and repack with quartz wool and magnesium perchlorate. Verify that particles of magnesium perchlorate can not enter the small tubing, thereby impeding the flow of gas creating back-pressure. Check pump tubing: Remove cassette from pump housing. Replace tubing on weekly basis.

5.5.4 Run macro "warmstrt": press F2, type "WARMSTRT" and press enter.

5.5.5 Run test optics macro after "warmstrt", Utilities, Diagnostics, select TEST OPTICS using cursor keys, press enter. The readings in microvolts should be within 1000 of each other and both should be above 450000. Imbalances can be adjusted using the aperture adjustment screws located on the cell. If the test optic value for the sample tube is greater than the reference tube, screw in the aperture for the sample tube (bottom screw) to block a portion of light and recheck as necessary until both are within 1000 of each other. Record final readings on instrument use log.

5.5.6 Data Storage. Set up file to receive data. Press Data, Folder, enter the name of folder then press enter. A batchname can be used to separate runs within a folder. Press F1, F4 to enter reports submenu, then press H for batcH, at prompt enter new batch name, then press enter. All results will be associated with this name for later retrieval for importing into the laboratory's database.

5.5.7 Instrument Calibration. Load standards onto standards rack, run "CAL6PT" macro, press F2, type CAL6PT, press enter. Instrument will now run standards 1 to 6 in triplicate. If curve linearity is greater than .998, and the deviation of blank is within 0.1ug/L, press A to accept the curve and press F3 to print out calibration curve.

5.5.8 Verify calibration with check standard and check blank. Load ICV solution into standard rack position C2, and check blank into C3. Press F6, then press 2 to run check standard 2 (ICV), then press F6, 3 to run check blank. If results are within control limits of 80 -120%, set frequency of the check samples to 10% and the instrument will automatically run check sample 2 and then check sample 3 every 10 samples.

5.5.9 Rack Entry: Press Autosampler, Rack Entry, type in initials then month, day, and a letter in the following format XXMMDDA. (If more than one rack will be prepared, use XXMMDDB.) At the prompt reply Y for new rackfile and begin entering sequence of tubes. Note that the weight and volumes fields will not be used (size and volume will be entered in a post-run file.)

5.5.10 Set up autosampler. Press F1, Autosampler, Set up, press 1, then enter name of rackfile for rack 1, then enter starting position and ending position. Press F8, then F8 again to begin autosampler run.

Trouble Shooting Guide. Refer to Leeman Labs Manual.

6.0 QUALITY CONTROL

6.1 Any results that exceed the highest calibration standard are diluted and reanalyzed. (LR = highest calibration standard)

6.2 The mercury auto-analyzer is capable of detecting parts per trillion levels of mercury when optimized. However, the laboratory reports to MDL.

6.3 Calibration standards must be prepared fresh daily from stock standards. The deviation of each standard must be within 5% of the standard's concentration or the run must be terminated and the instrument recalibrated. The correlation coefficient must be ≥ .995 or the run must be terminated and the instrument recalibrated.

6.4 Initial Calibration Verification Check solution. An ICV solution is prepared from an independent standard as the calibration standards are prepared. This solution is then digested with the samples and is the 1st check standard to be run. If recovery is outside 80-120% window, the run terminates. Recalibrate and rerun the ICV and ICB.

6.5 Continuing Calibration Check solution. The ICV solution is used as the CCV solution.

6.6 Initial and Continuing Blank Solution. A blank solution, separate from the calibration blank, is digested with the standards and analyzed at after each ICV and CCV. Criteria is +/- 0.2ug/L.

6.7 CRA solution. A solution of 0.2ug/L Hg is prepared as calibration standards are being prepared and is analyzed at the beginning of the run following the ICB.

6.8 Preparation Blanks are digested exactly as the samples. The same type of container, utilization of the same amount of reagents, and are assigned to the same digestion batch. The blanks are placed in sequence every twenty samples. Criteria is +/- 0.2 ug/L.

6.9 Laboratory Control sample. A blank solution is spiked at 1.0ug/L to check the spiking procedure and the digestion process. Acceptance criteria is based on statistical control charting for warning limits.

6.10 Spike Sample. 8mL of sample is spiked with 0.08mL of 0.1ppm Hg standard before addition of reagents or digestion. One spike is prepared every 20 samples of the same matrix. If the matrix spike is outside 75-125% criteria a post digestion spike must be analyzed. It also must be noted in the case narrative. If the sample is sufficiently high enough, a serial dilution should also

be performed when the matrix spike is outside criteria to detect interferences.

6.11 Post digestion spike - This is performed if the matrix spike is outside the criteria. The post digestion spike should fall within the midrange of the calibration curve and should be within 75-125%. If the post digestion spike is outside criteria and the sample result is above the reporting limit an MSA should be performed to quantify the result. The MSA should be used for all samples of similar matrix within the batch.

6.12 Serial Dilution - A serial dilution is performed if the matrix spike is outside criteria if the sample is sufficiently high > 1 ug/L. Dilute the sample 1:4 by pipetting 2mls of digested sample into a sample cup and adding 6ml of DI H_2O. The percent difference should be 10% or less. If the serial dilution is outside criteria an MSA should be performed to quantify the result. The MSA should be used for all samples of similar matrix within a batch.

6.13 MSA - An MSA is used to quantify results if the matrix spike and post digestion or serial dilution fall outside criteria. To perform an MSA, pipette 5ml of digested sample into four sample cups. Spike the second, third and fourth cups with 1/2 , 1 & 1 1/2 times the inherent sample concentration then add compensating water to have all cups at same volume. For example, if the one sample concentration is 2ppb, spike it with 1,2 & 3ppb respectively. Perform a linear regression to quantify the result using the four points. The correlation coefficient should be > 0.995. If the correlation coefficient is < 0.995, rerun the MSA once.

6.13 Duplicate. One duplicate every twenty samples will be performed. The duplicate is prepared before addition of any reagents or digestion.

7.0 SAFETY

7.1 Gloves, safety glasses, and lab coat must be worn when performing any aspect of the mercury digestion or analysis process.

7.2 Mercury vapor is toxic. Caution should be taken during all phases of the digestion and analytical process. Care should be exercised so that mercury has no chance to be absorbed through the skin or inhaled.

7.3 The acids used to digest mercury are used full strength. Extreme care should be taken so that acid does not spill or splash. Transport samples and empty bottles on one of the 3 high concentration room spill carts. Transport acid using the 4 liter plastic carrying buckets.

7.4 Additional safety equipment includes mercury sponges, acid neutralization media, shoe and leg splash protection, a mercury scrubber, and face shield.

8.0 DISPOSAL REQUIREMENTS

8.1 Collect all waste acid, samples, and standards into 20 liter plastic carboys or similar vessels and transport to waste disposal when container is 3/4 full for pour-off into 55 gallon drums (lined with polyethylene).

8.2 The main disposal concern of mercury digestates is the corrosivity and toxicity characteristics of mercury. The content of the waste can be as high as 30% acid. Varying concentrations of mercury will be present in the digestates and will be determined by waste disposal characteristic procedures prior to release to a disposal company.

9.0 REPORTING REQUIREMENTS

9.1 In addition to the accurate reporting and handling of raw data, there are records that need to be maintained for internal auditing purposes.

9.1.1 Before analysis is completed, record on the raw data the date of analysis, the analyst, the Mercury standard's source, lot number, and GP ID, the ICV's number, and GP ID, the LCSS's number and GP ID, a list of the cases included in the run, and the instrument upon which the analysis was performed. Note the source for the spike used in the matrix spike sample and % Recovery for the spike in the raw data.

9.1.2 Complete the Bench Sheet for Mercury with the following information: Instrument ID, Date of analysis, Analyst name and signature, Time analysis was initiated, case and SDG, work order numbers, sample sequence run, dilution factors and comments.

9.1.3 Complete the Instrument Use Log with the following information: Date, Method, Case, Analyst and Comments.

9.1.4 If maintenance or repair was required on the instrument, all relevant information must be recorded in the Maintenance Log. This Log will be maintained with all field service reports for each instrument.

Figure 1
Mercury Digestion Log

GP Environmental Services Mercury Digestion Log

Date of Digest: Method: Page No.: 251 of

Analyst: Filename: Document Control No.: GP138

Reviewed:- Water Bath Temp: Holding times OK? Y / N

GP Workorder	Frac	Client ID	Matrix	SIZE mL g	VOL (mL)	Spk.A. (mL)

Comments: Spiking Solution Conc:

Figure 2
Bench Sheet

BENCH SHEET
EG

95-07-175
115
104

95-07-133
9507-N1
07-097
07-148

Page 1

DATA FILE: AK72895
INSTRUMENT FILE: B:AK72895.PRN
CASE:
INSTRUMENT: PE200
SDG:
ANALYZED: 07/28/95

SEQ	LAB ID	CLIENT ID	MATRIX	DILUTION	SIZE	VOLUME	SOLIDS	ANALYZED	
1	CALBLANK	S0	WATER	1.00	100.000	100.000	100.00	07/28/95	15:33:33
2	0.1 ppb	S0.1	WATER	1.00	100.000	100.000	100.00	07/28/95	15:41:51
3	0.5 ppb	S0.5	WATER	1.00	100.000	100.000	100.00	07/28/95	15:50:06
4	1.0 ppb	S1	WATER	1.00	100.000	100.000	100.00	07/28/95	15:58:24
5	2.0 ppb	S2	WATER	1.00	100.000	100.000	100.00	07/28/95	16:06:43
6	5.0 ppb	S5	WATER	1.00	100.000	100.000	100.00	07/28/95	16:15:01
7	ICV	ICV	WATER	1.00	100.000	100.000	100.00	07/28/95	17:12:04
8	ICB	ICB	WATER	1.00	100.000	100.000	100.00	07/28/95	17:14:48
9	CRA	CRA	WATER	1.00	100.000	100.000	100.00	07/28/95	17:35:03
10	PBW	PBW	WATER	1.00	100.000	100.000	100.00	07/28/95	17:37:44
11	PBW2	PBW2	WATER	1.00	100.000	100.000	100.00	07/28/95	17:40:25
12	LCSW	LCSW	Water	1.00	100.000	100.000	100.00	07/28/95	17:43:06
13	LCSW2	LCSW2	Water	1.00	100.000	100.000	100.00	07/28/95	17:45:47
14	9507175-02A	W-1(FILTERED)	WATER	1.00	100.000	100.000	100.00	07/28/95	17:48:28
15	9507175-02AD	W-1(FILTERED)D	WATER	1.00	100.000	100.000	100.00	07/28/95	17:51:09
16	9507175-02AS	W-1(FILTERED)S	WATER	1.00	100.000	100.000	100.00	07/28/95	17:53:50
17	9507115-04A	A4 NOVOC	WATER	1.00	100.000	100.000	100.00	07/28/95	17:56:31
18	9507115-04AD	A4 NOVOCD	WATER	1.00	100.000	100.000	100.00	07/28/95	17:59:12
19	CL2	CCV1	Water	1.00	100.000	100.000	100.00	07/28/95	18:01:55
20	CL3	CCB1	Water	1.00	100.000	100.000	100.00	07/28/95	18:04:38
21	9507115-04AS	A4 NOVOCS	WATER	1.00	100.000	100.000	100.00	07/28/95	18:07:20
22	9507115-08A	B4 MT.	WATER	1.00	100.000	100.000	100.00	07/28/95	18:10:01
23	9507115-12A	C4 LING.	WATER	1.00	100.000	100.000	100.00	07/28/95	18:12:40
24	9507104-01E	E15-BU20-00-004	WATER	1.00	100.000	100.000	100.00	07/28/95	18:15:19
25	9507104-01ED	E15-BU20-00-004D	WATER	1.00	100.000	100.000	100.00	07/28/95	18:17:58
26	9507104-01ES	E15-BU20-00-004S	WATER	1.00	100.000	100.000	100.00	07/28/95	18:20:37
27	9507104-02A	E15-BU20-00-005	WATER	1.00	100.000	100.000	100.00	07/28/95	18:23:16
28	9507104-03E	E15-BU20-00-002	WATER	1.00	100.000	100.000	100.00	07/28/95	18:25:55
29	9507104-04A	E15-BU20-00-003	WATER	1.00	100.000	100.000	100.00	07/28/95	18:28:34
30	9507104-06E	E15-BU20-00-006	WATER	1.00	100.000	100.000	100.00	07/28/95	18:31:14
31	CL2	CCV2	Water	1.00	100.000	100.000	100.00	07/28/95	18:33:54
32	CL3	CCB2	Water	1.00	100.000	100.000	100.00	07/28/95	18:36:39
33	9507104-07A	E15-BU20-00-007	WATER	1.00	100.000	100.000	100.00	07/28/95	18:39:20
34	9507104-08E	E15-BU20-00-008	WATER	1.00	100.000	100.000	100.00	07/28/95	18:42:00
35	9507104-09A	E15-BU20-00-009	WATER	1.00	100.000	100.000	100.00	07/28/95	18:44:39
36	9507104-10E	E15-BU20-00-010	WATER	1.00	100.000	100.000	100.00	07/28/95	18:47:16
37	9507104-11A	E15-BU20-00-011	WATER	1.00	100.000	100.000	100.00	07/28/95	18:49:53
38	9507133-01E	E15-BU01-00-038	WATER	1.00	100.000	100.000	100.00	07/28/95	18:52:31
39	9507133-01ED	E15-BU01-00-038D	WATER	1.00	100.000	100.000	100.00	07/28/95	18:55:09
40	9507133-01ES	E15-BU01-00-038S	WATER	1.00	100.000	100.000	100.00	07/28/95	18:57:48
41	9507133-02A	E15-BU01-00-039	WATER	1.00	100.000	100.000	100.00	07/28/95	19:00:27

A. Kiecke AK 7/30/95
Analyst / Date

7/31/95
Lab Supervisor / Date

Figure 3
Instrument Use Log

GP ENVIRONMENTAL SERVICES
MERCURY RUN LOG: PS200

DATE_____ STD SOURCE_____ WORK ORDER # / FRACTION

PROTOCOL_____ FOLDER_____ _____/_____

BATCH NAME_____ CHKSTD SRC _____ _____/_____

TEST OPTICS: SAMPLE_____ REF_____ _____/_____

RACK1 _____ RACK2_____ _____/_____

MAINTENANCE _____ _____/_____

ANALYST'S NAME_____ _____/_____

COMMENTS_____ _____/_____

DATE_____ STD SOURCE_____ WORK ORDER # / FRACTION

PROTOCOL_____ FOLDER_____ _____/_____

BATCH NAME_____ CHKSTD SRC _____ _____/_____

TEST OPTICS: SAMPLE_____ REF_____ _____/_____

RACK1 _____ RACK2_____ _____/_____

MAINTENANCE _____ _____/_____

ANALYST'S NAME_____ _____/_____

COMMENTS_____ _____/_____

DATE_____ STD SOURCE_____ WORK ORDER # / FRACTION

PROTOCOL_____ FOLDER_____ _____/_____

BATCH NAME_____ CHKSTD SRC _____ _____/_____

TEST OPTICS: SAMPLE_____ REF_____ _____/_____

RACK1 _____ RACK2_____ _____/_____

MAINTENANCE _____ _____/_____

ANALYST'S NAME_____ _____/_____

COMMENTS_____ _____/_____

Figure 4
Maintenance Log

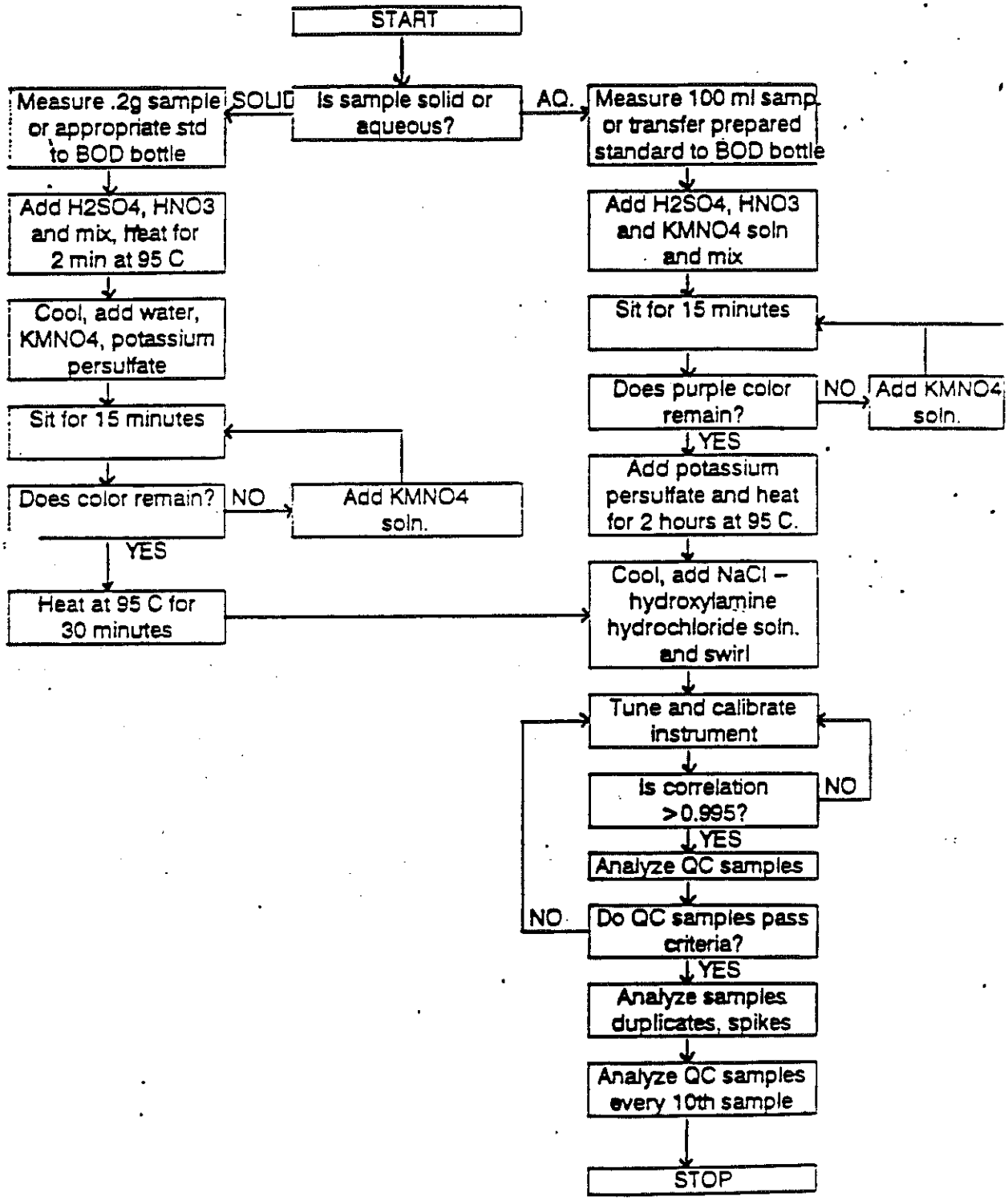
General Physics Environmental Services

Instrument Maintenance Logbook Document Number: GP_M_006

Instrument PS200

Date	Maintenance Performed	Performed By	Reviewed By
7/11/97	Preventive Maintenance: Clean optic cell, Lens and flush pump tubing with 1:1 HNO_3	CS	DH
	Flush PS200 with 20% HNO_3 for 15min		
	Rinse w/ 10% HCL for 20mins.		
7/22/97	Cleaned contacts on PS200's computer	CS	DH
	boards w/ eraser. Re-installed softwear.		
	Guy S. fixed cable from PS200 to Computer		
	(Problem... Halt 125 Sub. 99). Ran		
	standards in folder "Check" to see if PS200		
	needed to be restarted from "Warmstart".		
8/13/97	Flushed PS200 with 20% HNO_3 for 15min	CS	DH
	Rince w/ DI water 20mins then 10% HCL		
	for 30min till "~~Shutdo~~ Overnite" kicked in		
8/15/97	Changed Pump ~~tube~~ tubing and tips due	CS	DH
	to drop in preformance. Optic test passed		
	and remained at same intensity as start		
	of run. Staining Reductant was remade		
	and PS ~~200~~ 200 was rinsed w/ 50% HNO_3		
	and then rinsed w/ DI left to sit over		
	weekend		
9/5/97	clean optic cell and lenses	D.D.H.	CS
9/23/97	Clean Optic Cell and lenses, change lamp.	DDH	DH

Figure 5
Procedure Flow Chart



GP ENVIRONMENTAL SERVICES

Effective Date: October 1997
Version Number: 6
Initiated By :
Approved By :

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SOP No: 11.46

Title: Cyanide, Total (colorimetric, manual distillation)

Scope: This Standard Operating Procedure describes the distillation and analysis of water and soil samples for Total Cyanide in accordance with SW846 method 9010A.

1.0 PURPOSE

1.1 This method detailed the procedure to determine inorganic cyanide in water, wastewater, soils and leachates. The colorimetric method is suitable for concentrations between 5 and 200 ug/L CN. Samples with higher levels can be diluted to fall within this range.

1.2 Total Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system under acidic conditions and in the presence of magnesium ion. The liberated HCN is absorbed in a scrubber containing NaOH solution. The cyanide in the scrubber solution is converted to cyanogen chloride by reaction with chloramine-T at a pH < 8. Color is formed on the addition of pyridine-barbituric acid. The color is measured at 578 nm. The intensity of the color is proportional to the cyanide concentration.

2.0 REFERENCES

- SW846 method 9010A, Standard Methods for the Examination of Water and Wastewater, Method 4500-CN^- D.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Chlorine and other oxidizing agents can decompose cyanides. To remove these interferences, sodium arsenite or ascorbic acid crystals can be added.

3.2 Sulfide interferences can be removed by adding as excess of bismuth nitrate to precipitate out the sulfide.

3.3 Nitrate and/or nitrite present at levels > 10 mg/L can cause high CN results. They can be eliminated by adding sulfamic acid just before distillation.

3.4 Samples should be preserved with NaOH to a pH >12 when taken, and stored at 4^{oC}. Analysis must be performed within 14 days of sampling.

4.0 EQUIPMENT AND SUPPLIES

- Midi cyanide distillation unit (Kontes or equivalent)
- vacuum source
- cooling water source
- 50ml volumetric flasks
- 50 or 100ml class A graduated cylinders
- sample bottles, >50ml volume (plastic)
- Alpkem RFA 300 automated spectrophotometer (or equivalent) with CN manifold, with recorder; alternately:
- UV/Vis spectrophotometer, 1 cm or longer pathlength, capable of measurement at 578nm
- Fume hood
- Eppendorf and Oxford pipettors (calibrated)

5.0 REAGENTS

- ASTM Type II (or better) water should be used in the preparation of all standards and reagents.

- All chemicals must be ACS reagent grade

- All reagents and standards must be prepared in class A volumetric glassware

5.1 Distillation Reagents:

- NaOH solution (0.25N): Dissolve 20 grams NaOH in water and dilute to 1 liter
- Sulfuric acid: 1:1
- Magnesium chloride solution (2.5M): Dissolve 510 grams of $MgCl_2 \cdot 6\ H_2O$ in water and dilute to 1 liter
- Sulfamic acid (0.4N): Dissolve 40 grams H_2NSO_3H in water and dilute to 1 liter
- Lead acetate test paper
- Potassium iodide-starch test paper
- Ascorbic acid crystals
- Bismuth nitrate solution (0.062M): Dissolve 30 grams Bismuth nitrate in 100ml water. While stirring, add 250ml glacial acetic acid - stir until dissolved. Dilute to 1 liter.

5.2 Semi-automated Colorimetric Reagents:

- Phosphate Buffer: Dissolve 138 grams of $NaH_2PO_4 \cdot H_2O$ in water and dilute to 1 liter. Add 0.5ml Brij-35. Keep refrigerated. Prepare fresh monthly.

- Chloramine-T solution: Dissolve 0.40 grams water soluble chloramine-T in water and dilute to 100ml. Prepare fresh daily.

- Pyridine-barbituric acid color reagent: Prepare in a fume hood. Place 7.5 grams barbituric acid in a 500ml volumetric flask. Rinse down the sides of the flask with just enough water to wet the acid. Add a magnetic stir bar and place flask on a magnetic stir plate. Add, with stirring, 37.5ml pyridine and 7.5ml concentrated HCl. Slowly add 300ml water. Stir until barbituric acid has dissolved. Dilute to 500ml. Store in a dark bottle in the refrigerator. This solution is good for 6 months.

- 0.25N NaOH

- Brij-35 solution: a commercially available wetting agent

5.3 Manual Colorimetric Reagents:

- Phosphate Buffer: Prepare as above in the semi-automated method, but omit the Brij-35.
- Chloramine-T solution: Dissolve 1.0 gram white, water soluble chloramine-T in water and dilute to 100ml. Prepare fresh weekly.
- Pyridine-barbituric acid color reagent: Prepare in a fume hood. Place 15 grams barbituric acid in a 250ml volumetric flask. Rinse down the sides of the flask with just enough water to wet the acid. Add a magnetic stir bar and place flask on a magnetic stir plate. Add, with stirring, 75ml pyridine and 15ml concentrated HCl. Slowly add 300ml water. Stir until barbituric acid has dissolved. Dilute to 500ml. Store in a dark bottle in the refrigerator. This solution is good for 6 months.

- 0.25N NaOH

5.4 Stock Standards:

- 1000mg/L CN stock standard, commercially available with certification, this standard should be titrated weekly to recertify the concentration, see below:
- Separate source free cyanide standard for calibration verification
- Rhodamine indicator: Dissolve 20mg p-dimethylamino-benzal-rhodamine in 100ml acetone
- Standard silver nitrate solution (0.0192N): Commercially available with certification

To standardize the stock: Add 2.0ml CN stock standard to 100ml 0.25N NaOH. Add 0.5 ml rhodamine indicator. Titrate with 0.0192N silver nitrate to the first change in color from canary yellow to salmon.

1.0ml 0.0192N titrant = 1.0mg CN

6.0 PROCEDURE

6.1 Distillation

- Check sample pH, record in appropriate column in distillation log (see figure 1)
- Check sample for the presence of oxidizing agents with a strip of potassium iodide-starch test paper. If the paper turns yellow, place a portion of the sample in a beaker with stirring. Add ascorbic acid crystals until the sample no longer produces a color with the test paper. Record result of test in distillation logbook
- Check sample for the presence of sulfide with a strip of lead acetate test paper. If the paper darkens, treat a portion of the sample with 1.0ml additions of bismuth nitrate solution until a test strip comes out white. Record the result of the test in the distillation logbook.
- Check sample for presence of nitrate and nitrite. If the concentration is >10mg/L, or if bismuth nitrate has been added to remove sulfide interference; add a scoop of sulfamic acid crystals to the sample before distillation.
- If pH is below the required preservation pH of 12, notify supervisor and note in the comments section of the analytical logbook. If treatment to remove oxidizers or sulfide is required, note this in the comments section also. This information must be included in the data package case narrative.
- Set up the distillation apparatus as described in the manufacturers instructions. Start cooling water flowing.
- Place 50ml water sample, or 1.0gram soil in 50ml water, into the sample tube. Place sample tube into the heating unit and connect the inlet tube/condenser assembly to the tube.
- Add 50ml 0.25N NaOH to the absorber jacket and connect absorber to the sample tube. Connect absorber to vacuum source.
- Start a stream of air bubbles entering the boiling flask(sample tube) at approximately 3 bubbles per second. Monitor flow rate as samples begin to boil to ensure continuous airflow INTO the flask.
- If samples contain nitrate/nitrite interference, add 5.0ml sulfamic acid solution through the inlet tube. ALlow to mix for several minutes.

- Slowly add 5ml 1:1 sulfuric acid through the inlet tube. Let mix, then add 2ml magnesium chloride solution. Rinse the tube with a small amount of water.
- Turn on the heating block and set for 123-125^{oC}. Heat the samples to boiling, taking care to monitor airflow. Reflux for 1.5 hours.
- Turn off heat, continue the airflow for 15 minutes while cooling.
- Turn off the vacuum source, disconnect the scrubber and transfer the distillate to a clean plastic sample bottle. Label the bottle with the sample ID, date and analyst's initials. Refrigerate distillates until analysis.

6.2 Sample Analysis, semi-automated colorimetric

- Turn on autoanalyzer and allow to warm up.
- Set up manifold as shown in figure 2
- Filter reagents into erlenmeyer flasks and cover with parafilm. Cut a small slit in the parafilm to place the pump tubing through.
- Place the reagent lines into a wash solution (0.5ml Brij-35/500ml water) and allow the system to run for 10-15 minutes.
- Place the reagent lines into their respective reagents and allow the system to equilibrate and establish a stable baseline.
- "Sampler wash" as shown in figure 2 must be the same as the sample matrix, 0.25N NaOH.
- Prepare a series of standards for a calibration curve from a 10mg/L CN working solution prepared from the CN stock standard:

standard conc (ug/L)	ml working sol/50ml NaOH
0	0
5	0.025
10	0.050
50	0.250
100	0.500
200	1.00

- Transfer a portion of each calibration curve standard into a autosampler cup. The first sampler cup should contain the highest standard to mark the start of the run, then standards should be placed in order of increasing concentration, starting with the blank. After the calibration curve, load the ICV (Initial Calibration Verification; a midrange standard from a source different from the curve), ICB (Initial Calibration Blank), Prep Blank (blank distilled with the samples), and LCS's (distilled

standards). Then load samples, adding a CCV and CCB after every ten sample cups and at the end of the run.

- Set the sampling time to 10 and the wash time to 40 on the autosampler. Start the autosampler and recorder. Dilute any samples with a peak larger than the highest standard. The analytical run must be ended with a CCV and CCB after any sample dilutions (if necessary)
- When analysis is complete, place the reagents lines into the Brij-35 wash solution and allow the system to wash for 20 minutes. Then turn off the system, and unclamp the pump tubing to allow it to drain.
- Plot standard peak height vs concentration and perform a linear regression calculation on the calibration curve. The correlation coefficient must be 0.995 or greater, and the y-intercept must be lower than the lowest standard (method detection limit).
- Calculate sample concentrations from the plotted curve, taking into account any dilutions required.

  For water samples, the concentration in the distillate is equal to the concentration in the original sample if 50ml of sample was used for distillation.

  For soil samples:

$$\text{mg/Kg CN} = \frac{(\text{ug/L CN})(1000)(\text{50ml distillate volume})}{(\text{grams of sample distilled})(\%\text{solids})}$$

- Label all peaks on the printout and record all standard/sample peak heights and required dilutions in the Cyanide Analysis Logbook (figure 3). Label the top of the printout with the analyte, date and time the analysis was started and the analyst's initials.

6.3 Sample Analysis, Manual Colorimetric

- Turn on the UV/Vis spectrophotometer and set the wavelength to 578nm. ALlow to warm up for the manufacturer's recommended time.
- Prepare a series of calibration standards as above in the semi-automated method.
- Add 25ml of standard or sample to a 50ml volumetric flask, or a smaller portion of sample diluted to 25ml with 0.25N NaOH.
- Add 7.5ml of phosphate buffer and mix
- Add 1.0ml chloramine-T solution and mix. Wait 1 - 2 minutes.
- Add 2.5ml pyridine-barbituric acid color reagent and mix.
- Bring the sample/standard up to 50ml volume <u>with water</u>, and mix.

- Allow to develop for 8 minutes, then read absorbance at 578 nm within 15 minutes.
- Zero the spectrophotometer with a reagent blank.
- Plot the calibration curve as above, using standard absorbance vs. concentration.
- Calculate sample concentrations as above.
- Record all standard/sample absorbances and required dilutions in the Cyanide Analysis Logbook (figure 3)

7.0 QUALITY CONTROL

7.1 A distillation batch is defined as up to 15 samples of one matrix plus the associated QC samples listed below that are distilled using separate sets of distillation glassware. If sufficient glassware for this number is not available, batch size is defined as when the apparatus is broken down and washed.

7.2 A reagent blank must be distilled with every batch of samples, or less, per matrix. All preparation blanks will receive a unique ID number which will define one distillation batch. CBLK0001, etc. The result must be less than the detection limit. If the prep blank has a result greater than the detection limit, all samples associated with it must be redistilled.

7.3 All LCS samples will receive unique ID numbers which will define their distillation batch, LCSL0001, etc. Two Laboratory Control Samples (LCS) must be distilled with every batch of samples, or less, per matrix. Soil LCS's must be distilled along with soil samples. One LCS should be at the low end of the curve, and the other near the high end. The LCS recovery must be within 90-110%. If the standards do not meet this recovery, all associated samples must be redistilled.

7.4 The ICV/CCV standard should be prepared from a source different than that from which the calibration curve was prepared. Recovery must be 85-115%. If a CCV fails these limits, all samples after the last <u>passing</u> CCV must be reanalyzed.

7.5 The ICB/CCB samples must be less than half the detection limit.

7.6 One sample duplicate must be distilled and analyzed with every batch of samples, or less, per matrix. The sample and duplicate concentration RPD must be less than 20%, or the samples must be redistilled.

7.7 One matrix spiked sample must be distilled and analyzed with every batch of samples, or less, per matrix. Matrix spike must be added to the sample before any step in the distillation process is begun. The spike concentration should be approximately 40ug/L. Spike recovery should be 75-125%. If the recovery is outside these limits, check for matrix interference by analyzing a post-distillation spike.

8.0 SAFETY

8.1 All distillation and analysis should be performed in a closed system, or under a fume hood. Pyridine is aromatic and a carcinogen.

8.2 Keep all samples and standards away from acids to avoid liberating toxic HCN gas.

8.3 Wear safety glasses, labcoat, and gloves when handling samples and reagents.

8.4 Use special care when handling strong acids and NaOH solutions, and when working around the heated distillation unit.

9.0 DISPOSAL REQUIREMENTS

9.1 All waste should be collected from the analysis in a bottle for Cyanide Waste only. Label the bottle: Cyanide waste; contains pyridine. More details concerning disposal characteristics and procedures can be located in the SOP 9.1 "Analytical Division Laboratory Waste Handling and Disposal Procedure".

10.0 REPORTING REQUIREMENTS

10.1 A Multipro report must be generated for each analytical run. A copy of the Cyanide Analysis Logbook pages and the Cyanide Preparation Log must be attached to the report. If the semi-automated method is used, the recorder printout must be kept in the Cyanide Analysis Logbook, and a copy must be included with the raw data.

10.2 QC records are maintained in the form of control charts to document percent recovery of cyanide from laboratory control samples subjected to the distillation procedure. See SOP 3.12, Quality Control Charts for more information.

Figure 1

CYANIDE DISTILLATION LOG

Approval: _____ DOCUMENT NUMBER

Method: _____ Matrix: _____ Analyst _____

Date: _____

GP Work Order	Dash No.	Client	Client ID	Sample Amt. ml. / gm	PH	Res CL2	Sulfide	Final Vol

H2SO4 Spike ID and Conc.

NaOH LCS

MgCL2

Comments

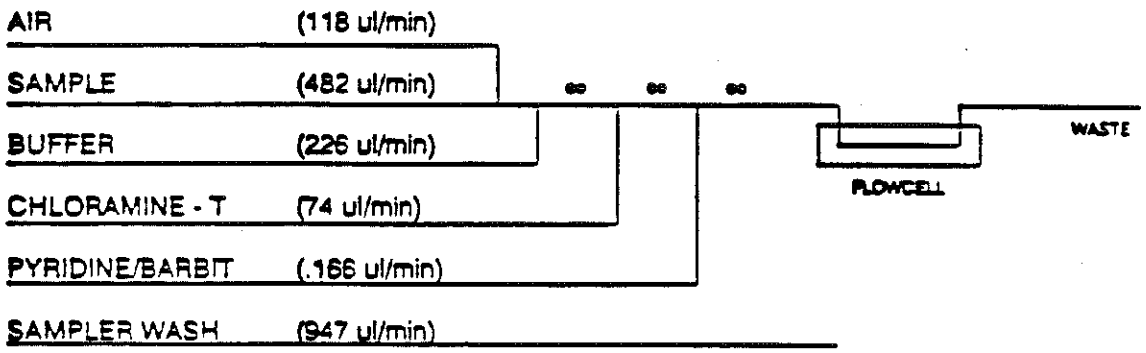
Figure 2

Autoanalyzer Cyanide Manifold

CYANIDE MANIFOLD

335.2 CLP - M

.005 - .200 mg/L CN⁻



AUFS	.5
DAMPING	1s
SAMPLE	34s
WASH	16s
FLOWCELL	12mm
WAVELENGTH	570nm
	COIL 5 TURNS

Figure 3

Cyanide Analysis Logbook

Method Title: Cyanide, Colorimetric, Manual Distillation
Method Reference: _____

Analyst: _____
Date: _____
Reviewed by/Date: _____
Work Order: _____
Work Order: _____
Work Order: _____

Work Order: _____
Work Order: _____
Work Order: _____

I. Instrument/Apparatus: _____

II. Calibration

A. 1000 ppm Stock Cyanide Solution
B. 20 ml Cyanide working standard

Standard	ml of Stock Solution	Final Volume	Absorbance
Calib Blank			
_____ ppm			
_____ ppm			
_____ ppm			
_____ ppm			
_____ ppm			
_____ ppm			

Corr. Coefficient: _____
y - intercept: _____
Slope: _____
Wavelength: _____

III. EPA QC Analysis
QC ID: _____
T.V.: _____
95% C.I.: _____

Found Value:
ICV _____ CCV1 _____ CCV2 _____

% Recovery:
ICV _____ CCV1 _____ CCV2 _____

IV. Duplicate Analysis
Sample ID #1/#2: _____ / _____
Init. Sample Value #1/#2: _____ / _____
Dup. Sample Value #1/#2: _____ / _____
RPD #1/#2: _____ / _____

V. Matrix Spike Analysis
Sample ID #1/#2: _____ / _____
Sample Value #1/#2: _____ / _____
Spike Sample Value #1/#2: _____ / _____
Spike Amount: _____
% Recovery #1/#2: _____ / _____

VI. Comments:

_____

Figure 3

Cyanide Analysis Logbook (Cont)

Method Title: Cyanide, Cobrimetric
Method Reference: _____
Method Detection Limit: _____

Analyst: _____
Date: _____
Reviewed by/Date: _____

RAW DATA

Client ID	CP ID	Sample Vol /Wt	Dilution	Absorbance	Conc	Final Results*

CALCULATION:
1. Prepare a Standard curve by plotting the absorbance of standards versus the corresponding CN concentrations.
2. Obtain concentration value of samples directly from Standard curve.
* Final Results = Dilution Factor X Concentration (if not detected report < _____)

GP ENVIRONMENTAL SERVICES

Effective Date: July 1995
Version Number: 1.0
Initiated By :
Approved By :

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SOP No.: 11.47

Title : Analysis of Water and Soils for Sulfide According to MCAWW Method 376.1 (titrimetric)

Scope : This Standard Operating Procedure describes the method for determination of sulfide for water and soil samples as required by MCAWW Method 376.1 (Titrimetric)

1.0 PURPOSE

This procedure describes the methodology used to determine the sulfide content of samples according to the method described in the Methods for Chemical Analysis of Water and Wastes (MCAWW), Method 376.1 (Titrimetric). The methodology is applicable to drinking, surface, and saline waters, domestic and industrial washes and soil and sediment samples.

2.0 REFERENCES

Methods for Chemical Analysis of Water and Wastes (MCAWW), EPA-600/4-82-055, Method 376.1 (Titrimetric)

3.0. EQUIPMENT AND SUPPLIES

- 10 ml buret, accurate to 0.25 ml
- 125 ml glass Erlenmeyer flask or beaker
- Electronic stir plate and magnetic stir bar

4.0 REAGENTS

6 N HCL (1:1)
Standard iodine solution, 0.0250 N
Standard sodium thiosulfate solution, 0.0250 N
Starch indicator

5.0 PROCEDURE

5.1 Sample holding time and preservation

Water samples which require sulfide analysis must be analyzed within 7 days of collection if zinc acetate is added as a preservative. Unpreserved samples must be analyzed immediately. Soil samples should be extracted within 7 days and the extracts analyzed immediately.

5.2 Standardization of sodium thiosulfate titrant

Add 5.0 ml of the 0.0250 N iodine solution to 20 ml of laboratory pure water. Acidify by adding 2.0 ml of 6 N HCl. Add 1.0 ml of starch indicator to form a blue color. Continue to titrate until the blue color disappears.

Adjust the concentration of the titrant until 5.0 ml of titrant is required to titrate 5.0 ml of iodine.

5.3 Sample analysis

Add 5.0 ml of iodine solution to 20 ml of sample. Titrate as above, with standardized sodium thiosulfate solution. Record the volume of titrant used.

NOTE: If 5.0 ml of iodine does not produce a yellow color in the sample, add additional 5.0 ml increments of iodine solution until color is seen. Record the volume of iodine solution added.

5.4 Soil sample extraction

Extract sulfide from soil samples by shaking 1.0 g to 2.0 g of sample in 50 ml of a dilute sodium hydroxide solution for 30 minutes. Filter the extract through Whattman grade 42 filter paper and analyzed immediately, as above.

5.5 Calculation

1.0 ml of 0.0250 N iodine solution reacts with 0.4 mg of sulfide present in the titration vessel:

$$\text{sulfide, mg/L} = \frac{400\ (A - B)}{\text{ml sample}}$$

where: A = ml of iodine solution added
B = ml of titrant used

6.0 QUALITY CONTROL

6.1 Because of the volatile nature of sulfide, no stable QC is available.

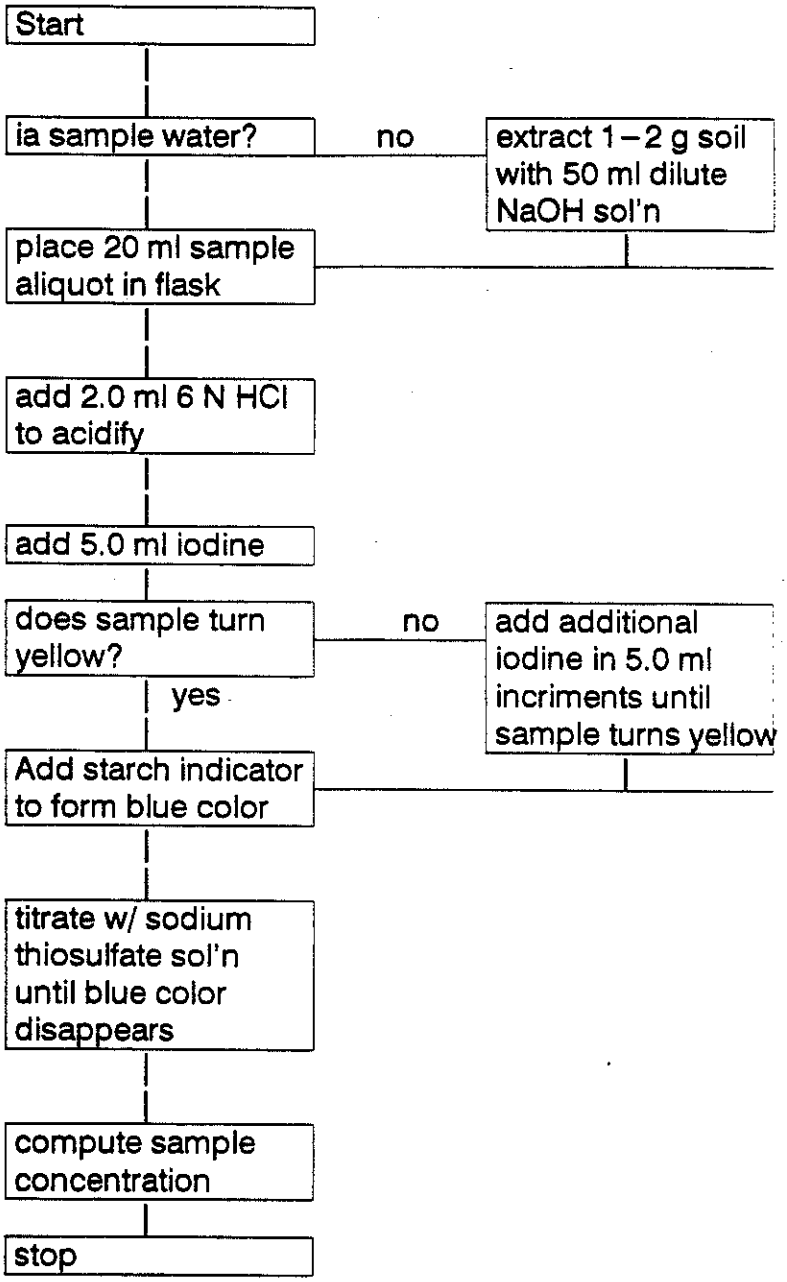
6.2 Control blanks will be analyzed at the beginning of the analysis, and continuing after every ten samples, as well as at the end of the analysis.

6.3 Duplicate titrations will be performed on 5% of the samples analyzed.

7.0 SAFETY

7.1 Care should be taken when handling reagents and samples.

Sulfide Analysis



SOP No: 11.62

Title: Trace ICP Quantitation of HSL Metals plus Boron, Molybdenum, Silicon, Strontium, Titanium, and Tin According to Method 6010A

Scope: The method detailed in this procedure is for the analysis of water, TCLP and EP extracts, soils, sludges, sediments and other solid wastes digestates for Hazardous Substance List (HSL) Metals by Inductively Coupled Plasma (ICP) spectroscopy in accordance with USEPA method 6010A. The use of ionization buffers, internal standards, and special background correction techniques is specified.

1.0 PURPOSE

1.1 The purpose of this procedure is to describe the simultaneous analysis of metals on the USEPA Hazardous Substances List (Antimony, Arsenic, Lead, Selenium, Silver, Thallium, Sodium, Potassium, Aluminum, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Vanadium, and Zinc) plus Boron, Molybdenum, Strontium, Titanium, and Tin at trace levels using a Thermo-Jarrell-Ash 61E Purged Trace Inductively Coupled Plasma Spectrometer and autosampler. Table 1 lists the elements and contract required detection limits. All samples are digested in accordance with SOP 11.35 or 11.36 prior to analysis. Filtered samples for dissolved metals analysis can be analyzed after either digestion or matrix matching. The digestate holding time is 180 days.

2.0 REFERENCES

- TJA ICAP 61E Operator's Manual (p/n 134542-00).
- SW846 method 6010A revision 1.

3.0 EQUIPMENT AND SUPPLIES

- 100mL volumetric flasks
- 200mL volumetric flasks
- 500mL volumetric flasks
- 1000mL volumetric flasks
- 100mL plastic storage bottles
- 250mL plastic storage bottles
- 500mL plastic storage bottles
- 20.0L Nalgene carboy

- 10.0L Nalgene carboy
- 1000mL graduated cylinder
- 200mL graduated cylinders
- 15mL disposable autosampler tubes
- 28mL disposable autosampler tubes
- Centrifuge tube holder
- Pipetters and Pipette Tips (1000mL Rainin, .100mL Eppendorf)
- 5, 10, 20 mL class A volumetric pipets
- Pump windings and tee fittings
- Argon gas (cryogenic liquid source)
- Nitrogen gas (cryogenic liquid source) used for purging of spectrometer

3.1 Instrumentation

3.1.1 TJA 61E Purge Trace ICP with meinhard nebulizer, cyclonic spray chamber, horizontal torch, and AS-192 autosampler.

3.1.2 Simultaneous background correction technique is used for the analysis of lead and selenium to acheive lower instrumental detection limits comparable to graphite furnace.

3.1.3 An argon humidifier is used for extracts and samples containing high salts. A high-solids "Bergener" nebulizer can be used for the analysis soil digestates.

3.1.4 Yttrium Internal standard - Lithium ionization buffer is added on-line using a mixing tee and coil with a ratio of 1:4 (one part standard: four parts samples, resulting in a dilution factor of 5 for the internal standard, approximated 10ppm is the final, "mixed-in" concentration.

4.0 REAGENTS

- A deionized water ASTM type II or equivalent
- Concentrated hydrochloric acid, trace metals grade
- Concentrated nitric acid, trace metals grade
- Flame Water - 5% hydrochloric acid, 1% nitric acid

<u>Preparation of Reagent Flame Water</u>

Fill a 20L Nalgene carboy half full with type II water. Add 200 ml concentrated nitric acid and 1000ml concentrated hydrochloric acid underneath a hood to contain noxious gases. Dilute to twenty liters with type II water and mix thoroughly.

- 2% nitric acid

  Preparation of 2% Nitric Acid

  Fill a 10L Nalgene carboy half full with type II water. Add 200 mL of concentrated nitric acid underneath a hood. Dilute to ten liters with type II water and mix thoroughly.

- 5ppm Arsenic Profile check solution

  Preparation of Arsenic Solution:

  Pipet 2.5mL of 1000ppm Arsenic stock solution into a 500mL volumetric flask. Dilute to volume with matrix matched water. Transfer to a bottle labelled 5ppm As. Record the date of preparation, expiration date and preparers initials on the bottle label. Prepare Arsenic Profile solution every three months or when depleted, whichever is more frequent.

- 50ppm Y-1500ppm lithium internal standards ionization buffer

  Preparation of 5ppm Y-1000ppm Lithium Internal standard-ionization buffer:

  Pipet 75mL of 10,000ppm Lithium standard and 25mL of 1000ppm Yttrium standard into a 500mL volumetric flask, bring to volume with matrix matched water (5% HCl+1% HNO3 or 2% HNO3).

5.0 GENERAL PRECAUTIONS

5.1 AVOID CONTAMINATION of STOCK STANDARDS. Always pour a small volume of standard stock solution into a new microbeaker before pipeting an aliquot. NEVER insert a pipet directly into the bottle. This precautionary measure also applies to quality control standards stock solutions (ICVA, ICl, etc.)

5.2 Check pipetters daily for leaks and proper calibration.

5.3 Empty Drain vessel at the end of each day. Transport waste to the waste disposal area for appropriate treatment prior to shipment. Fill vessel up to 6 inches using tap water prior to replacing vessel beneath instrument.

5.4 Clean up and neutralize all spills immediately to avoid corrosion damage to the instrument.

5.5 Purge the optics with nitrogen at all times. Leave the RF power unit on at all times. Never attempt to perform repairs to the High voltage

systems. Leave the instrument PM tubes and heater on at all times.

6.0 PROCEDURE

6.1 Preparation of Calibration Standards

6.1.1 To prepare calibration Standard 2 (standard 1 is a blank solution) in flame water, pipette 20mL of WS-1 and 20mL of WS-II, available from High Purity Standards, with Class A volumetric pipets to a 200mL flask, which has been half filled with flame water. Dilute the flask to volume with flame water. Mix the solution thoroughly, and transfer it to a plastic bottle.

6.1.2 To prepare calibration standard 2 in 2% nitric acid, follow the same procedure as with Standard 2 in flame water substituting 2% nitric acid for flame water.

True value of Standard 2. (WSI & WSII)

Element	Certified Std. Conc.(ug/ml)	Volume Added (ml)	Calibration Std. Conc. (ug/L)
Antimony	10ug/ml	20.0(mix)	1000
Arsenic	10	20.0(mix)	1000
Beryllium	1	20.0(mix)	100
Cadmium	10	20.0(mix)	1000
Chromium	10	20.0(mix)	1000
Cobalt	10	20.0(mix)	1000
Copper	10	20.0(mix)	1000
Lead	10	20.0(mix)	1000
Manganese	10	20.0(mix)	1000
Molybdenum	10	20.0(mix)	1000
Nickel	10	20.0(mix)	1000
Selenium	10	20.0(mix)	1000
Thallium	10	20.0(mix)	1000
Titanium	10	20.0(mix)	1000
Vanadium	10	20.0(mix)	1000
Zinc	10	20.0(mix)	1000
Barium	10	20(mix)	1000
Boron	10	20(mix)	1000
Strontium	10	20(mix)	1000
Tin	10	20(mix)	1000
Silver	1.0	2.0(mix)	100

Standard 2 (final volume = 200ml)

6.1.3 To prepare calibration Standard 3 in flame water, add 10ml each of the Mg, Ca, Na stock (10,000ppm) and 1ml of K stock standard (10,000ppm) standard from High Purity standard with a Class A volumetric pipets to a 200mL volumetric flask which has been half filled with flame water. Dilute the flask to volume with flame water, mix the solution thoroughly, and transfer to a plastic bottle.

6.1.4 To prepare calibration Standard 3 in 2% nitric acid, follow the same procedure as indicated for Standard 3 in flame water substituting 2% nitric acid for flame water.

Standard 3	Starting CONC	Volume Added	Final CONC.
Sodium	10,000ug/ml	10.0ml	500000ug/L
Potassium	10,000ug/ml	1.0ml	50000ug/L
Magnesium	10,000ug/ml	10.0ml	500000ug/L
Calcium	10,000ug/ml	10.0ml	500000ug/L

6.1.5 To prepare calibration standard 4 in flame water, pipette 2ml of the multi-element standard CLP-INF-1 from High Purity Standards with a class A volumetric pipette into a 200ml volumetric flask which has been half filled with flame water. Dilute to volume with flame water, mix solution thoroughly, and transfer to a plastic bottle.

6.1.6 To prepare calibration standard 4 in 2% nitric acid, follow the same procedure indicated for standard 4 in flame water substituting 2% nitric for flame water.

Standard 4	Certified Std. CONC	Volume Added	Calibration Std. CONC
Iron	5,000ug/ml	2ml	50,000ug/L
Aluminum	2,000ug/ml	2ml	20,000ug/L

NOTE 1: These formulations are subject to change without an update of SOP to suit various client requirements

NOTE 2: If the client requires multiple standards for each element, the standards above will be used as the high standard, with 1:10 and 1:100 dilutions used for medium and low standards. Alternatively, the low, middle, and high standard can be prepared from decimal dilutions of the CRDL stock solution with the non-CLP elements added separately.

6.1.7 Document the standard in the ICP Standards Logbook (Figure 1). Label the standard solution bottle. The label should include the preparers initials, the date of preparation, the expiration date, and the page number on which the standard has been recorded in the log book. The expiration date of standard solutions is three months from the date

of preparation or whenever one of the certified standards expires, whichever is first.

6.2 QC Preparation

6.2.1 Preparation of Low level linearity check Solution.(PQL)

Pipette 1ml of low check source solution from High Purity Standard using Class A volumetric pipette into a 100ml volumetric flask filled half way with flame water. Dilute to volume with flame water.

Note: This solution can also be made up with 2% HNO_3. Additional elements can be added, if necessary, according to client needs.

Element	Conc.(ppb)	Certified Stock Conc.(ppm)
Be	3	0.3
Cd	3	0.3
Cr	5	0.5
Co	5	0.5
Cu	5	0.5
Mn	5	0.5
Ni	5	0.5
V	5	0.5
Zn	10	1.0
Sb	5	0.5
As	10	1.0
Pb	3	0.3
Se	5	0.5
Ag	3	0.3
TL	10	1.0
Al	200	20
Fe	200	20
K	500	50
Mg	500	50
Na	1000	100
Ca	1000	100
Ba	10	1.0
Sn	5	0.5
Sr	5	0.5
Ti	5	0.5
B	50	5.0
Mo	5	0.5

Document the solution in the ICP Standards Log Book (Figure 1). Label the bottle as ICP CRI Stock and record the preparation date, the expiration date, the preparers initials, and the page number on which the solution has been recorded in the log book on the label. Prepare fresh solution every three months or when one of the

certified standards expires.

6.2.2 Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV):

Fill a 100mL volumetric flask halfway with flame water and add one mL of ICV, part 1 and part 2 certified stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICV. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICV solution using 2% nitric acid instead of flame water. These solutions should be prepared fresh weekly.

6.2.3 Interference Check Standard A (ICSA):

Fill a 100mL volumetric flask halfway with flame water and add 10mL of ICSA certified multi-element stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICSA. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICSA solution using 2% nitric acid instead of flame water. These solutions should be prepared fresh weekly.

6.2.4 Interference Check Standard AB (ICSAB):

Fill a 100mL volumetric flask halfway with flame water and add 10mL of ICSA certified stock solution, and 0.100mL of ANALCS-R certified stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICSAB. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICSAB solution using 2% nitric acid instead of flame water.
These solutions should be prepared fresh weekly.

6.3 Preparation of 1:5 Serial Dilution (L)

Obtain the sample digestates for the case or SDG to be analyzed. Take the original sample digestate that corresponds to the sample designated for duplicate and matrix spike digestions for each SDG and matrix and prepare its serial dilution as follows:

Transfer 5ml of sample into a 25ml volumetric flask and dilute with flame water.

If undigested filtered samples or drinking water samples are to be analyzed, then prepare the serial dilution using 2% nitric acid instead of flame water. Prepare the serial dilution immediately before analysis.

6.4 Preparation of Post Digestion Spike

Obtain the sampple digestates for the batch or SDG analyzed. Take the original sample digestate that corresponds to the sample designated for duplicate and matrix spike digestions for each batch and prepare the post spike as follows.

Transfer 10ml of sample into a sample cup and spike with 0.1ml of ICV part 1 and part 2.

Note: If the matrix spike recovery is outside criteria, the sample may require spiking at alternate concentrations.

6.5 Tuning and Calibration of the ICP

6.5.1 Conduct a pre-start up inspection.

6.5.1.1 Argon and Nitrogen gas supply and drain vessel

Make sure there is an adequate supply of Argon. Check the float gauge in the liquid argon dewar which is located in the cylinder storage room. The argon line pressure regulator should be set at 60 psi and the nitrogen line pressure should be set at 30 psi.

Check the drain vessel beneath the ICP and empty it if full.

6.5.1.2 Torch box

Make sure all connections are secure and air tight, including the drain hose, nebulizer cap, argon lines.

6.5.1.3 Peristaltic pump

Install new flexible pump tubing every other day (the windings have three stops which allow for an extra day of use) or if the old one shows signs of flattening or stretching, and connect to the nebulizer with capillary tubing.

6.5.2 Daily Start Up

6.5.2.1 Reset computer and instrument. Load the operating software called Thermospec by using the windows icon under Thermospec window or by typing "STNRUN" at the C: drive prompt in DOS.

6.5.2.2 Ignite plasma. Engage pump tubings. Under the menu heading SET UP, select CONTROL PANEL; then press F1 for Start Up followed by F9 for continue to begin the start up sequence which takes about 90 seconds.

6.5.2.3 Warm-up. Once the torch has been successfully lit, exit the start up submenu and go to the analysis menu. At the method prompt, enter "6010" and the peristaltic pump should begin turning and the levels adjusted to following:

Torch gas = HIGH
Auxilary gas = LOW
Nebulizer gas = 0.588 mL/min
Approximate RF Power (W) = 950
Pump rate (RPM) = 130

Fill the rinse water reservoir with the same matix as the samples and set rinse time for 60 seconds. Fill the internal standard -ionization buffer reservoir.

6.5.3 Profile and prepare for sample analysis.

6.5.3.1 Place a 28ml autosampler cup filled with 5 ppm As onto the last position (#19) on the "L" rack of the autosampler. Under the analysis submenu, press F6 to move autosampler and begin profile sequence. Once the autosampler has moved it will wait 35 seconds to allow for adequate uptake and equilibration of the test solution.

6.5.3.2 Start the profile sequence. Press F3 and then F1 to start the profile. The procedure takes approximately 63 seconds and returns a peak profile of the Arsenic line at 189.042 x 2 nm (second order line).

6.5.3.3 Record the peak position and intensity in the daily maintenance logbook. The peak position should be within 0.3 units of the 0 position and the intensity should be around 6000 "counts". Print out the profile report and include it with the raw data to demonstrate that the spectrometer was correctly profiled. A drift greater than the specified tolerance could indicate a drastic barometric or thermal change since the last profile

and warrants further investigation. (see trouble shooting.)

6.5.4 Prepare autosampler sequence.

Under Operation menu, select "Autosampler Setup". Load the default table name "trace" and enter the samples to be run under set 2. (maxinum 192).. Enter a CCV and CCB every 10 samples. Once finished, print out the table assignments by pressing F2.

6.5.5 Load autosampler with standards and samples according to the table printouts. A typical set-up should like like this:
(set 1) Load autosampler L rack with 28 mL cups

Position	Standard
5	std1-blank
4	std2
3	std3
2	std4
1	Linear range solution
6	ICV solution
7,8	ICB, CCB solution
9	(skipped)
10	ICSA solution
11	ICSAB solution
12	PQL solution
13,15,17	CCV solution (for long runs)
14,16,18	CCB solution

(set 2) Load autosampler (48 position racks):

Position	Name
1	PBW (BATCH #)
2	LCSW (BATCH #)
3	SAMPLE
4	DUPLICATE D
5	SPIKE S
6	SERIAL DILUTION L
7	POST DIGESTION SPIKE
8	SAMPLE2
9	SAMPLE3
10	SAMPLE4
(13) of L rack	CCV
(14) of L rack	CCB
11 .. 20	10 more samples
(13) of L rack	CCV
(14) of L rack	CCB
21 .. 30	10 more samples
(13) of L rack	CCV

(14) of L rack	CCB
31 .. 40	10
(15) of L rack	CCV2
(16) of L rack	CCB2
41 .. 48,	8 more samples
rack 2, 1 .. 2	2 more samples
(15) of L rack	CCV2
(16) of L rack	CCB2

(set 3) The final QC is entered in set #3 and begins with a CCV/CCB pair.

(6) of L rack	ICV
(7) of L rack	ICB
(10) of L rack	ICSA
(11) of L rack	ICSAB
(12) of L rack	PQL
(1) of L rack	CCV
(8) of L rack	CCB

NOTE 1: The autosampler assigns the positions of the samples and QC in the order in which they are entered. Modifying an existing run by inserting samples may change the assignments of the samples.

NOTE 2: In order to take multiple uptakes from the same QC cup, the identical name must be entered. This would not allow for the numbering of CCV1/CCB1, CCV2/CCB2, etc. or the suffix of "I" or "F" on ICSA, ICSAB, PQL check solution used in CLP type packages.

6.6 Sample Analysis

6.6.1 Initiate autosampler run. Under the Operation menu, select Analysis, enter the method, press F9 for autosampler run; enter the desired autosampler table file ("trace" if using example from 5.4.4) and press F1, to start operation.

6.6.2 If the samples to be analyzed have been digested then all the calibration standards and quality control solutions used should be prepared using flame water. If the samples to be analyzed are undigested filtered samples or drinking water samples, then all the calibration standards and quality control standards used should be prepared using 2% nitric acid.

6.6.3 Record the analysis sequence, the instrument identification, the date, the analyst's name, the analyst's signature, the time of analysis initiation, and the work order numbers on

the bench sheet (figure 3). Submit a copy of the bench sheet with the raw data.

6.7 Quality Control Requirements

6.7.1 LINEAR RANGE CHECK.

6.7.1.1 Linear ranges are determined for each analyte quarterly for each ICP used to analyze samples. To determine the linear range of the instrument, a standard is analyzed at the manufacturers estimated linear range. If the standard does not come within 5% of the true value, the standard concentration must be lowered and reanalyzed.

6.7.1.2 A linear range sample must be analyzed immediately after calibration when analyzing by method 6010A. This is the high standard used in the calibration process. The linear range sample must be within 5% of the true value. When measurements for any element exceed the control limit, the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

6.7.1.3 If any analyte in a field sample exceeds the linear range, the sample must be diluted to below the linear range.

6.7.2 ICV/CCV

The ICV is run immediately after calibration when analyzing samples by CLP method, or immediately after the linear range sample when running samples by method 6010. The CCV is run after every ten samples or every two hours. The ICV and CCV must be within 10% of the true value. When measurements for any element exceed the control limits the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

Acceptance Criteria
ICV

Element	Control Limits (ppb)	True Value (ppb)
Antimony	450 - 550	500
Arsenic	450 - 550	500
Lead	450 - 550	500
Selenium	450 - 550	500
Silver	45 - 55	50
Thallium	450 - 550	500
Aluminum	9000 - 11000	10000
Barium	450 - 550	500
Beryllium	45 - 55	50
Cadmium	450 - 550	500
Calcium	45000 - 55000	50000
Chromium	450 - 550	500
Cobalt	450 - 550	500
Copper	450 - 550	500
Iron	9000 - 11000	10000
Magnesium	45000 - 55000	50000
Manganese	450 - 550	500
Nickel	450 - 550	500
Vanadium	450 - 550	500
Zinc	450 - 550	500
Potassium	9000 - 11000	10000
Sodium	45000 - 55000	50000
Molybdenum	450 - 550	500
Boron	450 - 550	500
Silicon	450 - 550	500
Strontium	450 - 550	500
Titanium	450 - 550	500
Tin	450 - 550	500

6.7.3 ICB/CCB

The ICB and CCB are blank solutions. The ICB must be run immediately after the ICV. A CCB must be run immediately after each CCV. The absolute value of the ICB and CCB measurements should be less than or equal to the PQL. Otherwise, the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

Element	CRDL (ppb)
Antimony	5
Arsenic	10
Lead	3
Selenium	5
Silver	3
Thallium	10
Aluminum	200
Barium	10
Beryllium	3
Cadmium	3
Calcium	1000
Chromium	5
Cobalt	5
Copper	25
Iron	100
Magnesium	500
Manganese	5
Nickel	5
Vanadium	5
Zinc	10
Potassium	500
Sodium	1000
Molybdenum	5
Boron	50
Silicon	200
Strontium	5
Titanium	5
Tin	5

6.7.4 ICSAB

The ICSA and ICSAB must be run at the beginning and end of each analysis run or at a minimum of twice per eight hour shift. ICSAB must be run immediately following ICSA. ICSA contains interferents. ICSAB contains analytes plus interferents. The ICSAB measurements must be within 20% of the true values. If any element is outside this limit, then the analysis is void for that element. The problem must be corrected and the element should be reanalyzed.

Acceptance Criteria
ICSAB

Element	Control Limits (ppb)	True Value (ppb)
Antimony	480 - 720	600
Arsenic	80 - 120	100
Lead	40 - 60	50
Selenium	40 - 60	50
Silver	160 - 240	200
Thallium	80 - 120	100
Aluminum	400000 - 600000	500000
Barium	400 - 600	500
Beryllium	400 - 600	500
Cadmium	800 - 1200	1000
Calcium	400000 - 600000	500000
Chromium	400 - 600	500
Cobalt	400 - 600	500
Copper	00 - 600	500
Iron	160000 - 240000	200000
Magnesium	400000 - 600000	500000
Manganese	400 - 600	500
Nickel	400 - 600	1000
Vanadium	400 - 600	500
Zinc	800 - 1200	1000
Potassium	10000	8000-12000
Sodium	50000	40000-60000
Molybdenum	400 - 600	500
Boron	400 - 600	500
Silicon	400 - 600	500
Strontium	400 - 600	500
Titanium	400 - 600	500
Tin	400 - 600	500

6.7.5 PQL

The PQL is to verify linearity near the reporting limit. The PQL is prepared at approximately 3 - 5 times the IDL. The PQL must be run at least once during analysis. Specific acceptance criteria currently do not exist in the current

protocols but a range of +/- 15% will be used as rejection criteria.

6.7.6 PBW/PBS

The PBW and PBS are laboratory digested blanks. If any element concentration in the digested blank is above the reporting limit, then all the samples associated with that blank which have concentrations greater than the reporting limit and less than ten times the blank concentration must be redigested and reanalyzed for that element. If any element concentration in the digested blank is less than the negative of the reporting limit, then all samples associated with that blank must be reanalyzed.

Note: Exceptions may be made it the clients regulatory limit is higher than the reporting limit.

6.7.7 LCSW/LCSS

The LCSW and LCSS are digested control samples. The LCSW & LCSS measurements must be within laboratory determined control limits. If any element concentration in the LCSS or LCSW is outside the control limits, then all the samples associated with that LCSW or LCSS must be redigested and reanalyzed.

In house LCS control limits are generated once a year. LCS recoveries are also checked periodically to identify trends in the digestion/analysis.

6.7.8 Duplicates

One duplicate must be analyzed for each matrix type in each group of samples. If an element concentration is greater than or equal to five times the CRDL, then the % RPD should be 20%.

$$\%RPD = \frac{\text{sample - dup}}{\frac{\text{sample + dup}}{2}} \times 100$$

If the duplicate falls outside the criteria, it must be noted on the raw data and written in the case narrative.

6.7.9 Matrix Spike

The spike sample analysis is designed to provide information regarding the digestion and methodology used for analysis. One spike is prepared for each matrix type in each batch

of samples. If the spike recovery for an element is outside ± 25% of the true value, and if the sample concentration corresponding to the spiked sample is less than four times the spike added, then it should be noted in the case narrative and in the raw data. For purposes of calculating the % spike recovery, sample results less than the instrument detection limit reporting limit, should be assumed to be zero.

Spiking Levels

Element	Aqueous (ppb)	Solid (ppb)
Antimony	100	100
Arsenic	40	40
Lead	20	20
Selenium	10	10
Silver	50	50
Thallium	50	50
Aluminum	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	5000	5000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Magnesium	5000	5000
Manganese	500	500
Nickel	500	500
Vanadium	500	500
Zinc	500	500
Potassium	5000	5000
Sodium	5000	5000
Molybdenum	500	500
Boron	500	500
Silicon	500	500
Strontium	500	500
Titanium	500	500
Tin	500	500

6.7.10 Post Digestion Spike

A post digestion spike is analyzed for each batch of digested samples. The post digestion spike should be at 10-100 times the IDL. The post digestion spike can be analyzed on a diluted sample if the sample requires dilution. The post digestion spike criteria is 75-125%. If the spike addition is not insignificant. (Sample conc. is not greater than 4x the spike addition) If the SP

is outside criteria, the analystt should try spiking the diluted sample. If the PDS falls within criteria after dilution, all samples of similar matrix should also be diluted before quantitation. It the PDS is still outside criteria after dilution, an alternate method should be considered or it should be discussed in detail ni the case narrative.

6.7.11 Serial Dilution

Transfer 5.0mL of sample to 25mL flask, fill to marker. One serial dilution is prepared for one sample of each matrix type in each group of samples. If the element concentration is fifty times the reporting limit or greater, then the % difference between the serial dilution and the sample should be 10%.

$$\% \text{ Difference} = \frac{\text{sample} - \text{dilution}}{\text{sample}} \times 100$$

6.7.12 Internal Standard

The internal standard should be at approximately 10ppm. If the internal standard concentrate is significantly low, physical interference may be a problem and it should be noted in the case narrative. If the internal standard is significantly higher, yttrium may be present in the sample and an alternative method is necessary for analysis.

6.7.13 Interelement Correction factor determination (IEC)

OVERVIEW:

Inter-element interferances are false spectral signals arising from other elements in the sample besides the analyte. By measuring the apparent false signal of interfering elements at known concentrations, corrections factors can be determined and applied to unknown samples. These are determined annually or when routine interference check samples reveal the need for further adjustments.

PROCEDURE:

Set up, profile, and calibrate the icp. Introduce clean single element standards at the lenerar range concentrations. Determine the correction factor using the following equation:

$$\text{(eq. 1)} \quad k_1 = \frac{\text{apparent concentration of analyte}}{\text{known concentration of interferent}}$$

IEC's are then verified by introducing solutions of the interferences to determine the effectiveness of the IECs at cancelling th aapparrent concentrations. IEC's are entered into the software controlling the ICP for application on unknown samples.

REPORTING:

After all ilnter-element correction factors have been determined IEC's are entered onto CLP forms 11A and 11B in Telecations software and put into a binder along with the raw data.

6.8 Instrument Shut Down

6.8.1. Aspirate flame water for several minutes, followed by DI water, followed by 2% Triton-X 100, followed by DI water, to clean nebulizer tips and spray chamber.

6.8.2. Under Setup menu, select F7 (shutdown). This shuts off the torch and pump windings, goes through a cool down period of 90 seconds before shuting off the water recirculator and gas flows.

6.8.3. After the peristaltic pump stops, disengage the top two cartridges, leaving the tension setting untouched. The bottom cartridge supplies tension to the rinse reservoir and should be kept on to prevent back flowing of the rinse water.

6.8.4. Leave the circuit breaker on the RF power unit behind the instrument on at all times.

6.8.5. Leave the nitrogen purge gas on at all times.

6.9 Trouble shooting and corrective action

6.9.1 Problem: Stable plasma will not start.

Action: Make sure the pump tubing is clamped down and that there are no leaks in the tubing or spray chamber. Make sure the drain line is submerged under 6 inches of water in the drain waste vessel. Press reset on instrument, and there is adequate air suction on chimney.

6.9.2 Problem: Profile peak position greater than 0.3 units from zero position.

Action: ICP may not have reached purge or thermal equilibrium. Check the nitrogen purge gas flow, replace nitrogen dewar if empty or low pressure prevents sufficient purging. If purge is sufficient, try re-profiling and recalculate spectrum shifter position. Set new vernier position and verify profile. Record new vernier position in daily maintenance log.

6.9.3 Problem: ICV fails for an element.

Action: (a) The instrument will need to be recalibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICV solution or sample introduction system may have been contaminated, perform additional rinse, refill ICV/CCV, and rerun to verify. (f) The calibration standards may need to be remade. (g) IEC's have changed.

6.9.4 Problem: ICB fails for an element.

Action: (a) The instrument will need to be recalibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICB solution or sample introduction system may have been contaminated, perform additional rinse, refill ICB/CCB, and rerun to verify. (f) The calibration standards may need to be remade. (g) The torch is dirty and will need to be cleaned.

6.9.5 Problem: ICSA or ICSAB fails for an element.

Action: (a) The spectrum shifter may need to be reprofiled, (b) the Interelement correction files may need to be changed or (c) new background points may need to be selected and new IEC performed.

7.0 SAFETY

7.1 Equipment

- Lab coat
- Safety glasses
- Gloves

7.2 Potential hazards

7.2.1 All samples and solutions are maintained 5% HCl and may contain high concentrations of metals a well. Safety glasses should be worn to protect the eyes from acid splashes. Gloves and lab coats should be worn to protect the hands and skin from spills or splatter. If any solution comes in contact with the skin, wash the area immediately with plenty of water and notify a supervisor. If any solution is splashed in the eyes, flush immediately and thoroughly in an eyewash basin and contact a supervisor immediately.

7.2.2 The ICP uses high voltage electricity and generates an RF field, so there is a potential risk of electrocution if shielding is circumvented. The TJA ICP has numerous safety interlocks to shut off power to the RF coils if there is a break in the shielding around the coils, if the supply of cooling water is lost, or if there is a loss of argon pressure.

8.0 DISPOSAL REQUIREMENTS

8.1 After analysis sample digestates must be held for six months, after which they are disposed of in accordance with the Hazardous Waste Disposal Procedure.

8.2 All other non hazardous solutions may be washed down the drain with copious amounts of water.

9.0 REPORTING REQUIREMENTS

9.1 The case number, date, instrument ID, analyst's initials, and page number or source of all standard and quality control solutions must be recorded on the first page of raw data.

9.2 The ICP run log (figure 2) must be filled out for each day's operations. The method, date & time of start and end of each run, standard sequence and sources, QC sequence and sources, and sequence of samples analyzed and date for preparaton batch. In addition, each run must be recorded according to work orders, fraction numbers, corresponding multi-pro file name, elements completed, and analyst's initials.

9.3 If any maintenance is performed, routine or non-routine, the Maintenance log for the affected ICP shall be filled out if service people conduct maintenance on the instrument. The field service report is filed in a binder.

9.4 Record all solutions made in the ICP Calibration Standards logbook (figure 1).

9.5 Include copy of digestion log with weights and final volume for reviewer.

9.6 Include short narrative on why the run was needed, what problems were encountered, what actions were taken to correct them, and any future actions that will be needed.

Table 1
Contract Required Detection Limit

Element	CRDL (µg/L)	
Antimony	6	F
Arsenic	10	F
Lead	3	F
Selenium	5	F
Silver	10	F
Thallium	10	F
Aluminum	200	
Barium	200	
Beryllium	5	
Cadmium	5	
Calcium	5000	
Chromium	10	
Cobalt	50	
Copper	25	
Iron	100	
Magnesium	5000	
Manganese	15	
Nickel	40	
Vanadium	50	
Zinc	20	
Potassium	5000	A
Sodium	5000	A
Molybdenum	10	*
Boron	50	*
Silicon	200	*
Strontium	5	*
Titanium	50	*
Tin	40	*

A - May also be performed by FLAA
F - Element traditionally performed on GFAA
* - Element not on Hazardous Substances List.

FLAA = Flame Atomic Absorption
GFAA = Graphite Furnace Atomic Absorption

Figure 1
ICP CALIBRATION LOG BOOK

GP ENVIRONMENTAL SERVICES METALS WORKING STANDARDS LOGBOOK

Document Control No. 62/65 Page No.: 205

Type : _____ Date Prepared: _____ Initials: _____

Matrix: _____ Date of Expiration: _____ Supervisor: _____

Element	A Starting Conc(ppm)	B Volume Added(ml)	C Final Volume(ml)	A*B/C Final Conc(ppm)	Std Source page # or (if ID no)	Date of Expire
Zinc					Zn	
Beryllium					Be	
Cadmium					Cd	
Manganese					Mn	
Barium					Ba	
Cobalt					Co	
Copper					Cu	
Vanadium					V	
Chromium					Cr	
Nickel					Ni	
Iron					Fe	
Aluminum					Al	
Magnesium					Mg	
Calcium					Ca	
Arsenic					As	
Selenium					Se	
Silver					Ag	
Lead					Pb	
Thallium						

Comments: _____

Figure 2
ICP RUN LOG

Document Control No.:_____ Page____

GP ENVIRONMENTAL SERVICES TRACE ICP RUN LOG

Instrument ID Number: Trace Method :_____ File:_____

Start Date.:_____ End Date:_____ ICP FILENAME:_____

GPWorkorder	Clientcode	Type	Matrix	Prepdate	Comments:(Rush, Redigestion,etc)

AdditionalComments:_____

Maintenance: Pump windings _____ Waste _____ Nitrogen Purge:_____

Arsenic Profile Peak Position:_____ Intensity:_____

Traceability:

S1:_____ ICV :_____ Y INTERNAL STD:_____
S2:_____ CCV :_____ LITHIUM BUFFER:_____
S3:_____ ICSA :_____ Nebulizer ID :_____
S4:_____ ICSAB:_____ _____
S5:_____ CRI :_____ _____

Analyst:_____ Reviewed: _____

Figure 3
Bench Sheet

BENCH SHEET
SW6010

DATA FILE: [illegible] | BASE: | ANALYST: [illegible]
INSTRUMENT FILE: | INSTRUMENT: TRACE | ANALYZED: [illegible]

SEQ	LAB ID	SAMPLE ID	MATRIX	DILUTION	SIZE	VOLUME	DATE ANALYZED	
1	STANDARD 1	S0	WATER	1.00	100.000	100.000	[illegible]	[illegible]
2	STANDARD 2	S1000	WATER	1.00	100.000	100.000	[illegible]	[illegible]
3	STANDARD 3	S3	WATER	1.00	100.000	100.000	[illegible]	[illegible]
4	STANDARD 4	S4	WATER	1.00	100.000	100.000	[illegible]	[illegible]
5	[illegible]	[illegible]	Water	1.00	100.000	100.000	[illegible]	[illegible]
6	STANDARD 5	S5	Water	1.00	100.000	100.000	[illegible]	[illegible]
7	ICV	ICV	WATER	1.00	100.000	100.000	[illegible]	[illegible]
8	ICB	ICB	WATER	1.00	100.000	100.000	[illegible]	[illegible]
9	ICSA1	ICSA1	WATER	1.00	100.000	100.000	[illegible]	[illegible]
10	ICSAB1	ICSAB1	WATER	1.00	100.000	100.000	[illegible]	[illegible]
11	CRI1	CRI1	WATER	1.00	100.000	100.000	[illegible]	[illegible]
12	ICV	ICV1	Water	1.00	100.000	100.000	[illegible]	[illegible]
13	ICB	ICB1	Water	1.00	100.000	100.000	[illegible]	[illegible]
14	PBW/20/94	PBW	WATER	1.00	100.000	100.000	[illegible]	[illegible]
15	LCSW/20/94	LCSW	WATER	1.00	100.000	100.000	[illegible]	[illegible]
16	[illegible]	T7-22-EPS-[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
17	[illegible]	T7-22-EPS-[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
18	[illegible]	T7-22-EPS-[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
19	[illegible]	T7-22-EPS-[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
20	[illegible]	[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
21	[illegible]	[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
22	[illegible]	[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
23	[illegible]	[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
24	ICV	ICV2	Water	1.00	100.000	100.000	[illegible]	[illegible]
25	ICB	ICB2	Water	1.00	100.000	100.000	[illegible]	[illegible]
26	[illegible]	[illegible]	WATER	1.00	100.000	100.000	[illegible]	[illegible]
27	[illegible]	T7-22-EPS-[illegible](FILTERED)	WATER	1.00	100.000	110.000	[illegible]	[illegible]
28	[illegible]	T7-22-EPS-[illegible](FILTERED)LD	WATER	1.00	100.000	110.000	[illegible]	[illegible]
29	[illegible]	T7-22-EPS-[illegible](FILTERED)L	WATER	1.00	100.000	110.000	[illegible]	[illegible]
30	ICV	ICV	Water	1.00	100.000	100.000	[illegible]	[illegible]
31	ICB	ICB	Water	1.00	100.000	100.000	[illegible]	[illegible]
32	[illegible]	[illegible]	Water	1.00	100.000	100.000	[illegible]	[illegible]
33	[illegible]	[illegible]	Water	1.00	100.000	100.000	[illegible]	[illegible]
34	CRI1F	CRI1F	Water	1.00	100.000	100.000	[illegible]	[illegible]
35	ICV	ICV	Water	1.00	100.000	100.000	[illegible]	[illegible]
36	ICB	ICB	Water	1.00	100.000	100.000	[illegible]	[illegible]

GP ENVIRONMENTAL SERVICES

Effective Date: August 1995
Version Number: 1
Initiated By:
Approved By:

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SOP No: 11.48

Title: Determination of Inorganic Anions in Water and Aqueous Extract Samples by Ion Chromatography

Scope: This method is used to identify and quantify inorganic anions aqueous samples.

I: PURPOSE

To identify and quantify the amount of inorganic anions: bromide, chloride, nitrate, nitrite, phosphate, and sulfate; in aqueous samples.

II: REFERENCES

Determination of Inorganic Anions by Ion Chromatography (SW846 method 9056)
The Determination of Inorganic Anions in Water by Ion Chromatography (MCAWW method 300.0)

III. EQUIPMENT AND SUPPLIES

A. Ion Chromatograph (Dionex Model 4000)

B. Guard column (Dionex AG4A)

C. Anion separator column (Dionex AS4A)

D. Anion membrane suppressor (Dionex AMMS-II)

E. Anion Trap Column (Dionex ATC)

F. Integrator

G. Class A volumetric flasks (100ml)

H. Pipettes (volumetric and mechanical, adjustable 10-100ul)

I. Polypropylene syringe filters (0.45um)

IV. REAGENTS

A. Eluent: 0.003M $NaHCO_3$/0.0024M Na_2CO_3
Dissolve 1.0080 g of sodium bicarbonate and 0.0176 g of sodium carbonate in reagent water and dilute to 4 L.

B. Suppressor Reagent: 0.025 N sulfuric acid
Add 100 mL of 1N H_2SO_4 to 3 L of reagent water and dilute to 4 L.

V. STANDARDS

Store all standards at 4°C

A. Stock Standards: 1,000mg/L of the anions of interest
Certified standards can be purchased

B. Working Solutions (100mg/L): Add 10.0ml of stock standard to 100ml volumetric flask; bring to volume with deionized water.

C. Calibration Standards:

Standard	ml Working Sol'n	Final Volume	Std Concentration
STD 1	0	10.0ml	0ug/L
STD 2	0.010	10.0ml	100ug.L
STD 3	0.050	10.0ml	500ug/L
STD 4	0.150	10.0ml	1000ug/L
STD 5	0.200	10.0ml	2000ug/L
STD 6	0.500	10.0ml	5000ug/L

VI. EXTRACTION

A. Water Samples: Extraction is not required.

B. Soil Samples: Weigh 2.0g of sample into a 50ml plastic centrifuge tube. Add 30ml of deionized water. Gently shake tube using the mechanical wrist-action shaker for 30 minutes. Allow the layers to separate (centrifuge if necessary). Filter the extract through a 0.45um membrane filter. Store extract at 4°C.

VII. ION CHROMATOGRAPHY

A. Instrument Parameters

1. Flow rate: 2.0ml/minute
2. Detector range: 10uS full-scale
3. Injection loop: 200ul

B. Initial Calibration

Analyze all calibration standards; starting with the blank, followed by standards run in order of decreasing concentrations. Calculate linear correlation coefficients by plotting the concentration vs. the area of the standard peaks for IMPA and MPA.

The correlation coefficient must be 0.995 or better.

C. Initial and Continuing Calibration Verification

The calibration curve must be verified at the beginning of every work day by injecting an Initial Calibration Verification (ICV) sample prepared from a source independent of the solutions used for the preparation of the calibration standards. The Continuing Calibration Verification (CCV) samples will be run after every ten samples and at the end of the run.

All ICV and CCV samples must produce a recovery of 80-120%. If this criterion is not met, samples analyzed prior to the QC which failed, must be reanalyzed.

D. Sample Analysis

After the calibration curve has met and passed the acceptance criteria,, the samples and sample extracts can be analyzed. The samples are analyzed under the same conditions as the standards. If the concentration of a sample falls outside of the calibration curve, dilute the sample and re-analyze. Concentrations are calculated by comparing the peak area (of a peak with the proper retention time) of the sample to the calibration curve linear plot.

Samples must be filtered through a 0.45um membrane filter before they are injected into the instrument to prevent clogging ports and tubing.

Samples must be spiked with 0.10mL of 100X concentrated eluent to 10mL sample to avoid a water dip in the chromatogram.

Interpretation of sample chromatograms are performed using retention times (listed below) Samples which produce peaks in the retention time windows for the anions of interest will be spiked with those anions. The samples are then reanalyzed to verify the presence of the added anions as separate peaks or to determine if the analytes add to the peaks in the sample.
Samples which contain anions that interfere with the interpretation of the chromatograms, must be diluted until the peaks are interpretable.

E. Retention Times

All times are approximate and will change with changing conditions cl 3.4min, Br. 4.0min, NO_2 4.5min, PO_4 9.0min, NO_3 11.3min, SO_4 21.4min

IX. QUALITY CONTROL

A. Preparation/Extraction Blank

The method blank for soil is 2.0g of the standard blank soil which is treated exactly as a sample.

1. A method blank must be extracted with every set of samples.

2. The analytes of interest reported on the method blank, must have concentration values which are less than the CRQL.

B. Analytical Spike

An analytical spike must be analyzed every 20 samples of a particular matrix. The sample is pre-treated with cleanup columns, and a known amount of anion is added to the sample. The spike amount utilized will depend on the chromatographic results of the individual sample.

C. Matrix Spike

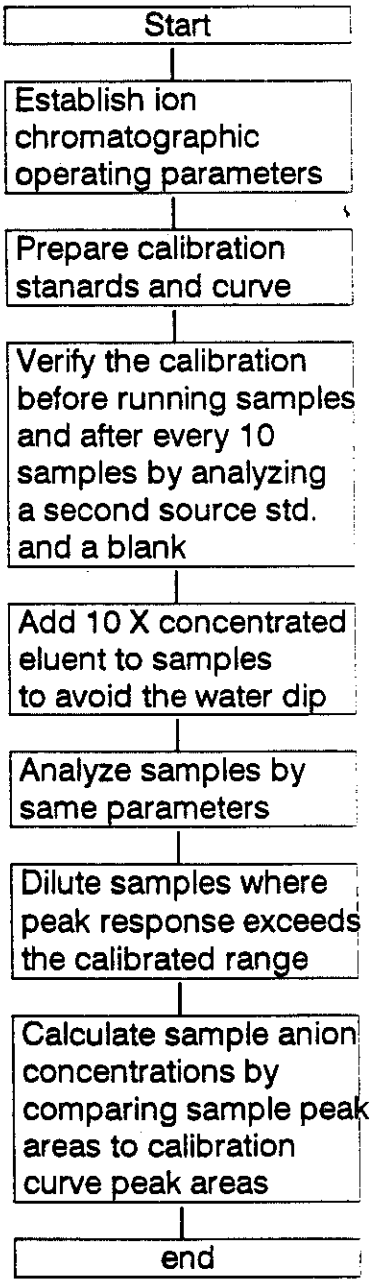
A matrix spike must be extracted for every 20 soil samples extracted. The sample is spiked with a known amount of IMPA and MPA prior to extraction.

X. SAFETY

A. A lab coat, safety glasses, and gloves must be worn at all times during the extraction and sample preparation steps.

B. Label all reagents and standards indicating the date prepared, the chemist initials, and the concentration of the solution.

Determination of Inorganic Anions
by Ion Chromatography



GP ENVIRONMENTAL SERVICES

Effective Date: October 1997
Version No: 1
Initiated By:
Approved By:

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SOP No: 11.90

Title: Cation-Exchange Capacity of Soils

Scope: This Standard Operating Procedure describes the Method for the Determination of Cation-Exchange Capacity of soil samples According to SW846 Method 9081

1.0 PURPOSE

1.1 This method is applicable to the analysis of calcareous and noncalcareous soil samples.

1.2 The soil sample is mixed with an excess of sodium solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the absorbed sodium with ammonium. The concentration of displaced sodium is then determined by flameAA.

2.0 REFERENCES

- SW846 Method 9081
- GP SOP 11.19, determination of sodium by flameAA.

3.0 INTERFERENCES

3.1 Interferences can occur during analysis of the extract for sodium content.

4.0 EQUIPMENT AND SUPPLIES

- Centrifuge tubes with caps - 50ml, round bottom
- Mechanical shaker
- Centrifuge
- Volumetric flasks - 100ml, Class A

5.0 REAGENTS

5.1 Sodium acetate (NaOAc), 1.0N: Dissolve 136g of sodium acetate trihydrate in water and dilute to 1 liter. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the pH to 8.2.

5.2 Ammonium acetate (NH4OAc), 1N: Dilute 114ml of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138ml of concentrated ammonium hydroxide (NH4OH) and add water to obtain a volume of about 1,980ml. Check the pH of the resulting solution, add more NH4OH, as needed to obtain a pH of 7. Dilute to 2 liters.

5.3 Isopropyl alcohol: 99%.

6.0 PROCEDURE

6.1 Weigh 4g of medium to fine textured soil or 6g of coarse textured soil into a 50ml centrifuge tube.

6.2 Add 33ml of 1.0N NaOAc solution, cap the tube and shake it on a mechanical shaker for 5 minutes.

6.3 Centrifuge the tube until the supernatant liquid is clear. Decant the liquid.

6.4 Repeat steps 6.2 and 6.3 three more times.

6.5 Add 33ml of isoproryl alcohol to the centrifuge tube, cap and shake for 5 minutes.

6.6 Centrifuge the tube until the supernatant liquid is clear. Decant the liquid.

6.7 Repeat steps 6.5 and 6.6 two more times.

6.8 Add 33ml NH4OH solution to the centrifuge tube, cap and shake for 5 minutes.

6.9 Centrifuge the tube until the supernatant liquid is clear. Decant the liquid into a 100ml volumetric flask.

6.10 Repeat steps 6.8 and 6.9 two more times.

6.11 Dilute the combined washings to volume with NH4OH solution.

6.12 Analyze the extract for sodium according to SOP 11.19.

7.0 QUALITY CONTROL

- Extract one method blank with each batch of 20 or fewer samples.
- Extract an LCS using a cation exchange resin of known capacity.
- Provide a portion of the NaOAC and NH4OH solutions used along with the batch of extracts.

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EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280 AND DFLMO1.1

TLI SOP No. DSP224	Version: 8	Effective Date:	June 5, 1995
Author:	Belen Rueda	Date Written:	June 3, 1997
Technical Approval: Phil Albro (Technical Director)		Date Approved:	6/4/97
Authorization: (Production Manager)		Date Authorized:	6/4/97

I. **SCOPE AND APPLICATION:** The purpose of the SOP is to describe soxhlet extraction of PCDD/PCDF from solid samples using methods 8280 and DFLMO1.1.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid sparks and flames. Avoid contact with skin and eyes. Avoid breathing vapors. They may cause irritation, nausea, dizziness, and in extreme cases, death. For additional safety information, see TLI Safety and Health Manual and appropriate MSDS.

III. **REAGENTS:**

- Toluene- Pesticide grade or better quality.
- Sodium sulfate- powder, anhydrous, pre-extracted with methylene chloride
- Tridecane- Sigma, carbon filtered.
- Hexane- Pesticide grade or better quality
- Filtered n-heptane

IV. **GLASSWARE PREPARATION:**

Each extraction setup requires:

A. 150 mL or 250 mL beaker

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B. 500 mL flat bottom flask, pre-Soxhleted

C. small or large (depending on availability) thimble holder, pre-Soxhleted

D. scintillation vial

E. spatula

V. For method **DFLMO1.1** samples, also:

A. Dean-Stark apparatus, pre-Soxhleted

B. Rinse every item from the above list with hexane or heptane.

C. After rinsing invert all flasks, thimble holders, etc. and allow to fully drain.

D. Label each container by placing a color coded sample label on top of a strip of colored tape.

NOTE: All flat bottom flasks require two labels with sample ID - one on the side of the flask and one on the neck. Also, place on the flask a label, or write with a marker, name of the solvent inside and the next step.

1. Add 400 mL of toluene and 5-6 boiling chips to the boiling flask. Place thimbleholder in the mouth of the flask.

2. Place small or large (depending on availability) pre-extracted thimble in the beaker.

VI. **EXTRACTION PROCEDURE:**

A. **NOTE:** Percent moisture should be determined for each sample before the extraction step.

1. Remove the samples from storage (cooler) and place them on clean aluminum foil laid out on a lab bench. Allow sufficient time for samples to reach ambient temperature.

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2. Check sample IDs on sample containers against sample IDs on the Sample Preparation Tracking and Management Form. If there are any discrepancies contact the Project Manager for further instructions.

3. Take gross weight of sample container and record on Sample Preparation Tracking and Management Form (SPTMF) in folder.

4. Open sample jar and mix sample thoroughly with a solvent rinsed spatula. Place beaker with pre-Soxhleted thimble on the calibrated scale, and tare the scale.

5. Using spatula, transfer scoops of sample to the thimble, until about 10 g (wet weight) has been delivered for extraction. Do not transfer rocks, glass, organic matter or any other debris unless the entire sample is debris.

   NOTE: Use 10g of sodium sulfate for blank and any LCS/LCSD samples.

6. Record the weight of extraction sample in the MILES and on the SPTMF.

7. Record observations of the physical appearance of samples in MILES (Wet Lab Observation menu).

8. Weigh sample container and record the weight on SPTMF.

9. Add ~30 g or more of anhydrous sodium sulfate to the thimble. The amount depends on the moistness of the sample. The wetter the sample, the more sodium sulfate that must be added.

10. Mix the sample and the sodium sulfate thoroughly inside the thimble.

11. Spike all samples in the extraction batch with 100 µL of 8280 Internal Standard at 0.5 µg/mL. Spike any LCS/LCSD and/or MS/MSD samples with 250 µL of 8280 Matrix Spike at 0.1µg/mL - for **Method 8280** samples, and for **Method DFLMO1.1** samples (see attachment 1 for spiking table). Spike directly into the sample. Record the volume, lot number, concentration and expiration date of each standard added to the samples.

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12. Place the thimble in the Soxhlet extractor, place the Soxhlet extractor on the heating mantle, connect with the condenser.

    NOTE: Dean-Stark apparatus must be added to Soxhlet extractor for all method **DFML01.1** samples.

13. Cap the top of the condenser with aluminum foil. Wrap the thimble holder and Dean-Stark extractor with foil. Place a piece of colored tape on the condenser to indicate it is being used for a sample and needs to be pre-Soxhleted after the sample extraction is completed. Write **3X** on the tape.

14. Adjust the heat so the solvent cycles completely through the system at least 5 times per hour.

15. Check units after one hour. Each unit should be refluxing, have no leaks and have sufficient solvent. Make adjustment as needed. If adjustments were required, check the units again in one hour. Otherwise, check again in six hours.

16. Extract sample for 16 hours.

17. After 16 hours turn off the heater. Allow the sample to cool off for 20-30 minutes. Drain and discard water from SDS trap.

18. Remove flat bottom flask. Discard toluene from thimble holder and SDS into the appropriate waste container. The extract is ready for concentration.

VII. CONCENTRATION AND DIVIDING PROCEDURES:

A. Add 500 µL of carbon filtered Tridecane to the flask with the extract.

B. Concentrate the sample to 0.5 mL in the rotary evaporator at a temperature of 42-45°C.

C. Solvent exchange the sample twice with 20 mL of filtered n-heptane.

   NOTE: In extreme cases, iso-octane may be substituted for n-heptane.

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D. Add 10 mL of hexane to the sample flask, sonicate well.

E. Transfer the extract to a scintillation vial calibrated to 20 mL. Rinse the sample flask twice with 5 mL of hexane, add rinses to the vial.

F. Adjust volume in the vial to exactly 20 mL, mix well then immediately transfer required portion (usually 20% - 4 mL) back to the original flask.

G. Spike the sample portion in the flask with 100 µL of 8280 Surrogate Standards at 0.05µg/mL, and relinquish to cleanup room (cleanup - DSP225 (if necessary), and DSP260).

H. Mark the level of the sample extract remaining in the scintillation vial. Archive the sample extract in the cooler #2.

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EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280 AND DFLMO1.1	
TLI SOP No. DSP224 Version: 8	Date Written: June 3, 1997

SPIKING TABLE

	STANDARD	8280	DFLMO1.1
ALL SAMPLES	IS @ 0.5µL/mL	100µL	100µL
LCS/LCSD	MS @ 0.1µL/mL	250µL	250µL
MS/MSD	MS @ 0.1µL/mL	250µL	250µL

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ACID/BASE CLEANUP OF PCDD AND PCDF EXTRACTS - METHOD 8280

TLI SOP No. DSP225	Version: 8	Effective Date:	June 5, 1997
Author:	Patty Ragsdale	Date Written:	June 3, 1997
Technical Approval: Phil Albro Technical Director		Date Approved:	6/4/97
Authorization: S Van Alen Production Manager		Date Authorized:	6/4/97

I. **SCOPE AND APPLICATION:** The purpose of the SOP is to describe the procedure for acid/base cleanup of PCDD and PCDF extracts using method 8280.

II. **SAFETY CONSIDERATIONS:** Wear labcoat, appropriate eyewear and gloves. Carry out these operations in a hood. Sulfuric acid and potassium hydroxide are corrosive substances. Avoid contact with skin and clothing. Hexane is flammable; avoid flames and sparks. Do not breathe vapors, as it may cause irritation, nausea, and dizziness. For additional safety information, see TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

Hexane- pesticide grade or better quality

Sulfuric acid- concentrated, ACS grade

Sodium chloride (NaCl) - analytical reagent grade, 5% (w/v) in distilled water

Potassium hydroxide (KOH)- ACS grade, 20% (w/v) in distilled water

Sodium sulfate (powder, anhydrous)- pesticide grade

Tridecane- sigma, carbon filtered

HPLC water

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IV. **Glassware Preparation**

A. The following glassware is needed for each sample:

1 250 mL separatory funnel

1 glass powder funnel

1 100 mL round bottom flask

NOTE: The extraction setup also requires (2) 100 mL graduated cylinders.

B. Assemble the separatory funnel(s) with stopcock(s) and stopper(s).

C. Rinse the following with hexane or n-heptane:

separatory funnel(s)

glass powder funnel(s)

round bottom flask(s)

graduate cylinder(s)

D. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a wasted container.

E. After rinsing, invert all flasks and allow to fully drain.

F. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

G. Label each container by placing a color coded sample label on the top of a strip of colored tape.

NOTE: All extraction flasks require two labels with the sample ID - one on the side of the flask and one on the neck. Also place on the flask a label, or write with a marker, name of solvent(s) inside.

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V. **PROCEDURE:**

NOTE: Perform acid/Base cleanup only on 20% sample aliquots following the 80:20 division and spike with 8280-C.. DO NOT perform acid/base cleanup on the entire sample aliquots after solvent exchange.

A. Add 10 mL hexane to sample flask and sonicate. Transfer to 250 mL separatory funnel containing 10 mL sulfuric acid. Rinse sample flask two (2) more times with 10 mL hexane each time. Transfer to separatory funnel.

B. Add 30 mL sulfuric acid to sample flask, sonicate, transfer to separatory funnel.

C. Shake separatory funnel for two (2) minutes. Discard acid layer (bottom layer). Repeat acid washing until no color is visible in acid layer (or for a maximum of four times).

D. Add 40 mL 5% (w/v) sodium chloride shake for two (2) minutes. Discard aqueous layer (bottom layer).

NOTE: Perform following step sample by sample. DO NOT ALLOW SAMPLE TO SIT IN KOH FOR ANY LENGTH OF TIME. Once final KOH shake is drained add 40 mL of 5% $NaCl_2$ then proceed to the next sample,

E. Add 40 mL 20% (w/v) potassium hydroxide and shake for two (2) minutes. Discard base layer (bottom layer) as soon as hexane separation ends. Repeat base washes until no color is visible in the bottom layer (or for a maximum of four times).

NOTE: Strong base is known to degrade certain PCDDs/PCDFs; therefore, contact time should be minimized.

F. Add 40 mL 5% (w/v; 5 g/100 mL) sodium chloride. Shake for two (2) minutes. Discard the aqueous layer (bottom layer).

G. Drain the organic layer through funnel with appropriate amount of sodium sulfate into a 100 mL round bottom flask containing 500 mL of tridecane. Rinse the separatory funnel twice with 10 mL hexane and drain through sodium sulfate. Rinse the sodium sulfate twice with 10 mL of hexane into the round bottom flask.

H. Concentrate extract to 0.5 mL and proceed using SLICC SOP.

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PCDDs AND PCDFS BY GC/MS METHOD 8280			
TLI SOP No. DHR183	Version: 2	Effective Date:	June 5, 1997
Author:	Mike Matthews	Date Written:	June 2, 1997
Technical Approval:	Technical Director	Date Approved:	6/4/97
Authorization:	Production Manager	Date Authorized:	6/4/97

I. **SCOPE AND APPLICATION:** This method provides procedures for the analysis of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) from matrices including but not limited to soil, sludge, fly ash, and water. This procedure is an adaptation of SW 846 Method 8280.

II. **SAFETY CONSIDERATIONS:** The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in the 2,3,7,8 positions are known to have toxicities comparable to that of 2,3,7,8-TCDD. Extreme care must be exercised in all handling of extracts and standards in the application of this SOP. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDSs.

III. **EQUIPMENT:**

A. GC/MS - equipment utilized for this analysis consists of one of the following systems:

VG 12-250 Quadrapole
VG 7070EQ
VG 70 SE

The VG 7070EQ and VG 70SE units are high resolution mass spectrometers which are operated at low resolution (1000 - 3000) for this analysis. Each instrument is operated in the selected ion recording mode (SIR).

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Two quantitation ions (M and M+2 or M+2 and M+4) are monitored for each target analyte and standard.

Note: Only one quantitation ion is monitored for the cleanup standard.

A confirmation ion which monitors the loss of the $[COCl]^-$ is also monitored for each analyte. See table 8 in the 8280 Data User Manual for the description of each ion monitored.

The GC of each instrument is equipped for temperature programming and capillary columns.

B. GC Injection Port - The GC injection port is designed for capillary columns. 2 µL injection volumes are used unless otherwise noted.

C. GC Column - In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one GC/MS analysis, the 60 m DB-5 fused silica capillary column is used. Operating conditions known to produce acceptable results with the DB-5 column are shown in Table 2.

D. Gas Chromatograph/Mass Spectrometer(GC/MS) Interface -

1. The GC/MS interface conditions are set so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. See Table 1 for the specific conditions for each instrument

2. The GC column is fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules may be used.

E. Data System - A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored) are acquired during the analyses and stored. Quantitation is reported based upon computer generated peak areas. The data system is set to acquire data as low as 10 ions in a single scan. The data system is set to switch to different sets of ions (descriptors) at specified times

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during an GC/MS acquisition. The data system provides hard copies of individual ion chromatograms for selected gas chromatographic time intervals.

NOTE: The detector ADC zero setting must be set to allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power.

IV. STANDARDS:

A. Calibration Solutions (Table 3) - Five nonane solutions containing the labeled and unlabeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (0.15 npg/µL) and the highest values for the octachlorinated congeners (1000 npg/µL). See Table 3 for the exact composition of each standard solution.

Note: Only the mid-range calibration standard (CC3) contains the clean-up standard ($^{37}CL_4$-2,3,7,8-TCDD) and all of the unlabeled analytes.

B. Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at 500 pg/µL per compound. 20 µL of this solution is added to each sample extract before the GC/MS analysis.

C. GC Column Performance/Retention Window Check Solution (RTCHK)- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. Table 4 lists the first and last eluting isomer for each congener.

D. Acceptance Criteria for Newly Prepared Standards -Data for newly prepared standards is reviewed by Standards Preparation Chemist. For Acceptance Criteria for Newly Prepared Standards refer to Standards Preparation SOP.

E. Storage Conditions - Standards are stored in 1/2 dram amber glass vials at room temperature.

V. PROCEDURE:

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A. Initial Calibration (ICAL)- Initial calibration of the instrument is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any continuing calibration does not meet the criteria listed in Section B.

1. All five calibration solutions listed in Table 1 must be used for the initial calibration and each must be analyzed in triplicate.

2. Tune the instrument with Perfluorokerosene (PFK) to achieve a static resolving power of 1000 - 3000 (10% valley).

3. Inject 2 µL of the GC column performance check solution (RTCHK) and acquire SIM mass spectral data as described earlier in the *EQUIPMENT* section of this SOP. The total cycle time must not exceed 1 second.

4. The RTCHK must meet the acceptance criteria listed below in section C.

5. Using the same instrument conditions that produced acceptable results for the RTCHK (i.e. acquisition windows and TCDD resolution), analyze a 2 µL portion of each of the five calibration standards. Remember, each calibration solution must be analyzed in triplicate.

6. Calculate the relative response factor for all components of the standards using :

$$RRF_{(\alpha)} = \frac{A_{(\alpha)} * Q_{i(\beta)}}{Q_{(\beta)} * A_{(\alpha)}}$$

where:

α = an analyte, internal or cleanup standard

β = the appropriate standard (see Table 13 in the 8282 Data User Manual for the relationship of standards to analytes and other standards)

$A_{(\alpha)}$ or $A_{(\beta)}$= the integrated ion of the quantitation ion characteristic of the analyte, internal or cleanup standard

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$Q_{(\alpha)}$ or $Q_{(\beta)}$= the amount of analyte, internal or cleanup standard

7. Calculate the average response factor for each component of the standards using data from all fifteen (15) analyses. This average response factor is used

8. ICAL Acceptance Criteria:

   a) The integrated ion current ratios for each labeled and unlabeled component must be within the following limits:

Congeners	ions	Ratio Limits	
TetraCDD	320/322	0.65 - 0.89	*
PentaCDD	356/358	1.33 - 1.82	*
HexaCDD	390/392	1.08 - 1.45	*
HeptaCDD	424/426	0.89 - 1.20	*
OCDD	458/460	0.75 - 1.01	
TetraCDF	304/306	0.65 - 0.89	
PentaCDF	340/342	1.33 - 1.82	*
HexaCDF	374/376	1.08 - 1.45	*
HeptaCDF	408/410	0.89 - 1.20	*
OCDF	442/444	0.75 - 1.01	

   * For consistency with the other dioxin methods (particularly 8290 and 1613), these ratios have been presented as the inverse of the presentation in method 8280.

   b) The signal to noise ratio for the m/z 320 ion of 2,3,7,8-TCDD must be ≥ 50:1 in all analyses of the CC1 standard.

   c) The percent relative standard deviations (%RSD), based on the triplicate analyses, Must be ≤15%.

   %RSD = $STDS_{RF}$/ AVG RF X 100
   Where $STDS_{RF}$ = the standard deviation of the response factors

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B. Continuing Calibration Check (CONCAL) - Continuing calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and RTCHK.

1. Inject 2 µL of the CONCAL solution CC3 standard (Table 3),. using the GC/MS conditions as used in Tables 1 and 2.

2. Calculate relative response factors for all analytes, internal and cleanup standards.

3. Acceptance Criteria for Continuing Calibration - The following criteria must be met before further analysis is performed.

   a) The relative response factors obtained for the unlabeled standards during the continuing calibration analysis must be within ± 30 percent of the mean values established during the initial calibration (Section A above).

   b) The relative response for up to two of the labeled internal standard compounds in the continuing calibration analysis may be greater than 30%, but less than 40% of the mean values established by the initial calibration.

   c) The ion-abundance ratios for each labeled and unlabeled component must be within the limits shown in section V.A.8.a above.

   d) If either one of the criteria in presented above in a) and b) is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire continuing calibration process must be reviewed.

   e) If an acceptable CONCAL cannot be achieved, the GC/MS system must be evaluated. If the instrument is determined fit to run, an acceptable initial calibration must be obtained before any sample may be analyzed.

C. GC column performance check solution (RTCHK)

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1. Must be analyzed prior to the analysis of a sample or standard (either initial or continuing)

2. Must be analyzed within 3 hours after the sample marking the end of the 12 hour period which was started with the analysis of the first ICAL standard or with the CONCAL standard.

3. Acceptance criteria for the initial RTCHK solution are:

   a) The resolution between 2,3,7,8-TCDD and the closest eluting TCDD isomer must produce a valley whose height above the baseline is no greater than 25% of the height of the 2,3,7,8-TCDD peak.

   b) The first and last eluting isomer for each class must be present in the associated retention time window.

4. Acceptance criteria for the ending RTCHK solution are:

   a) The resolution between $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-2,3,7,8-TCDD must produce a valley whose height above the baseline is no greater than 25% of the height of the $^{13}C_{12}$-2,3,7,8-TCDD peak.

   b) The resolution between 2,3,7,8-TCDD and the other close eluting isomers must produce a valley whose height above the baseline is no greater than 40% of the height of the 2,3,7,8-TCDD peak.

5. See Work Area Guidelines if initial or ending RTCHK does not meet Acceptance Criteria described above.

D. **ANALYSIS**

1. Requirements for analyzing samples:

   a) The instrument must have a valid ICAL.

   b) The instrument must have a valid RTCHK analysis immediately prior to the analysis of the CONCAL

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c) The instrument must have a valid CONCAL analysis which was obtained after the RTCHK and less than 12 hours prior to the sample analysis.

2. Sample analysis:

a) Remove the sample extract (blown to dryness) or blank from storage. Add 20 µL of recovery standard and mix thoroughly

NOTE: A final volume of 20 µL or more should be used whenever possible. A 10 µL final volume is difficult to handle, and injection of 2 µL out of 10 µL leaves little sample for confirmations and repeat injections, and for archiving.

b) Inject a 2 µL aliquot of the extract into the GC, operated under the instrument conditions that produced acceptable CONCAL and RTCHK results.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined.

c) Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

(1) The ion-abundance ratios must be within the following limits:

Tetra congeners	0.65 - 0.89
Penta Congeners	1.32 - 1.78
Hexa Congeners	1.05 - 1.43
Hepta Congeners	0.88 - 1.20
Octa Congeners	0.76 - 1.02

(2) The retention time for the analytes that have a corresponding ^{13}C-labeled internal or recovery standard must maximize within three (3) seconds of the corresponding labeled standard.

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(3) The relative retention time (RRT) of an analyte that does not have a corresponding ^{13}C-labeled standard must be within 0.005 RRT units of the RRT established by the CONCAL. The RRT equals the retention time of the analyte divided by the retention time of the nearest internal standard.

(4) Non-2,3,7,8-substituted compounds (tetra-hepta) must elute within the retention time window established by the window defining mix.

(5) The two monitored ions and the confirmation ion ($[COCl]^-$ loss) for the analyte must maximize within two seconds of each other. See Table 12 in the 8280 Data User Manual for the relationships.

(6) The signal to noise (S/N) for the analyte quantitation ions must be ≥ 2.5 . For internal standards, the S/N must be $\geq$ 10. The analyte confirmation ion does not have to meet the 2.5 S/N criteria, but must meet all other criteria. If the analyte confirmation ion is less than 2.5 S/N, the peak may be marked for deletion by the analyst.

Note: Signal to noise refers to a comparison of the analyte peak areas to the areas of the background noise as a ratio. See SOP on noise calculation for additional detail and information.

(7) For the identification of PCDFs, no signal should be observed in the corresponding polychlorinated diphenyl ether (PCDPE) channel that is greater than 2.5 S/N. If a PCDPE is detected above 2.5 S/N and the intensity is greater than 10% of the intensity of the co-eluting PCDF, the PCDF peak is calculated as an estimated maximum possible concentration (EMPC).

(8) Sample Concentrations:

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$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{\overline{RF}}_n}$$

where:

C_X	=	analyte concentration
A_X	=	sum of integrated quantitation ions - analyte
A_{IS}	=	sum of integrated quantitation ions - internal standard
Q_{IS}	=	quantity of internal standard added (in pg)
W	=	sample weight in g
$\overline{\overline{RF}}$	=	mean response factor for analyte, from initial calibration

E. QUALITY CONTROL REQUIREMENTS

1. Samples

a) Internal standard recoveries in the sample are expected to be within 40 - 120 % for tetra - hepta internal standards and 25 - 120 for the OCDD internal standard. Samples having very complex matrices may not achieve the specified recoveries, but a S/N ≥ 10:1 must be achieved.

b) The target detection limits (TDL) must be achieved, unless prohibited by a limited sample size or the need to dilute a high concentration sample.

Congener	Water TDLs	Soil TDLs
Tetras - Penta	10 ppt	1 ppb
Hexas- Heptas	25 ppt	2.5 ppb
Octas	50 ppt	5.0ppb

c) Samples which fail to meet acceptance criteria must be re-extracted and reanalyzed.

2. Laboratory Method Blank: Required for every extraction batch of samples

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a) Unlabelled analyte concentrations in the method blank should be less than the target detection limits listed directly above.:

b) If a blank contains analytes at levels above the target detection limits the blank is out of control and the associated samples are re-extracted and re-analyzed. If the analyte(s) found in the blank are not detected in the associated samples or are present at a level greater than 20 times the level in the blank, the contamination is deemed to have had no affect on the sample quality. In this case, the data may be reported but must be addressed in the case narrative.

c) Internal standard recoveries in the blank must be within 40 - 120 % tetra - hepta and 25 - 120% octa.

d) The target detection limits described in 1.B must be met for each analyte.

e) Failure to meet c) or d) above, invalidates the blank and the associated samples must be re-extracted and re-analyzed.

3. Spiked Samples

a) A matrix spike (MS) and matrix spike duplicate sample are prepared per extraction batch not to exceed 20 samples per batch as scheduled according to client requirements. If sufficient client sample is not available for matrix spikes and duplicates, laboratory control spikes may be prepared in duplicate using a blank matrix. A single laboratory control spike is always prepared with each set of matrix spikes for control purposes.

b) Recoveries must be within the 50 - 150% for all analytes in the laboratory control spikes. If an LCS fails to meet criteria, the analysis is suspect and sample re-extraction is expected.

c) Recoveries are expected to be within 50 - 150% for all analytes in the matrix spikes. If a matrix spike and a matrix spike duplicate fail to meet this criteria, but the corresponding LCS meets criteria, a matrix effect is assumed to the cause of the failure.

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d) Relative percent difference (RPD) for LCS/LCSD pairs are expected to be ≤ 50%. If this criteria is not met, the analysis is suspect and re-extraction and analysis of the affected samples is required.

$$RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

e) Relative percent difference for MS/MSD pairs are expected to be ≤ 50%. If this criteria is not met, but the corresponding LCS/LCSD pair meets criteria, a matrix effect is assumed to be the cause of the failure.

Original stamped in blue:

ORIGINAL

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TABLE 1: MASS SPECTROMETER CONDITIONS

Instrument	VG 7070EQ & VG 70SE	VG 12-250
Source	265° C	250° C
Interface	Direct, 270°C	Direct, 290° C
Electron Energy	70 eV	125 eV

TABLE 2: GAS CHROMATOGRAPHY CONDITIONS

Column type	**DB-5**
Length (m)	60
i.d. (mm)	0.25
Film Thickness (um)	0.25
Carrier Gas	Helium
Carrier Gas Flow (mL/min)	1-2
Injection Mode	⇐ splitless ⇒
Valve Time (s)	30
Program Temperature	The exact temperature porgram is specified in the specific instrument amintenance manual.

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TABLE 3 COMPOSITION OF INTERNAL STANDARD SOLUTIONS

Compound	Concentrations (pg/mL) Sol. Number: 1	2	3	4	5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDD	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.1	0.25	0.5	1.0	2.0
2,3,4,7,8-PeCDF			0.5		
1,2,3,4,7,8-HxCDD			1.25		
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
1,2,3,7,8,9-HxCDD			1.25		
1,2,3,4,7,8-HxCDF			1.25		
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,7,8,9-HxCDF			1.25		
2,3,4,6,7,8-HxCDF			1.25		
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,7,8,9-HpCDF			1.25		
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-2,3,7,8-TCDF	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	1.0	1.0	1.0	1.0

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$^{13}C_{12}$-OCDD	1.0	1.0	1.0	1.0	1.0
Cleanup Standard					
$^{37}Cl_4$- 2,3,7,8-TCDD			0.25		
Compound	**Concentrations (pg/mL) Sol. Number:**				
	1	**2**	**3**	**4**	**5**
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5

TABLE 4: COMPOSITION OF RTCHK SOLUTION

Analyte	Amount (ng)
2,3,7,8-TCDD	10
2,3,7,8-TCDF	10
1,2,3,7,8-PeCDD	25
1.2.3.7.8-PeCDF	25
2,3,4,7,8-PeCDF	25
1,2,3,4,7,8-HxCDD	25
1,2,3,6,7,8-HxCDD	25
1,2,3,4,7,8-HxCDF	25
1,2,3,6,7,8-HxCDF	25
2,3,4,6,7,8-HxCDF	25
1,2,3,7,8,9-HxCDF	25
1,2,3,4,6,7,8-HpCDD	25
1,2,3,4,6,7,8-HpCDF	25
1,2,3,4,7,8,9-HpCDF	25
OCDD	50
OCDF	50

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GEOTECHNICAL LABORATORY TESTING CAPABILITIES

Index Properties:

- visual classification and water content
- grain-size distribution
- organic content
- reactive sulfate
- total carbonate content
- liquid, plastic and shrinkage limits
- specific gravity
- pH level
- total salt content
- cation exchange capacity

Compaction Testing:

ASTM methods are used to determine the moisture-density relationships for soils to be used in fill placement. Both mechanized and hand-operated compactors are available as may be required to provide specified compaction energy levels.

Permeability:

The laboratory is equipped to perform constant-head and falling-head permeability tests by the appropriate ASTM standards. Both flexible-wall and fixed-wall cells are available. Twenty back-pressure saturation and consolidation stations are used to perform the falling-head tests. Five of these stations are constant- flow stations which use mercury manometers for precise measurement of pore water movement through low-permeability clays and geosynthetic clay liner materials.

Compressibility:

One-dimensional consolidation properties are obtained using fixed-weight loading frames. These frames may be monitored using automated data acquisition equipment. Controlled rate-of-deformation consolidation tests may be performed using specially adapted triaxial cells.

Static Strength:

The laboratory is equipped to perform unconfined and triaxial compression testing of soil and rock specimens. Triaxial cells manufactured by Brainard-Kilman and Trautwein Equipment are used for specimen diameters up to 4-in.-diameter (100 mm) specimens and effective confining pressures up to 120 psi (830 kPa). Twenty back-pressure saturation/consolidation stations are available.

GEOTECHNICAL TESTING CAPABILITIES
Rust Cincinnati Division

Test	Sample Size inches (mm)	Maximum Pressure Limits, psi (kPa)	Applicable ASTM Standard	Comments
Triaxial Compression	Diameters: 1.5 to 4 (38 to 100)	Cell Pressure: 120 (830)	D2850 D4767	Unconsolidated-Undrained Consolidated-Undrained
Unconfined Compression	Diameters: 1.5 to 4 (38 to 100)	N/A	D2166	
Direct Shear	Diameter or Width: 2.0 to 12.0 (50 to 305)		D3080	
Consolidation Incremental Controlled-Strain	Diameters: 2.5 to 4 (63 to 100)	350 (2450)	D2435 D4186	Dead-Weight Load Frame
Permeability Constant Head Falling Head	2 to 4 (50 to 100) 1.5 to 4 (38 to 100)		D2434 D5084	
Liquid and Plastic Limits			D4318	
Specific Gravity			D854	
Moisture Content			D2216	
Grain-Size Aggregate Sieve Hydrometer			D422 D422	Controlled Temperature Bath
Organic Content			D2974	
Compaction	4 and 6 (100 and 150)		D698 D1557	Mechanical Compactor

ADDITIONAL EQUIPMENT (Field Testing):

- RocTest Pressuremeter
- Troxler Nuclear Density Gauges
- HydroPunch

STANDARD OPERATING PROCEDURE FOR RECEIVING INCOMING SAMPLES

STEP 1

Log sample into Sample Log Book, include project name, number, client, sample number, location and testing required, assign a number to the Assignment Sheet and date received.

- Alternatively, the Soil Request Records may be used as the Sample Log Book (currently used in Baton Rouge).

STEP 2

After completing the Log-in process, place the sample to be tested in the appropriate testing area, i.e., Proctors, Classifications, Strength and Permeability, etc.

STEP 3

Complete all required project information on each data sheet including sample locations, stations, elevation, numbers, etc.

STEP 4

If separate, setup the soil laboratory worksheet. Include all information as completed in Step 1. Circle all required testing and any special information that may have been supplied by the project, Project Manager or other. Place the Soil Laboratory Worksheet with the sample.

Prepared by: B. M. Griggs 3/30/95
Reviewed by: Kirk Lowery 11/10/95
Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE FOR PROCESSING BULK SAMPLES

STEP 1

Set up Soil Laboratory Worksheet. See SOP-GT-001, Step 4 for reference. Weigh entire content of the bulk sample and record in Remarks Section on worksheet.

STEP 2

Lay out entire sample on a flat pan in proctor area.

STEP 3

Completely fill out two sample tags and place one with sample and one on a bucket for use later. Include project name and number, sample number or I.D. Collect approximately 1500 grams for sieve analysis, place into bucket or flat pan and set aside.

STEP 4

Collect a representative 300-500 gram sample for Natural Moisture Content (NMC) prior to any drying of the bulk sample. Place into a sealed plastic bag and leave with bulk sample. (The NMC sample may be used for P-200, See SOP-GT-07.4).

NOTE: Should the bulk sample be in excess of 10% greater than the estimated Optimum Moisture Content (OMC), allow the entire bulk sample to air dry until the moisture content has been reduced to about 6% greater than the estimated OMC. Then proceed with STEP 5.

STEP 5

Dice and chop bulk sample in the flat pan and remove, weigh and record on worksheet any large stones; place bulk samples into the Rapid Soil Processor. Make the necessary hook-ups on the Soil Processor. Place the larger black tub under, and the smaller black tub towards the back of the Soil Processor. Turn on the Soil Processor and allow it to shave the entire bulk sample until all the soil has been "Processed". USE CAUTION!

STANDARD OPERATING PROCEDURE FOR PROCESSING BULK SAMPLES (continued)

STEP 6

From the Processed Bulk Sample, collect about 200 grams of moist soil for Atterberg and place into a marked container. Record container's ID on worksheet in Atterberg Limits Section. Place distilled water in container covering soil and place in classification testing area of the laboratory.

STEP 6.1

From the Processed Bulk Sample, collect approximately 200 grams of moist soil for the hydrometer analysis (Wet Method) and place into a marked container. Record container ID on worksheet in Hydrometer Section. Place distilled water in container covering soil and place in classification testing area.

STEP 7

Check worksheet for completeness. Leave worksheet with bulk samples

Prepared by: B. M. Griggs 3/3/95
Reviewed by: Kirk Lowery 11/10/95
Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE FOR ASTM D4318 - ATTERBERG LIMITS (Wet Method)

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect 200 gms from the processed bulk sample - see SOP-GT-002, Step 5, or place the 200 gms into a marked container and place tap or distilled water into the container just covering the soil. Allow to soak until mixing. Mix the material in the blender for 1 minute. Pour the soil/water mixture over a #40 sieve which has been previously placed on top of a oven dried "Dog Bowl". Allow soil slurry to dry until a thick paste has developed. Collect approximately 40 grams of this material for plastic limits and place this sample to the side for testing later.

STEP 3

Calibrate drop of liquid limit cup using the grooving tool handle. Place approximately 150 gms of the soil into a mixing dish and thoroughly mix. Spread soil into the liquid limit cup approximately 10 mm thick. Cut a grove through the center of the filled cup using the grooving tool. Turn the handle on the limit cup at a rate of about two blows (drops) per second and count the number of blows (drops) of the limit cup required to close the grove between the two halves approximately ½ inch. Point one should require 20 to 30 blows to close the groove. Collect a sample of this material perpendicular to and across the closed groove and place in a tare. Cover tare until wet weight plus tare is determined.

STEP 4

Repeat the above steps one additional time for verification of point one. After completing both points of the liquid limit, weigh and record the weight of both samples plus tare on the data sheet and place them in the drying oven.

STANDARD OPERATING PROCEDURE
FOR
ASTM D4318 - ATTERBERG LIMITS (Wet Method)
(continued)

STEP 5

Take the plastic limit samples and roll them out on a glass plate. Continue rolling and kneading until the soil sample can no longer be rolled out to an 1/8" thread. Collect 2 samples of this rolled out material and place in a tare (approximately 12 gms each). Weigh and record the weight of each sample and tare and place them in the drying oven.

STEP 6

Check the data sheet for completeness.

Prepared by: B. M. Griggs 3/3/95
Reviewed by: Kirk Lowery 11/10/95
Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE
FOR
SOIL CLASSIFICATION - GRAIN SIZE ANALYSIS OF SOIL ASTM D422

STEP 1

Complete all project information on the soil classification data sheet.

STEP 2

Oven dry at least 1,500 grams or the appropriate weight depending on maximum particle size, obtained from the bulk or tube sample. Place sample into container for drying. Record the container's I.D. number on the soil classification data sheet, grain size section.

NOTE: All Hydrometers Samples Shall be Tested using the Wet Method, SOP-GT-07.2 , unless instructed otherwise, inwhich case, use SOP-GT-07.1.

STEP 3

After drying, record dry weight of sample minus any tare weight on worksheet. Place sample into Beaker or Plastic Bucket. Record container's Id on worksheet and cover sample with tap water in container. Allow sample to soak.

STEP 4

After soaking, agitate sample in container using a wire wisp. Wash thoroughly over a # 10 sieve or # 200 sieve depending on type of test, see note.

NOTE: If Hydrometer is in progress, wash over # 10 sieve. If a grain-size with # 200 wash has been requested, wash sample over a # 200 sieve.

STANDARD OPERATING PROCEDURE
FOR
SOIL CLASSIFICATION - GRAIN SIZE ANALYSIS OF SOIL ASTM D422
(continued)

STEP 5

After washing, return sample to tare and place into over for drying. Record tare Id on worksheet.

STEP 6

After drying, pass the soil over a nest of sieves as: $1^1/_2$, 1, $^3/_4$, $^1/_2$, $^3/_8$, $^1/_4$, #4 and #10 (# 40 and # 200 if a grain-size with wash # 200 has been requested).

Record the weights of the material retained on each sieve cumulatively. Once the total weight retained on the #10 or # 200, has been determined and recorded, place sieved sample into a labeled plastic bag. DO NO DISCARD SAMPLE. Check the data sheet for completeness. Return paperwork to the Hydrometer Testing Area or Data Reduction Basket.

Prepared by: B. M. Griggs 3/3/95
Revised by: B. M. Griggs 4/01/96
Reviewed by: Kirk Lowery 4/01/96
Reapproved by: Kirk Lowery 4/03/96

STANDARD OPERATING PROCEDURE
FOR
ASTM D2216 - NATURAL MOISTURE CONTENT

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect 50 to 1500 gms of wet sample depending on particle size of sample and place in tare. Weigh wet soil and tare. Record weight on data sheet. Place tare and sample in drying oven.

STEP 3

Leave data sheet in basket next to oven.

NOTE This specimen may be used for P-200, see SOP-GT-07.4.

Prepared by: B. M. Griggs 3/3/95
Reviewed by: Kirk Lowery 11/10/95
Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE FOR ASTM D422 - HYDROMETER ANALYSIS (Dry Method)

STEP 1

Complete all project information on the data sheet. Riffle split 200 gms from the 1500 gm sample obtained from the Proctor area. Pulverize sample using a mortar and pestel and pass material over a #10 sieve. Discard the plus #10 material. (See SOP-GT-003, Step 2 for reference).

STEP 2

Mix the minus #10 material and collect a 50 gm sample for hygroscopic moisture. Obtain and record weight of soil and tare and place in drying oven. Collect 50-70 gms of minus #10 material for hydrometer testing. Record sample and tare weight on data sheet. Mix this 50-70 sample with 125 ml of hydrometer solution and allow to soak at least 16 hours.

STEP 2.1

Prepare a control flask consisting of distilled water and 125 ml of hydrometer solution which is at the same temperature as the Hydrometer test specimen. From the control flask, the composite correction and temperature readings will be obtained during the Hydrometer test.

STEP 3

After soaking, pour soil/solution mixture into the blender and mix for 1 minute. After 1 minute of mixing, transfer soil/solution mixture into hydrometer flask. Use a squirt bottle to remove all soil from the blender. Fill the hydrometer flask to just below the fill line with distilled water and the soil/solution mixture. Thoroughly mix the distilled water and soil/solution mixture by inverting and reversing the flask for 1 minute. Wash down any remaining soil on the sides of the flask and bring the water level (bottom of the meniscus) up to the fill line using a squirt bottle with distilled water.

STEP 4

After 1 minute, place the hydrometer bulb into the hydrometer flask and take your first hydrometer reading at two minutes. Readings should be taken at exactly 2, 5, 15, 30, and 60 minutes and at least 720 minutes (12 hours) and recorded on a sieve sheet. Record temperature from the control flask at the start of the test and at the end.

STANDARD OPERATING PROCEDURE
FOR
ASTM D422 - HYDROMETER ANALYSIS (Dry Method)
(continued)

STEP 5

After taking final reading; wash all soil/solution over the #200 sieve. Transfer the material retained on the #200 sieve into tare and place in the drying oven. After drying, pass the material over a nest of two sieves (#40 and #200 sieve). Weigh the material collected on each sieve and record on sieve sheet.

STEP 6

Check the data sheet for completeness.

Prepared by: B. M. Griggs 3/3/95
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Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE
FOR
ASTM D422 - HYDROMETER ANALYSIS (Wet Method)

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect approximately 200 grams of soil from the processed bulk. See SOP-GT-002, Step 6.1. Place the 200 gram sample into a marked plastic container; record container's ID on the worksheet and cover the soil in the plastic container with distilled and allow to soak or slake until soil will easily break down.

STEP 3

After soaking, use a wire wisp or spatula to thoroughly mix soil/water slurry. Pour slurry over a previously placed #10 sieve over a oven dried "Dog Bowl". Work the retained soil, as much as practical, through the sieve. Allow the minus #10 slurry in the "Dog Bowl" to dry to a thick paste. Record "Dog Bowl" number on worksheet in Hydrometer Section.

STEP 4

When a thick paste has developed, using a spatula cut four quarters into the soil paste. Remove opposite quarters and place into a pre-weight tare can for hygroscopic moisture content. Record tare can number, tare weight and wet weight of soil and tare on worksheet under hydro hydroscopic Moist. Content. Place into drying oven. Slice the two remaining quarter into halves. Remove opposite slices for hydrometer test. Place the removed slices into a tared or weighed glass beaker. Record soil weight and beaker ID on worksheet. Place 125 ml of hydro solution over the soil and allow to soak at least 16 hours.

STANDARD OPERATING PROCEDURE
FOR
ASTM D422 - HYDROMETER ANALYSIS (Wet Method)
(continued)

STEP 5

After soaking, pour soil/solution mixture into the blender and mix for 1 minute. After 1 minute of mixing, transfer soil/solution mixture into hydrometer flask. Use a squirt bottle to remove all soil from the blender. Fill the hydrometer flask to just below the fill line with distilled water and the soil/solution mixture. Thoroughly mix the distilled water and soil/solution mixture by inverting and reversing the flask for 1 minute. Wash down any remaining soil on the sides of the flask and bring the water level (bottom of the meniscus) up to the fill line using a squirt bottle with distilled water.

STEP 6

After 1 minute, place the hydrometer bulb into the hydrometer flask and take your first hydrometer and temperature reading. Readings should be taken at exactly 2, 5, 15, 30, and 60 minutes and at least 720 minutes (12 hours) and recorded on a sieve sheet. Record temperature from the control flask at the start of the test and at the end.

STEP 7

After taking final reading; wash all soil/solution over the #200 sieve. Transfer the material retained on the #200 sieve into tare and place in the drying oven. After drying, pass the material over a nest of two sieves (#40 and #200 sieve). Weigh the material collected on each sieve and record on sieve sheet.

STEP 8

Check the data sheet for completeness.

Prepared by: B. M. Griggs 3/3/95
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Approved by: Kirk Lowery 11/14/95

Standard Test Method for pH of Soils[1]

This standard is issued under the fixed designation D 4972; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of the pH of soils for uses other than for corrosion testing. Such measurements are used in the agricultural, environmental, and natural resources fields. This measurement determines the degree of acidity or alkalinity in soil materials suspended in water and a 0.01 *M* calcium chloride solution. Measurements in both liquids are necessary to fully define the soil's pH. This variable is useful in determining the solubility of soil minerals and the mobility of ions in the soil and assessing the viability of the soil-plant environment. A more detailed discussion of the usefulness of this parameter is not warranted here; however, it can be found in many discussions of the subject. A few such discussions are given as Refs **(1)**[2] through **(6)** at the end of the text.

1.2 The values given in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials[3]

D 1193 Specification for Reagent Water[4]

G 51 Test Method for pH of Soil for Use in Corrosion Testing[5]

3. Summary of Test Method

3.1 Measurement of the pH of soils in both suspensions of water and a calcium chloride solution are made with either a potentiometer using a pH sensitive electrode system (Method A), or pH sensitive paper (Method B). The potentiometer is calibrated with buffer solutions of known pH. The pH sensitive paper is a less accurate measurement and should only be used for a rough estimate of the soil pH. The electrode must be used for this measurement unless the pH sensitive paper is specified.

4. Significance and Use

4.1 The pH of the soil is a useful variable in determining the solubility of soil minerals and the mobility of ions in the soil and assessing the viability of the soil-plant environment.

4.2 pH measurements are made in both water and a calcium chloride solution because the calcium displaces some of the exchangeable aluminum. The low ionic strength counters the dilution effect on the exchange equilibrium by setting the salt concentration of the solution closer to that expected in the soil solution. The pH values obtained in the solution of calcium chloride are slightly lower than those measured in water due to the release of more aluminum ions which then hydrolyses. Therefore, both measurements are required to fully define the character of the soil's pH.

4.3 For the purpose of this test method the test soil must be sieved through a No. 10 sieve (2 mm sieve mesh openings). Measurements on soils or soil fractions having particle sizes larger than 2 mm by this test method may be invalid. If soil or soil fractions with particles larger than 2 mm are used, it must be stated in the report since the results may be significantly different.

4.4 All water used for this test method must be ASTM Type III or better. Type III water is defined by Specification D 1193. It is prepared by distillation, ion exchange, reverse osmosis, or a combination thereof.

5. Interferences

5.1 This test method as measured by a pH probe has possible interferences due to a suspension effect or sedimentation potential. Users interested in a detailed discussion of the mechanism of this effect can find it in Refs **(5)** and **(6)**.

5.2 This effect is the main reason Test Method G 51 can not be used for general measurement of pH outside of that for corrosion analysis. Test Method G 51 measures pH (an aqueous parameter) without adding any aqueous phase to the soil. This results in excessive soil particle-pH probe contact that overestimates the activity of the hydrogen ions in solution and is therefore unacceptable for general soil analysis.

5.3 The suspension effect can be mitigated by careful attention to 9.1.

6. Apparatus

6.1 *Method A, pH Meter*—Potentiometer equipped with glass-calomel electrode system. Follow the manufacturer's instructions for the pH meter used. A silver/silver chloride electrode system or similar is also acceptable.

6.2 *Method B, pH Paper*—pH paper sensitive to a pH range from 1 to 12, with resolution to the nearest 0.2 pH unit.

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.22 on Soil as a Medium for Plant Growth.

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[2] The boldface numbers in parentheses refer to a list of references at the end of the test method.

[3] *Annual Book of ASTM Standards*, Vol 04.02.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 03.02.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—All water used for this test method must be ASTM Type III or better. Type III water is defined by Specification D 1193. It is prepared by distillation, ion exchange, reverse osmosis, or a combination thereof.

7.3 *Acid Potassium Phthalate Buffer Solution* (0.05 *M*)—Dissolve 10.21 g (dried 1 h at 105°C) of potassium phthalate in water and dilute to 1 L. The pH of this solution should be 4.0 at 20°C. Protect the solution against evaporation and against contamination with molds. Replace the solution when mold is noticed. The effect of temperature is as follows:

°C	pH
5 to 37	4.0

This illustrates that the pH of the solution does not change over the range in temperature from 5 to 37°C.

7.4 *Calcium Chloride Stock Solution* (1.0 *M*)—Dissolve 147 g of $CaCl_2 \cdot 2H_2O$ in water in a 1-L volumetric flask, cool, dilute to volume with water, and mix.

7.5 *Calcium Chloride Solution* (0.01 *M*)—Dilute 20.0 mL of stock 1.0 *M* $CaCl_2$ solution to 2 L with water. The pH of this solution should be between 5 and 7.

7.6 *Phosphate Buffer Solution* (0.025 *M*)—Dissolve 3.40 g of KH_2PO_4 and 3.55 g of KH_2HPO_4 in water and dilute to 1 L. Dry salts 2 h at 130°C before use. The pH of this solution should be 6.9 at 20°C. The effect of temperature is as follows:

°C	pH
0	7.0
10	6.9
20	6.9
30	6.8
40	6.8

8. Calibration of pH Meter

8.1 Calibrate the pH meter using the acid potassium phthalate and phosphate buffer solutions. Adjustment of the pH meter should follow the manufacturer's direction.

9. Procedure

9.1 When making measurements with the pH electrode, place the electrode into the partially settled suspension to mitigate the suspension effect.

9.2 For both methods, begin with an air dried soil that has been sieved through a No. 10 sieve (2 mm holes) to remove the coarser soil fraction. Air drying the soil is necessary to accomplish sieving and to control the amount of water present at the time of measurement.

9.3 *pH in Distilled Water*—For both methods, weigh out approximately 10 g of air dried soil. Place the soil into a glass container and add approximately 10 mL of water. Mix thoroughly and let stand for 1 h.

9.4 *Method A*—Read pH on pH meter.

9.5 *Method B*—Read pH on pH paper.

9.6 *pH in 0.01 M Calcium Chloride Solution*—For both methods weigh out approximately 10 g of air dried soil. Place the soil into a glass container and add approximately 10 mL of the 0.01 *M* $CaCl_2$ solution. Mix thoroughly and let stand for 1 h.

9.7 *Method A*—Read pH on pH meter.

9.8 *Method B*—Read pH on pH paper.

9.9 The mixture should be at approximately room temperature (15 to 25°C) at the time of pH measurement.

10. Report

10.1 Report the pH of the soil to the first decimal place. Specify which of the pH measurements is in water and which is in the calcium chloride solution. Also specify whether the determinations were made with Method A or Method B. If size fractions other than sieved through the No. 10 sieve are used, it must be stated in the report since the results may be significantly different.

11. Precision and Bias

11.1 *Precision:*

11.1.1 *Within-Laboratory Precision*—The within laboratory standard deviations for Method A are 0.031 (pH units) for the water mixture and 0.139[7] (pH units) for the calcium chloride mixture. Therefore, results of two properly conducted tests in the same or different laboratories should not differ by more than 0.065[7] (pH units) for the water mixture and 0.389 pH units for the calcium chloride mixture. The within-laboratory standard deviations for Method B are 0.189 (pH units) for the water mixture and 0.212[7] (pH units) for the calcium chloride mixture. Therefore, results of two properly conducted tests in the same or different laboratories should not differ by more than 0.53[7] (pH units) for the water mixture and 0.60 pH units for the calcium chloride mixture.

11.1.1.1 The precision of Method A presented was determined by the National Technical Center of the United States Department of Agriculture. In their evaluation they used 174 replicates for the water mixture and 32 replicates in testing the calcium chloride mixture.

11.1.1.2 The precision of Method B presented was determined by the United States Army Environmental Hygiene Agency. In their evaluation they used 25 replicates in testing each mixture.

11.1.2 *Between-Laboratory Precision*—The between-laboratory standard deviation has not been determined for either method. Subcommittee D18.22 is actively seeking data to evaluate the between laboratory precision of this test method.

11.2 *Bias*—There is no accepted reference value for this test method; therefore, bias cannot be determined.

12. Keywords

12.1 acidity; alkalinity; pH; reaction; soil

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[7] These data satisfy the 1S and D2S requirements outlined in Practice C 670.

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Designation: D 2974 – 87 (Reapproved 1995)

Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils[1]

This standard is issued under the fixed designation D 2974; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the measurement of moisture content, ash content, and organic matter in peats and other organic soils, such as organic clays, silts, and mucks.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Summary of Test Methods

2.1 *Test Method A*—Moisture is determined by drying a peat or organic soil sample at 105°C. The moisture content is expressed either as a percent of the oven dry mass or of the as-received mass.

2.2 *Test Method B*—This is an alternative moisture method which removes the total moisture in two steps: (*1*) evaporation of moisture in air at room temperature (air-drying), and (*2*) the subsequent oven drying of the air-dried sample at 105°C. This method provides a more stable sample, the air-dried sample, when tests for nitrogen, pH, cation exchange, and the like are to be made.

2.3 *Test Methods C and D*—Ash content of a peat or organic soil sample is determined by igniting the oven-dried sample from the moisture content determination in a muffle furnace at 440°C (Method C) or 750°C (Method D). The substance remaining after ignition is the ash. The ash content is expressed as a percentage of the mass of the oven-dried sample.

2.4 Organic matter is determined by subtracting percent ash content from one hundred.

3. Apparatus

3.1 *Oven*, capable of being regulated to a constant temperature of 105 ± 5°C.

NOTE—The temperature of 105°C is quite critical for organic soils. The oven should be checked for "hot spots" to avoid possible ignition of the specimen.

3.2 *Muffle Furnace*, capable of producing constant temperatures of 440°C and 750°C.

3.3 *Evaporating Dishes*, of high silica or porcelain of not less than 100-mL capacity.

3.4 *Blender*, high-speed.

3.5 *Aluminum Foil*, heavy-duty.

3.6 *Porcelain Pan, Spoons*, and equipment of the like.

3.7 *Desiccator.*

4. Preparation of Sample

4.1 Place a representative field sample on a square rubber sheet, oil cloth, or equivalent material. Reduce the sample to the quantity required by quartering and place in a moisture-proof container. Work rapidly to prevent moisture loss or perform the operation in a room with a high humidity.

MOISTURE CONTENT

5. Test Method A

5.1 Record to the nearest 0.01 g the mass of a high silica or porcelain evaporating dish fitted with a heavy-duty aluminum foil cover. The dish shall have a capacity of not less than 100 mL.

5.2 Mix thoroughly the representative sample and place a test specimen of at least 50 g in the container described in 5.1. Crush soft lumps with a spoon or spatula. The thickness of peat in the container should not exceed 3 cm.

5.3 Cover immediately with the aluminum foil cover and record the mass to the nearest 0.01 g.

5.4 Dry uncovered for at least 16 h at 105°C or until there is no change in mass of the sample after further drying periods in excess of 1 h. Remove from the oven, cover tightly, cool in a desiccator, and record the mass.

6. Test Method A Calculation

6.1 Calculate the moisture content as follows:

$$\text{Moisture Content, \%} = [(A - B) \times 100]/A$$

where:

A = mass of the as-received test specimen, g, and

B = mass of the oven-dried specimen, g.

6.1.1 This calculation is used primarily for agriculture, forestry, energy, and horticultural purposes and the result should be referred to as the moisture content as a percentage of as-received or total mass.

6.2 An alternative calculation is as follows:

$$\text{Moisture Content, \%} = [(A - B) \times 100]/B$$

where:

A = as-received test specimen, g, and

B = mass of the oven-dried specimen, g.

[1] These test methods are under the jurisdiction of ASTM Committee D-18 on Soil and Rock and are the direct responsibility of Subcommittee D18.18 on Peats and Related Materials.

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6.2.1 This calculation is used primarily for geotechnical purposes and the result should be referred to as the moisture content as a percentage of oven-dried mass.

6.3 Take care to indicate the calculation method used.

7. Test Method B

7.1 This test method should be used if pH, nitrogen content, cation exchange capacity, and the like are to be tested.

7.2 Mix the sample thoroughly and select a 100 to 300 g representative sample. Determine the mass of this sample and spread evenly on a large flat pan. Crush soft lumps with a spoon or spatula and let the sample come to moisture equilibrium with room air. This will require at least 24 h. Stir occasionally to maintain maximum air exposure of the entire sample. When the mass of the sample reaches a constant value, calculate the moisture removed during air drying as a percentage of the as-received mass.

7.3 Grind a representative portion of the air-dried sample for 1 to 2 min in a high-speed blender. Use the ground portion for moisture, ash, nitrogen, cation exchange capacity tests, and the like.

7.4 Thoroughly mix the air-dried, ground sample. Weigh to the nearest 0.01 g the equivalent of 50 g of test specimen on an as-received basis. Determine the amount, in grams, of air-dried sample equivalent to 50 g of as-received sample, as follows:

$$\text{Equivalent Sample Mass, g} = 50.0 - [(50 \times M)/100]$$

where:

M = moisture removed in air drying, %.

7.5 Place the sample in a container as described in 5.1 and proceed as in Method A.

8. Test Method B Calculation

8.1 Calculate the moisture content as follows:

$$\text{Moisture Content, \%} = (50 - B) \times 2$$

where:

B = oven-dried sample, g.

8.1.1 This calculation gives moisture content as a percentage of as-received mass.

8.2 An alternative calculation is as follows:

$$\text{Moisture Content, \%} = [(50 - B) \times 100]/B$$

8.2.1 This calculation gives moisture content as a percentage of oven-dried mass.

ASH CONTENT

9. Test Method C

9.1 Determine the mass of a covered high-silica or porcelain dish.

9.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen.

9.3 Remove the cover and place the dish in a muffle furnace. Gradually bring the temperature in the furnace to 440°C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

9.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass.

9.5 This test method should be used for all geotechnical and general classification purposes.

10. Test Method D

10.1 Determine the mass of a covered high-silica or porcelain dish.

10.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen.

10.3 Remove the cover and place the dish in a muffle furnace. Gradually bring the temperature in the furnace to 750°C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

10.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass.

10.5 This test method should be used when peats are being evaluated for use as a fuel.

11. Calculation for Test Methods C and D

11.1 Calculate the ash content as follows:

$$\text{Ash Content, \%} = (C \times 100)/B$$

where:

C = ash, g, and

B = oven-dried test specimen, g.

ORGANIC MATTER

12. Calculation

12.1 Determine the amount of organic matter by difference, as follows:

$$\text{Organic matter, \%} = 100.0 - D$$

where:

D = ash content, %.

13. Report

13.1 Report the following information:

13.1.1 Results for organic matter and ash content, to the nearest 0.1 %.

13.1.2 Furnace temperature used for ash content determinations.

13.1.3 Whether moisture contents are by proportion of as-received mass or oven-dried mass.

13.1.3.1 Express results for moisture content as a percentage of as-received mass to the nearest 0.1 %.

13.1.3.2 Express results for moisture content as a percentage of oven-dried mass as follows:

(*a*) Below 100 % to the nearest 1 %.

(*b*) Between 100 % and 500 % to the nearest 5 %.

(*c*) Between 500 % and 1000 % to the nearest 10 %.

(*d*) Above 1000 % to the nearest 20 %.

14. Precision and Bias

14.1 The precision and bias of these test methods have not been determined. Data are being sought for use in developing a precision and bias statement.

STANDARD OPERATING PROCEDURE (SOP)

1. **TITLE**-Data Validation Procedures for EPA Level III Data

2. **PRINCIPLE REFERENCE**-

   U.S. EPA "National Functional Guidelines for Organic Data Review", December 1990, revised June, 1991.

   U.S. EPA "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analysis", October 1989.

   U.S. EPA "Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses", July 1, 1988.

3. **APPLICATION**-The purpose of this Standard Operating Procedure (SOP) is to establish a uniform procedure for evaluating the quality of data obtained from laboratories. The validation procedures contained in this SOP are applicable to data where a summary Quality Control (QC) package has been required. Data may be validated against criteria in SW846, EPA 600 Series Methods, CLP, or other reference methods. The contents of the QC package can be determined by the client or specified in the Quality Assurance Project Plan (QAPP) or Sampling Analysis Plan (SAP), however, the following quality control results are generally reviewed:

Organics	Inorganics
Holding Times	Holding Times
Laboratory Blanks	Laboratory Blanks
Surrogate Spikes	Laboratory Duplicates
Matrix Spike/Matrix Spike Duplicates (MS/MSDs)	Laboratory Control Samples
Field Blanks	Matrix Spikes
Field Duplicates	Field Blanks
	Field Duplicates

Additional quality control results will be reviewed if required by the project. These include:

Organics	Inorganics
Tuning Results	Initial/Continuing Calibrations
Initial and Continuing Calibrations	ICP Serial Dilution
Internal Standard Areas	Post Digestion Spikes (PDS)
	Method of Standard Additions (MSA)

Note: This SOP is written mainly for water matrix samples, and limits may vary slightly for other matrices.

4. **SUMMARY OF PROCEDURE** - The goal of data validation is to document noncompliance to the QAPP/SAP or method criteria and to determine the affects of noncompliance on data usability/project objectives. During validation, qualifiers are placed on the data to identify quality control deviations as defined below; the following definitions are brief explanations of the validation qualifiers.

U - The analyte was analyzed for, but not detected above the reported quantitation limit.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

General Guidelines:

During the validation process it is important to document noncompliances to the method and/or QAPP/SAP (and samples affected) to ensure incorporation of these noncompliances into the validation report. A form has been included in Attachment 1 which may be useful to cite problems with data packages and indicate which QC parameters were evaluated.

Data qualifiers should be written directly on the analytical reports during validation. The reason for the qualifiers should be stated at the bottom of the sheet. Any changes to the qualifiers should be crossed out with a single line, initialized and dated. A red pen should be used for applying codes.

The QAPP/SAP and the field forms are tools for the validation process. The QAPP/SAP defines specific quality control limits required for the project and other pertinent information (completeness criteria for project). The field forms are necessary to identify field quality control samples since these samples are often blind to the lab and may be blind to the data reviewer.

5. PROCEDURE-

A. Completeness Evaluation

Assure that the following information is included in the data package, for each analyte and for each sample, as applicable. If this information is not available, contact the laboratory and obtain the missing data.

1. Chain-of-Custody Form

2. Cooler Receipt Form

3. Analytical results for each requested sample and analyte - the results received should be backchecked against the custody form to assure all requested analyses have been received.

4. QC data should also undergo a completeness check; the requested quality control data should be present for each sample.

5. Any reanalysis results due to out-of-control surrogates or internal standards (if reported).

6. Date of Analysis.

7. Date of Extraction (where applicable).

8. Method of Analysis.

9. Contract Required Quantitation Limits for aqueous samples should meet those which were requested (in QAPP/SAP); if not, verify that the sample was diluted. Detection limits achieved may not always be those requested for soil samples due to moisture content.

10. Batch number - Each sample for each type of analysis should be associated with a batch number so that the correct laboratory QC can be associated with it.

B. Organic Data Validation

The following guidelines are applicable to all organic analyses. When analyses are non-routine the reviewer should be thoroughly familiar with QAPP/SAP and method requirements.

1. Holding Times/Preservatives

Holding times are determined from the date of the samples

collection to the date of analysis (or extraction).

a. Evaluate chain-of-custodies to determine sample collection date and the analytical report for the analysis and extraction dates. Chain-of-custodies should also be evaluated for correct preservation. Samples submitted for Volatile Organic Compounds (VOCs) should be preserved with 1:1 hydrochloric acid to a pH <2. At this time, it is also convenient to check that a trip blank is present in the specified frequency for aqueous VOCs.

b. The following table summarizes holding time requirements. For non-routine organics the QAPP/SAP should be reviewed for the correct holding time.

PARAMETERS	AQUEOUS	SOLIDS
Volatiles	14 days if preserved, 7 days if not preserved	14 days
Semivolatiles	Extraction - 7 days Analysis - 40 days from extraction	Extraction -14 days Analysis - 40 days from extraction
PCB/Pesticides	Extraction - 7 days Analysis - 40 days from extraction	Extraction -14 days Analysis - 40 days from extraction

c. All results for samples with holding time exceedances are qualified . If the holding time exceedance is minor (ie. within twice the holding time), results are qualified as estimated for nondetects and positive results (UJ and J, respectively). Samples exceeding twice the holding time (excessive holding time exceedance) are qualified as rejected (R) for nondetects and estimated (J) if a positive result. Samples exceeding holding time requirements are considered to have a potential for low bias due to constituent degradation during the prolonged holding times.

1. If aqueous VOCs were not preserved this should be noted in the validation report and holding time qualifications are based on 7 days.

2. If a trip blank is not present in the specified frequency for aqueous VOCs, this should be stated in the validation report and associated samples listed.

d. Sample temperature on arrival at the laboratory should be 4°C±2°C. Samples arriving at temperature outside this range should be qualified as follows:

<u>VOCs</u>

- Intact samples between 2-6°C. No qualifiers.
- Samples between 6-10°C. All results qualified as estimated (UJ and J).
- Samples greater than 10°C. All nondetect results qualified R. Positive results qualified J.

<u>BNAs, PCB/Pesticides and Herbicides</u>

- Intact samples between 2-6°C. No qualifiers.
- Samples greater than 6°C. All results qualified as estimated (UH and J).

2. **GC/MS Tuning**

Results of GC/MS tunes (often reported on CLP form V) should be reviewed to insure that ion abundance criteria as stated in the method of analysis is achieved. If criteria has not been met, contact the lab to verify that a transcription error has not been made (request raw data). If critical ion abundance criteria as defined below are not met, both non detect results and positive results should be rejected (R). If relative abundances of non-critical ions are outside criteria, nondetects and positive results should be qualified as estimated (UJ and J, respectively).

BFB:

Characteristics Ions
50
75
95/96
174/175
174/176
176/177
173

DFTPP:

Critical Ions	Non-critical Ions
198/199	51
442/443	127
68	275
70	
197	
441	
365	

Tune forms should also be reviewed to verify samples were analyzed within the 12 hour tune period. The 12 hour tune period starts at the injection time of the tuning compound (BFB or DFTPP). All subsequent sample injections should be within this twelve hour time frame. If exceedances are evident (usually minor) note these in the validation report. If the reviewer has reason to believe the exceedance of the 12 hour tune period has affected data quality/usability; results should be qualified.

3. **Calibration**

a. Initial Calibration

The initial calibration curve for volatile and semivolatile analyses must contain five calibration points, include all compounds reported and reflect the linear range of the instrument. The percent Relative Standard Deviation (%RSD) and Relative Response Factors (RRFs) for each compound must be reported.

1. %RSDs must be ≤30% for CCC compounds (VOA and SVOA). Positive results associated with the CCC compounds exceeding this limit should be qualified (J). Nondetects associated with high %RSDs should also be qualified (UJ) if the exceedance is excessive (ie.,>50%RSD).

2. If an SPCC has any initial calibration RRF which is <0.05 for SVOA or <0.3 for VOA, except bromoform, <0.25, qualify positive results for this compound as estimated (J) and nondetects as rejected (R) in associated samples.

The initial calibration curve for GC analyses (PCB/pesticides, herbicides) require five calibration points for single component compounds and three calibration points for multi-component compounds (ie aroclors, toxaphene & chlordane), must include all compounds reported (including surrogates), and reflect the linear range of the instrument. The percent Relative Standard Deviation (%RSD) for each compound must be reported. If the %RSD criteria is not met (20% for single component and 30% RSD for multi-components), qualify associated positive results as estimated (J). If the exceedance is excessive (>40%RSD), qualify both positive and nondetects (J and UJ, respectively) per SW-846.

b. Continuing Calibration

The continuing calibration standards for volatile and semivolatile analyses must be analyzed at the start of each 12 hour analysis period and must include all compounds reported including surrogates. The Percent Difference (%D) and the Relative Response Factor (RRF) for each compound must be reported.

1. %Ds must be ≤25% for VOA CCC compounds or ≤30% for SVOA CCC compounds. Positive results associated with CCC compounds exceeding this limit should be qualified J. Nondetects associated with high %Ds should also be qualified (UJ) if the exceedance is excessive (ie., >50%D).

2. If an SPCC compound has a continuing calibration RRF which is less than 0.05 (SVOA) or 0.3 (VOA; except bromoform, 0.25), quality positive results for this compound as estimated (J) and nondetects as rejected (R) in associated samples.

Continuing calibration checks for GC analyses (PCB/Pesticides, herbicides) are to be analyzed every ten analyses and must include all single component Pesticides reported (including surrogates). If the %D reported is greater than 15%, associated positive results should be qualified as estimated (J). Nondetects associated with high %D should also be qualified (UJ) if the exceedance is excessive (ie.,>30%D).

4. Blanks

The purpose of the laboratory blanks (or field blanks) is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The procedure for evaluating blanks applies to all types of blanks (ie., method blanks, instrument blanks, trip blanks, and field blanks); however, there is an order (or hierarchy) in which they should be evaluated (ie. method/instrument blanks, trip blanks, and lastly field blanks). Results must <u>not</u> be corrected by subtracting any blank values.

Frequency - The frequency of blanks should be as stated in the QAPP/SAP or method (usually daily or every 20 samples) and blanks should be submitted for every matrix analyzed. If the frequency criteria has not been met, this should be stated in the validation report.

a. Laboratory Blanks - The B qualifier used by the laboratory should be eliminated and a U qualifier applied as discussed below. If a compound is found in the blank but not the associated samples, no action is taken.

Common Lab Contaminants:

Volatiles	Semivolatiles
Methylene Chloride	Phthalates
Acetone	
2-Butanone	
Toluene	

The 10Xs rule applies to common lab contaminants: A compound detected in the sample and also detected in the blank is qualified U if the sample concentration is less than 10Xs the blank concentration. The quantitation limit should also be evaluated:

If the reported value is less than the quantitation limit, this value should be raised to the quantitation limit and qualified U. Example (using 10Xs rule):

Blank result	7
Quantitation limit	5
Sample result	3J
Validated result	5U

If the reported value is greater than the quantitation limit, the value should remain as reported and qualified U. Example (using 10Xs rule):

Blank result	7
Quantitation limit	5
Sample result	50
Validated result	50U

Data users should be made aware of elevated detection limits due to blank contamination in the validaton report. The 5Xs rule follows the same procedure; however, it applies to target compounds which are not common lab contaminants.

b. Trip Blanks (VOCs) - If trip blanks show contamination that is not related to the lab, associated samples should be qualified using the 5Xs rule.

c. Rinsate Blanks - In general, results for rinsate blanks are only applicable to aqueous samples. Positive results in the rinsate blank, that are not related to the lab or shipment (trip blank) are considered to be contamination from inadequate field decontamination procedures. Associated field samples should be qualified using the procedure discussed above (5Xs rule).

5. **Surrogate Spike**

Surrogate recoveries should be evaluated using limits as specified in the QAPP/SAP. Every sample should have surrogate recovery results if required in the method.

a. High recovery: Qualify positive results J; a high bias is present. Non detects are unaffected.

b. Low recovery (but greater than 10%): Qualify both nondetects (UJ) and positive results (J); a low bias is present.

c. Very low recoveries (less than 10%): Qualify positive results as J and nondetects as R.

d. Both a low recovery and high recovery are present: Qualify as in (b) unless a recovery is less than 10%; use (c) in this case.

When evaluating semivolatiles, 2 surrogate recoveries need to be out-of-control in the same fraction (ie. 2 acids or 2 base/neutrals) and only compounds of the out-of-control fraction are qualified as in (a) and (b) from above. If any one surrogate recovery for semivolatiles is less than 10%, the associated fraction is qualified as in (c).

If surrogate recoveries are outside the established limits for VOCs, a reanalysis may be required; refer to the QAPP/SAP to confirm if this requirement exists. If the reanalysis results are within the surrogate limits, only the reanalysis results should be reported. If both analyses are outside surrogate limits, the results associated with the sample producing surrogate recoveries closer to the established limits should be used.

6. **Matrix Spikes/Matrix Spike Duplicates**

Quality control limits as specified in the QAPP/SAP should be used to evaluate MS/MSD recoveries. RPD's are reported for all organics, but the limits are not applicable per SW-846. Generally, only the unspiked sample is qualified if the MS/MSD is outside established limits.

a. High recovery: Qualify the compound exhibiting the high recovery J in the unspiked sample if the result is positive; a high bias is present. Nondetects are unaffected.

b. Low recovery (but greater than 10%); Qualify both nondetects and positive results (UJ and J, respectively) for only the compound which exhibited the low recovery in the unspiked sample; a low bias is present.

c. Very low recoveries (less than 10%): Qualify the compound exhibiting the very low recovery J if the result of this compound in the unspiked sample is positive and R if nondetected.

d. Both a low recovery and high recovery are present: Qualify as in (b) unless a recovery is less than 10%; use (c) in this case.

7. **Laboratory Control Samples**

Qualify samples based on limits as presented in the QAPP/SAP. If limits are not presented in the QAPP/SAP, use limits submitted by the laboratory. Quality recoveries as in 6 a-d.

8. **Internal Standard Areas**

Internal standard area counts are evaluated for GC/MS analyses (volatiles and semivolatiles) to ensure that the sensitivity and response are stable during each analysis.

Internal standard area counts must not vary by more than a factor of two (-50% to +100%) from the associated calibration standard. If the area count for each sample or blank is outside - 50% or +100% of the area of the associated standard:

a. Positive results for compounds quantitated using that internal standard should be qualified J.

b. Nondetected compounds quantitated using an internal standard count greater than 100% should <u>not</u> be qualified.

c. Nondetected compounds quantitated using an internal standard count less than 50% are reported as the associated sample quantitation limit and qualified as UJ.

d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. A severe loss of sensitivity is defined as an area count less than 25% of the lower limit or less than a 5000 area count. Nondetected target compounds should then be qualified as unusable (R). Positive results should be qualified as estimated (J).

Internal standard retention times: If the internal standard retention time varies more than 30 seconds, the data must be re-evaluated by the lab and raw data submitted for data review.

9. **Confirmation**

Positive results need to be confirmed via a second chromatography column for analyses performed via GC or LC analyses (not required for GC/MS analyses). The parameters which specifically require second column confirmation are PCB/pesticides. For positive results, verify that the results were confirmed. If the positive results were not confirmed, qualify the result as estimated (J).

10. **Field Duplicates**

The Relative Percent Difference (RPD) should be calculated for positive results and results presented in table format with the validation report. If one of the values is a nondetect, the quantitation limit should be used to calculate the RPD.

Qualifiers are generally not assigned based on high RPDs; however, if field duplicates do not agree with QAPP/SAP requirements, it should be noted in the validation report.

C. **Metals Data Validation**

The following guidelines are applicable to all metals analyses. The reviewer should be thoroughly familiar with QAPP/SAP and method requirements. If a CLP reporting format is submitted, the B qualifier which indicates that the concentration is less than the Contract Required Detection Limit (CRDL) but greater than the instrument detection limit (IDL), should be removed to eliminate confusion as to what this qualifier means (it is often thought to be lab contamination).

1. **Holding Times/Preservatives**

Holding times are determined from the date of the sample collection to the date of analysis.

a. Evaluate chain-of-custodies to determine sample collection date and the analytical report for the analysis dates. Chain of custodies should also be evaluated for correct preservation. Aqueous metals samples should be preserved with 1:1 nitric acid to a pH <2 and aqueous cyanide samples preserved with sodium hydroxide to a pH>12.

b. The following table summarizes holding time requirements.

Parameters	Holding Times
Mercury	28 days
Other Metals	6 months
Cyanide	14 days

c. All results for samples with holding time exceedances are qualified. If the holding time exceedance is minor (ie. within twice the holding time) nondetects and positive results are qualified as estimated (UJ and J respectively). Samples exceeding twice the holding time (excessive holding time exceedance) are qualified as rejected (R) for nondetects and estimated (J) if a positive result.

1. If aqueous metals or cyanide are not preserved at the time of collection, qualify positive results and nondetects as estimated (UJ and J, respectively).

2. Sample temperature is not a concern for metals. Cyanide samples should be maintained at 4±2°C. If cyanide samples were received at a temperature >6° C, qualify results of nondetects and positive results as estimated (UJ and J, respectively).

2. **Calibration**

A blank and at least 3 standards (4 standards for mercury) must be used in establishing the initial calibration curve. If not, qualify data as unusable (R). A mid-range standard must be distilled for cyanide. The correlation coefficient should be ≥0.995, if not qualify nondetects and positive results as estimated (UJ and J, respectively).

Initial and continuing calibration verification (ICV and CCV) control limits:

Metals (excluding mercury):	90-110% Recovery
Mercury:	80-120% Recovery
Cyanide:	85-115% Recovery

If the ICV or CCV % recoveries fall outside the acceptance windows within the ranges of:

Metals (excluding mercury):	75-89%
Mercury:	65-79%
Cyanide:	70-84%

Qualify both nondetects and positive results as estimated (UJ and J).

Metals (excluding mercury):	<75%
Mercury:	<65%
Cyanide:	<70%

Qualify both nondetects and positive results as unusable (R).

Metals (excluding mercury):	111-125%
Mercury:	121-135%
Cyanide:	116-130%

Qualify positive results as estimated (J). Nondetects are usable.

Metals (excluding mercury):	>125%
Mercury:	>130%
Cyanide:	>135%

Qualify positive results as unusable (R). Nondetects are usable (no qualifiers).

3. Blanks

The purpose of laboratory blanks (or field blanks) is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The procedure for evaluating blanks applies to all types of blanks (ie. method blanks, instrument blanks, and field blanks); however, there is an order (or hierarchy) in which they should be evaluated (ie. first method/instrument blanks, and last field blanks).

Frequency - The frequency of blanks should be as stated in the QAPP/SAP or method (usually every 20 samples) and blanks should be submitted for every matrix analyzed. If the frequency criteria has not been met, this should be stated in the validation report.

a. Laboratory Blanks - If a metal is found in the blank but <u>not</u> the associated samples, no action is taken.

If the concentration of an analyte in the blank exceeds the CRDL (or reporting limits if CLP forms are not used) qualify associated positive results within five times the concentration of the blank as U. (See reference #3).

For analytes with negative results whose value exceeds - the CRDL (or reporting limit if CLP forms are not used), nondetects should be qualified as unusable (R). Positive results within 3X the CRDL should be qualified as estimated (J) and are considered to have a potential for low bias. Positive results greater than 3Xs the CRDL are acceptable.

b. Field Blanks - In general, results for field blanks are only applicable to water samples. If contamination that is not related to the lab is found, associated field samples should be qualified using the procedure discussed above.

4. Laboratory Control Samples (LCS)

Aqueous LCSs:

All results should be within 80-120% recovery or as defined in the QAPP/SAP.

If the recovery for a metal is low (50-79% recovery), qualify associated nondetects and positive results as estimated (UJ and J, respectively). The qualified results have a potential for low bias.

If the recovery for a metal is very low (<50%), qualify associated sample results as unusable (R).

If the recovery is high (>120%), do not qualify associated nondetects; qualify associated positive results as estimated (J). Positive results qualified have a potential for high bias.

5. Laboratory Duplicates

For sample results greater than 5Xs the CRDL (or reporting limit): duplicate results should be within 20 RPD. If not, qualify associated positive results as estimated (J).

If one or both sample results are less than 5Xs the CRDL: duplicate results should be within ± the CRDL. If not, qualify the associated positive results as estimated (J).

The direction of the sample bias cannot be determined due to laboratory duplicate imprecision.

6. **Matrix Spikes**

Spike recoveries must be within 75-125% recovery or as defined in QAPP/SAP, however, these limits do not apply when the concentration of the metal in the sample exceeds the concentration of the spike by a factor of 4 (this QC data cannot be used for qualifying samples).

If the recovery for a metal is low (30-74% recovery), qualify associated results as estimated (UJ and J). The qualified results have a potential for low bias.

If the recovery for a metal is very low (<30%), qualify associated positive results as estimated (J) and nondetects as unusable (R). Positive results have a potential for a low bias while nondetects are unusable - the presence or absence of this analyte cannot be verified.

If the recovery is very high (>120% recovery), do not qualify associated nondetects; qualify associated positive results as estimated (J). Positive results qualified have a potential for high bias.

7. **Furnace QC**

Post Digestion Spikes: Metals ran via furnace methodologies are required to run post digestion spikes (PDSs). Recovery limits for PDSs are 85-115% recovery.

a. If the recovery is ≥10% and <85% qualify both nondetects and positive results as estimated (UJ and J, respectively).

b. If the recovery is >115% qualify positive results as estimated (J).

c. If the recovery is <10% qualify positive results as estimated (J) and nondetects as unusable (R).

Method of Standard Additions (MSA): If it is evident that MSA is required but has not been performed, qualify nondetects and positive results as estimated (UJ and J, respectively). If the MSA correlation coefficient is <0.995, qualify nondetects and positive results as estimated (UJ and J, respectively).

8. ICP Serial Dilution

ICP metals with a sufficiently high sample concentration should be evaluated for chemical interferences due to matrix effects. Only metals with sample concentrations greater than 50 times the IDL should be evaluated. The original result and a five fold dilution must agree within 10% Difference (%D). If this criteria is not met, qualify associated sample results for that analyte as estimated (J) if the sample concentration is greater than 50 times the IDL.

9. Field Duplicates

Field Duplicates - The relative percent difference (RPD) should be calculated for positive results and results presented in table format with the validation report. If one of the values is a nondetect, the reporting limit should be used to calculate the RPD. If one or both of the results are less than five times the reporting limit, a control limit of +/- 2Xs will be used.

Qualifiers are generally not assigned based on high RPDs, however, if field duplicates do not agree with QAPP/SAP requirements, this should be discussed in the validation report.

6. DOCUMENTATION-

A validation report is required for all data validated and is submitted as a technical memorandum. It should include QC parameters which were evaluated and all noncompliances to the QAPP/SAP or analytical methods. If noncompliances affect data quality and validation codes are applied, the affected samples should be listed with a discussion regarding the affects of the noncompliance on the data included (ie. whether sample bias can be determined). An overall discussion is also necessary which states whether the data has met the objectives of the project (completeness evaluation), if resampling needs to occur (usually this is evident to the project chemist before the validation stage), and the effects of rejected data on the project.

A final comparison of codes reported in the validation report should be made to codes present on hardcopy reports. The reviewer should evaluate the validation report and the hardcopy results (and database results) to verify that codes discussed in the report are present on hard copies (and in the database).

7. CALCULATIONS-All calculations are per the WMX Environmental Monitoring Laboratories, Inc., Comprehensive Quality Assurance Plan (QAPP).

8. REFERENCES-

WMX Environmental Monitoring Laboratories, Inc., Comprehensive Quality Assurance Plan (QAPP), August 5, 1994.

U.S. EPA "Test Methods for Evaluating Solid Waste Physical/Chemical Methods", SW-846 3rd. Edition November, 1986, Final Update July, 1992.

Any method references cited in facility's permit, QAPP or SAP.

ATTACHMENT A

Level III Data Quality Review
Data Review Worksheets

Site Name_____

REVIEW OF ORGANIC DATA PACKAGE

The hardcopied (laboratory name)_____data package has been reviewed and the quality assurance and performance data summarized. The data review included:

No. of Samples_____
Matrix_____
VOCs, SVOCs, PCB/Pesticides

Sampling Date(s)_____
Shipping Date(s)_____
Date Received by Lab_____

Sample Nos:

Trip Blanks No.:

Rinsate Blank No.:

Field Dup. Nos:

The general criteria used to determine the performance were based on an examination of:

___Data Completeness
___Holding Times
___GC/MS Tuning
___Calibrations
___Lab Control Samples
___Laboratory and Field Blanks
___Surrogate Recoveries
___Mat.Spikes/Mat. Spike Duplicates
___Internal Standards
___Quantitation Limits
___Field Duplicate Precision

Overall Comments:

Reviewer:_____ Date:_____

Level III Data Quality Review
Data Review Worksheets

Site Name_____

I. DATA COMPLETENESS

MISSING INFORMATION	DATE LAB CONTACTED	DATE RECEIVED

Level III Data Quality Review
Data Review Worksheets

Site Name_____

II. HOLDING TIMES

Complete table for all samples and circle the fractions which are not within the criteria.

SAMPLE ID	DATE SAMPLED	VOA DATE	BNA DATE EXTR	BNA DATE ANAL.	PEST DATE EXTR.	PEST DATE ANAL.

VOA Aqueous (unpreserved) - 7 days
Aqueous (preserved) - 14 days
BNA & PEST. Waters: Extract within 7 days, analyze within 40 days

ACTION:
1. If holding times are exceeded all positive results are estimated (J) and non-detects are estimated (UJ)
2. If holding times are grossly exceeded (2 weeks or greater) the reviewer may determine that nondetects are unusable (R).

Level III Data Quality Review
Data Review Worksheets

Site Name_____

III GC/MS TUNING

_____ The DFTPP performance results were reviewed and found to be within the specified criteria and samples analyzed within the 12 hour tune period.

If no,
Samples affected:_____

_____ The BFB performance results were reviewed and found to be within the specified criteria and samples analyzed within the 12 hour tune period.

If no,
Samples affected:_____

If mass calibration is in error to the validation guidelines for expanded criteria. If necessary, qualify all associated data as unusable (R).

Describe specific problems below:

Level III Data Quality Review
Data Review Worksheets

Site Name_____

IV. CALIBRATIONS

Fraction:_____ Dates of Initial Calibration:_____
Instrument ID:_____ Dates of Continuing Calibration_____

DATE	COMPOUNDS	EXCEEDANCES	SAMPLES QUALIFIED

1. Average RRF's and RRF's must be ≥0.05 (SVOC's, SPCC's) or ≥0.3 (VOC's, SPCC's except Bromoform ≥ 0.25).

2. %RSD's must be ≤30% (VOCs & SVOCs) for CCC compounds. %RSD's must be ≤20% for GC.

3. %D's must be ≤25% (VOC's) or ≤30% (SVOC's) for CCC compounds. %D's must be ≤ 15% (GC).

Level III Data Quality Review
Data Review Worksheets

Site Name_____

V. LABORATORY CONTROL SAMPLE

List any recoveries not within the SAP/QAPP criteria and the sample affected.

Matrix_____

DATE	LAB ID.	EXCEEDANCES	RESULTS QUALIFIED

Level III Data Quality Review

Site Name_____

Data Review Worksheets

VI. BLANK ANALYSIS RESULTS

List the contaminants in the blank below.

1. Laboratory Blanks

DATE	LAB ID	FRACTION/ MATRIX	COMPOUND DETECTED/ CONC.	SAMPLES QUALIFIED

2. Rinsate and Trip Blanks

DATE	FIELD ID.	FRACTION/ MATRIX	COMPOUND DETECTED/ CONC.	SAMPLES QUALIFIED

Level III Data Quality Review
Data Review Worksheets

Site Name_____

VII. SURROGATE RECOVERIES

List the percent recoveries which do not meet the criteria for surrogate recovery.

Matrix_____

FIELD ID	VOA DCE	VOA TOL	VOA BFB	BN NZB	BN FBP	BN TPH	ACID PHL	ACID 2FP	ACID TBP	PCB/ PEST TCMX	PCB/ PEST DCP

Surrogate Actions:

	PERCENT RECOVERY		
	<10%	<RRR	>RRR
Positive Sample Results	J	J	J
Non-detected Results	R	UJ	Acceptable

RRR=Required Recovery Range (SAP or QAPP)

Level III Data Quality Review
Data Review Worksheets

Site Name_____

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

1. Matrix Spike/Matrix Spike Duplicate Recoveries and Precision

List the samples spiked.

FRACTION	FIELD ID	LEVEL	MATRIX

List the percent recoveries and RPD's of compounds which do not meet the criteria in the SAP/QAPP. (Criteria not applicable to SW846 methods, RPDs reported only).

MS or MSD	COMPOUND	%REC/RPD	QC LIMITS

QUALIFICATION IS LIMITED TO THE UNSPIKED SAMPLE ONLY.

1. If any compound does not meet the Required Recovery Range (RRR) as specified in the SAP/QAPP follow the actions stated below.

	PERCENT RECOVERY		
	≤10%	10%-RRR	> RRR
Positive Sample Results	J	J	J
on-detected Results	R	UJ	Acceptable

Level III Data Quality Review Site Name_____
Data Review Worksheets

IX. INTERNAL STANDARD PERFORMANCE

List the internal standard areas of samples which do not meet the criteria of +100% or -50% of the internal standard area in the associated continuing calibration standard.

FIELD ID	DATE	IS OUT	IS AREA/RT	ACCEPTABLE RANGE	ACTION

ACTION:

1. If an IS area count is outside the criteria -50% or +100% of the associated standard:

a. Positive results for compounds quantitated using that IS are flagged as estimated (J) for that sample fraction.

b. Nondetects for compounds quantitated using that IS are flagged as estimated (UJ) for that sample fraction.

c. If extremely low area counts are reported, or if performace exhibits a major drop-off, then a severe loss of sensitivity is indicated. Nondetects should be flagged as unusable (R).

2. If an IS retention time varies more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exists. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

X. QUANTITATION

List samples/fraction which did not meet QAPP/SAP quantitation limits with an explanation.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

XI. FIELD DUPLICATE PRECISION

Sample Nos._____ , _____ Matrix:_____

List the concentrations and RPD of the compounds detected in the field duplicate. Circle RPDs that do not meet QAPP/SAP criteria.

FRACTION	COMPOUND	SAMPLE CONC.	FIELD DUP CONC.	RPD

Level III Data Quality Review
Data Review Worksheets

Site Name_____

REVIEW OF INORGANIC DATA PACKAGE

The hardcopied (laboratory name)_____data package has been reviewed and the quality assurance and performance data summarized. The data review included:

No. of Samples_____ Sampling Date(s)_____

Matrix_____ Shipping Date(s)_____

Date Rec'd by lab_____

Sample Nos:

.insate Blank Nos:

Field Dup Nos.

The general criteria used to determine the performance were based on an examination of:

___Data Completeness
___Holding Times
___Calibrations
___Blanks
___Matrix Spike Recoveries
___Laboratory Duplicates
___Laboratory Control Samples
___Furnace AA Results
___ICP Serial Dilution Results
___ICP Interference Check
___Quantitation
___Field Duplicates

Overall comments:

.eviewer:_____ Date:_____

Level III Data Quality Review
Data Review Worksheets

Site Name_____

I. DATA COMPLETENESS

MISSING INFORMATION	DATE LAB CONTACTED	DATE RECEIVED

Level III Data Quality Review
Data Review Worksheets

Site Name_____

II. **HOLDING TIMES** Complete table for all samples and circle the fractions which are not within the criteria.

SAMPLE ID.	DATE SAMPLED	Hg ANALYSIS DATE	CYANIDE ANALYSIS DATE	OTHERS ANALYSIS DATE	pH	ACTION

METALS 180 DAYS FROM SAMPLE COLLECTION
MERCURY 28 DAYS FROM SAMPLE COLLECTION
CYANIDE 14 DAYS FROM SAMPLE COLLECTION

ACTION:

1. If holding times are exceeded all positive results are estimated (J) and nondetects are estimated (UJ).

2. If holding times are grossly exceeded, the reviewer may determine that nondetects are unusable (R).

Level III Data Quality Review
Data Review Worksheets

Site Name_____

III.A. CALIBRATIONS

1. Recovery Criteria

List the analytes which did not meet the percent recovery (%R) criteria for Initial or Continuing Calibration.

DATE	ICV/CCV#	ANALYTE	% R	ACTION	SAMPLES AFFECTED

ACTIONS:

If any analyte does not meet the %R criteria follow the actions stated below:

For Positive Results:

	ACCEPTED	ESTIMATED (J)	REJECTED (R)
METALS	90-110%R	75-89%R, 111-125%R	<75%R, >125%R
MERCURY	80-120%R	65-79%R, 121-135%R	<65%R, >135%R
CYANIDE	85-115%R	70-84%R, 116-130%R	<70%R, >130%R

For Nondetect Results:

	ACCEPTED	ESTIMATED (UJ)	REJECTED (R)
METALS	90-125%R	75-89%R	<75%R, >125%R
MERCURY	80-135%R	65-79%R	<65%R, >135%R
CYANIDE	85-130%R	70-84%R	<70%R, >130%R

Level III Data Quality Review
Data Review Worksheets

Site Name_____

III B. **CALIBRATIONS**

2. Analytical Sequence

A. Did the laboratory use the proper number of standards for calibration as described in the analytical method?
YES or NO

B. Were calibrations performed at the beginning of each analysis?
YES or NO

C. Were calibration standards analyzed at the beginning of sample analysis and at a minimum frequency of ten percent of every two hours during analysis, whichever is more frequent?
YES or NO

D. Were the correlation coefficients for the calibration curves for AA, Hg and CN $\geq$0.995?
YES or NO

E. Was a standard at 2xCRDL analyzed for all ICP analyses?
YES or NO

If NO, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

IV. BLANK ANALYSIS RESULTS

List the contaminants in the blanks below.

1. Laboratory Blanks

Matrix_____

DATE	ICB/CCB#	PREP BLANK	ANALYTE DETECTED/CONC.	SAMPLES QUALIFIED

2. Rinsate Blanks

DATE	FIELD ID	ANALYTE DETECTED	CONC.	SAMPLES QUALIFIED

3. Frequency Requirements

A. Was a preparation blank analyzed for each matrix, for every 20 samples and for each digestion batch? YES or NO

B. Was a calibration blank run every 10 samples or every 2 hours whichever is more frequent? YES or NO

Level III Data Quality Review
Data Review Worksheets

Site Name_____

V. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

1. Matrix Spike/Matrix Spike Duplicate Recoveries and Precision

Sample No._____,_____ Level:_____ Matrix:_____

List the percent recoveries and RPD's of compounds which do not meet the criteria stated on Form 3.

MS or MSD	ANALYTE	%REC/RPD	QC LIMITS

Matrix Spike Actions apply to all samples of the same matrix.

ACTIONS:

1. If the sample concentration exceeds the spike concentration by a factor of 4 or more, no action is taken.
2. If any analyte does not meet the %R criteria, follow the actions below.

	PERCENT RECOVERY		
	<30%	30%-RRR	>RRR
Positive Sample Results	J	J	J
Nondetected Results	R	UJ	Acceptable

RRR=Required Recovery Range (QAPP or SAP)

2. Frequency Criteria

A. Was a matrix spike prepared at the required frequency? YES or NO
B. Was a post digestion spike analyzed for elements that did not meet required criteria for matrix spike recovery? YES or NO

Level III Data Quality Review
Data Review Worksheets

Site Name_____

VI. LABORATORY DUPLICATES

List the concentrations of any analyte not meeting the criteria for laboratory duplicate precision. Indicate what criteria was used to evaluate precision by circling either the RPD or reporting limit for each element.

Matrix:_____

ELEMENT	REPORTING LIMIT WATER	SAMPLE #	DUP. #	RPD	ACTION

Laboratory duplicate actions should be applied to all other samples of the same matrix.

ACTIONS:

1. Estimate (J) positive results for elements which have RPD greater than SAP (QAPP) limits.

2. If sample results are less than 5X the reporting limit, estimate (J) positive results for elements whose absolute difference is the reporting limit.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

VII. LABORATORY CONTROL SAMPLE

1. AQUEOUS LCS

List any LCS recoveries not within the 80-120% (or SAP/QAPP) criteria and the samples affected.

Matrix:_____

DATE	ELEMENT	%REC	ACTION	SAMPLES AFFECTED

Level III Data Quality Review
Data Review Worksheets

Site Name_____

VIII. FURNACE ATOMIC ABSORPTION ANALYSIS

1. Duplicate Precision

_____ Duplicate injections and one-point analytical spike were performed for all samples; duplicate injections agreed within ±20%.

_____ Duplicate injections and/or spikes were not performed for the following samples/elements:

_____ Duplicate injections did not agreed within ±20% for all samples/elements:

2. Post Digestion Spike Recoveries

_____ Spike recoveries met the 85-115% recovery criteria for all samples.

_____ Spike recoveries did not meet the 85-115% criteria, but did not require MSA for the following samples/elements:

_____ MSA was used to quantitate analytical results when required:

_____ Correlation coefficients ≥0.995, accept results.
_____ Correlation coefficients <0.995 for samples/elements:

_____ MSA was not performed as required for samples/elements:

ACTION:

1. Estimate (J) positive results if duplicate injections are outside ±20% RSD.

2. If the post digestion spike recovery was outside the required limits:

	Percent Recovery		
	≤10%	11%-84%	≥115%
Positive Results	J or R	J	J
Nondetected Results	R	UJ	Acceptable

3. Estimate (J) sample results if the MSA was required and not performed.

4. Estimate (J) sample results if coefficient was <0.995.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

IX. ICP SERIAL DILUTIONS

_____ Serial Dilutions were performed for each matrix and results of the diluted sample analysis agreed within 10% of the original undiluted analysis.

_____ Serial Dilutions were not performed for the following:

_____ Serial Dilutions were performed, but analytical results did not agree within 10% for analyte concentrations greater than 50X the IDL before dilution.

Matrix_____

ELEMENT	IDL	50xIDL	SAMPLE RESULT	SERIAL DILUTION	%D	ACTION
Aluminum						
Barium						
Beryllium						
Cadium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Nickel						
Potassium						
Silver						
Vanadium						
Zinc						

Actions apply to all samples of the same matrix.

ACTIONS:
1. Estimated (J) positive results if %D >15.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

X. ICP INTERFERENCE CHECK SAMPLE

1. Recovery Criteria

List any element in the ICS AB solution which did not meet the criteria for % recovery.

DATE	ELEMENT	%R	ACTION	SAMPLES AFFECTED

ACTIONS:

If an element does not meet the %R criteria, follow the actions stated below:

	PERCENT RECOVERY		
	<50%	50%-79%	>120%
Positive Results	R	J	J
Nondetected Results	R	UJ	Acceptable

2. Frequency Requirements

Were Interference QC samples run at the beginning and end of each sample analysis run or minimum of two per 8 hour working shift, whichever is more frequent? YES or NO

If NO, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

XI. QUANTITATION

List samples/analytes which did not meet QAPP/SAP quantitation limits with an explanation.

Level III Data Quality Review
Data Review Worksheets

Site Name_____

XII. FIELD DUPLICATE PRECISION

Sample Nos._____,_____ Matrix_____

List the concentrations and RPD of the analytes detected in the field duplicates.

Circle RPDs that do not meet SAP/QAPP criteria.

ANALYTE	SAMPLE CONC.	FIELD DUP CONC.	RPD

9. **APPROVAL-**

The original copy of this document was approved and signed:

Author	Date
Director, Administration	Date
resident, EML	Date

GUIDELINES FOR THE PREPARATION OF STANDARD OPERATING PROCEDURES (SOPS)

FOR

FIELD AND LABORATORY MEASUREMENTS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION V

MONITORING AND QUALITY ASSURANCE BRANCH

QUALITY ASSURANCE SECTION

536 S. CLARK STREET

CHICAGO, ILLINOIS 60605

MARCH 16, 1989

GUIDELINES FOR THE PREPARATION OF STANDARD OPERATING PROCEDURES (SOPS) OF FIELD AND LABORATORY MEASUREMENTS

Field and laboratory protocol for qualitative and quantitative measurements, that are selected for a specific project shall be submitted to the Region V Quality Assurance Section (QAS) as an attachment to the sit-specific Quality Assurance Project Plan (QAPjP) for review/approval prior to the start of the measurement activity.

The field and laboratory measurement protocol should be documented in a standard operating procedure (SOP) format. This SOP shall describe in "cookbook" details the exact instructions to follow and the equipment and materials required to make the measurement.

This document outlines the elements that are to be considered for inclusion 'n all SOPs.

1. Parameter(s) to be measured.

2. Range of Measurement (Working Linear Range).

3. Limit of Detection. (Where appropriate procedure used for determination of method detection limit shall be specified).

4. Sample Matrix.

5. Principle, Scope and Application.

6. Interferences and Corrective Actions. (Specify method/steps to be taken to eliminate the interferences. Method shall be matrix-specific).

7. Safety Precautions.

8. Sample Size, Collection, Preservation, and Handling (Describing for each matrix which measurement procedure is applicable).

9. Apparatus (including instrument and instrumental parameters) and Materials.

10. Routine Preventative Maintenance, including procedures and frequency.

11. Reagents and Calibration Standards (including preparation procedures, storage and shelf life).

12. Calibration Procedures (including instrument tuning and routine performance checks, etc. If appropriate, specify whether internal standard or external standard techniques are to be used).

13. Sample Preparation (i.e., Extraction, Digestion, etc.)

14. Analytical Measurement (Describing in cookbook detail. Include separate details for each sample matrix if the procedure is applicable to more than one sample matrix).

15. Flow Chart or Table that describes the method step by step.

16. Data Treatment (Details of calculation, including equations).

17. Data Deliverables (define the content of data packages), as a minimum, the following shall be provided:

    a) Case narrative, briefly describe the sample preparation and analysis, problems encountered and corrective action taken during the process of sample preparation and analysis.

    b) Summary of initial calibration and continuing calibration check results.

    c) Summary of Sample Analysis, arranging in increasing order of sample number.

    d) Summary of QC sample analyses.

    e) Raw data including instruments printout, mass spectra, Chromatograms, etc.

    f) Instrument logbook (including serial number, date of purchase, date brought on line, maintenance and repair history over the period of service provided for this specific project. Daily entries should include name of analyst, parameter measured, instrument setting, comments on the sample analysis and any other information that may be deemed of interest.

18. Quality Control Requirements (Specify internal requirements for blanks, spikes, duplicates, and external requirements for reference and QC samples).

19. References.

20. Method Validation Data (if available) should be included to support the validity, limitation and the applicability of the measurement method. If the method is a "Standard Method", i.e., EPA APHA, ASTM or AOAC, this element need not be addressed. If the method has not been validated, then the description of the SOP should include the process for method validation to be conducted for approval prior to the use of the method for sample measurements. If the parameter(s) being measured is for health and safety requirement for field screening to select sampling locations, then method validation data is not required.

STANDARD OPERATING PROCEDURE FOR THE
FIELD MEASUREMENT OF VOLATILE ORGANICS BY HNu

I. PARAMETER(S)

Volatile organics with ionization potentials of less than 10.2 eV.

II. RANGE OF MEASUREMENT

The linear range is 0.1-400 ppm, the useful range is 0.1-2000 ppm.

III. LIMIT OF DETECTION

The detection limit of 0.1 ppm was determined by the manufacturer based on the response of benzene at a span setting of 9.8 and a 10.2 eV probe.

IV. SAMPLE MATRICES

Headspace above soil samples collected in split spoon samplers or with trowels.

V. PRINCIPLE, SCOPE AND APPLICATION

The analyzer measures the concentration of trace gases present in the atmosphere by photoionization. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and become a positive ion. This will occur when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The source of photons is an ultraviolet lamp with an energy of 10.2 eV.

Sample gases enter through the inlet into the ion chamber and are exposed to photons emanating from the ultraviolet lamp. Ionization occurs for those molecules having ionization potentials near to or less than that of the lamp. A positive-biased polarizing electrode causes these positive ions to travel to a collector electrode in the chamber. Thus the ions create an electrical current which is amplified and displayed on the meter. This is proportional to the concentration of trace gas present in the ion chamber and to the sensitivity of that gas to photoionization.

In service, the analyzer is first calibrated with a gas of known composition equal, close to, or representative of that to be measured. Gases with ionization potentials near to or less than 10.2 eV will be ionized. These gases will thus be detected and measured by the analyzer. Gases with ionization potentials higher than 10.2 eV will not be detected.

Ionization potentials for various atoms, molecules and compounds are given in the Instruction Manual Appendix. The ionization potential of the major components of air, i.e., oxygen, nitrogen, and carbon dioxide, range from about 12.0 eV to about 15.6 eV and are not ionized by any of the three lamps. Gases

with ionization potentials near to or slightly higher than the lamp are partially ionized, with low sensitivity.

VI. INTERFERENCES AND CORRECTIVE ACTIONS

Air currents or drafts in the vicinity of the probe tip may cause fluctuations in readings. Soil, dust, or debris drawn into the probe will result in low readings and/or negative deflection of the meter. High ambient humidity and high percent moisture samples will cause negative deflection of the meter.

To obtain stable, reproducible readings, corrective actions such as shielding the probe from drafts or currents and rain should be done. Sample moisture content is not controllable as representativeness dictates that no special handling of the sample occurs that might bias chemical results. Any drying of the sample would result in loss of volatiles. The field records should indicate which samples were wet and note any negative meter deflection.

VII. SAFETY PRECAUTIONS

Do not look at the light source closer than 6 inches with unprotected eyes. Observe only if necessary, then only briefly. Continued exposure to ultraviolet energy generated by the light source can be harmful to eyesight.

The instrument measures gases in the vicinity of the operator and a high reading when measuring toxic or explosive gases should be cause for action for operator safety.

Use HNu only in an emergency with a low battery when on battery charge.

Turn the function switch on the control panel to the OFF position before any disassembly. Otherwise, high voltage of 1200 vdc will be present. Use great care when operating the analyzer with the readout assembly outside its case due to the presence of 1200 vdc.

Do not interchange lamps of different eV ratings in a probe. Amplifier and components are selected for a specific eV lamp. A probe with the wrong lamp will not operate properly.

VIII. SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING

Soil

Measurement is done on the soil contained in the split spoon sampler or trowel placed in a clean 8-ounce jar with a teflon-lined lid. Measurement should be made within 5 minutes of collection in the field. The jar should be half full.

IX. APPARATUS

- Clean 8-ounce clear glass jars with teflon-lined lid, hole the diameter of the HNu probe drilled in top.

12. Sample Preparation.

There is no sample preparation for this procedure other than allowing the electrode system and sample solution to reach thermal equilibrium (steady thermometer reading).

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).
13.2 Remove electrode system and ATC Probe from buffer solution and rinse them with distilled water.
13.3 Immerse the electrode system and ATC Probe into the sample solution and allow sufficient time for the electrode system and sample solution to reach thermal equilibrium.

Notes: Thermal equilibrium normally requires about 1 minute, but will vary depending upon temperature difference between electrode system and sample.

13.4 Read the pH value of sample from the digital display and record on the Well Purging and Sample Collection form. Remove electrode system and ATC probe from sample and rinse with distilled water. Repeat step 13.3 and 13.4 for remaining samples.
13.5 ON-OFF switch to OFF after last measurement.

14. Data Deliverables.

The pH accuracy will be assessed by performing two measurements on three standard buffer solutions. Each measurement will be within ±0.05% standard unit of the certified value for the buffer solutions. Precision will be assessed through replicate measurements on field samples. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit. The electrode will be withdrawn, rinsed with dionized water, and re-immersed between each replicate. Calibration and verification will be done in the field before the first replicate and after the last. The instrument used will be capable of providing measurements of 0.01 standard unit. The instrument will be calibrated at least once daily and every 10 samples and results recorded on the Field Meter Instrument Calibration Log. Field replicates will be done at a frequency of every 10 samples. This will be done in quadruplicate. All field sample measurements will be recorded on the Well Purging and Sample Collection form.

15. Quality Control Requirements.

Quadruplicate samples will be done every 10 samples by rinsing the electrode after the initial reading, waiting 1 full minute, and then measuring the next sample. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Fisher Accumet Model 955 Portable pH/mV Temperature Meter, Catalog No. 69348.

17. Method Validation Data.

The parameter of pH is being measured for field screening to select sampling locations and method validation data is, therefore, not required.

Standard Operating Procedure
for the
Measurement of Specific Conductance in the Field
Using the Cole Parmer Model 4070 Conductivity Meter

1. Parameter to be measured: Specific Conductance.

2. Range of Measurement: Range (a) 0 to 19.99 mS
(b) 0 to 1999 uS
(c) 0 to 199.9 uS
(d) -30.0 to ±150.0°C

Resolution (a) 0.01 mS
(b) 1 uS
(c) 0.1 uS
(d) 0.1°C

3. Sample Matrix.

This method is applicable to drinking, surface, saline, and groundwater samples; domestic and industrial wastes.

4. Principle, Scope, and Application.

The specific conductance of a sample is measured using a self-contained portable conductivity meter equipped with an Automatic Temperature Compensation (ATC) probe.

5. Interferences and Corrective Action.

5.1 Precipitation reactions and absorption of carbon dioxide from the air can affect the specific conductance. This can be avoided by taking the measurement as soon after sampling as possible.

5.2 Specific conductance is affected by temperature changes. The use of the ATC probe will eliminate this problem.

5.3 Any constituent of the sample which can coat the conductivity probe such as oil or grease, algae, or sedimentation can cause incorrect or sluggish response. Dried salts or particulate matter allowed to build up on the cell plates may cause the readings to be erroneous. It is important to rinse the cell carefully with deionized water.

5.4 Ensure that no air bubbles are trapped in the cell area between the plates. Failing to do so could cause a false reading.

6. Safety Precautions.

Common sense is the best safeguard against any potential hazards. Obviously, one must never pipette samples or standard solutions by mouth. Handle the probes carefully to avoid breakage. Since the meter will be measuring potentially hazardous material, the probes must never be placed in the mouth.

7. Sample Size, Collection, Preservation, and Handling.

Samples should be collected in clean glass or plastic containers. The volume should be such that the cell plates of the probe are completely immersed in the sample. Samples may be filtered through a 4.5 m filter before analysis if necessary. Specific conductance should be measured as soon after sampling as possible, however, if readings cannot be taken immediately, samples should be stored at 4°C and measured as soon as possible.

8. Apparatus and Material.

8.1 Cole Parmer Conductivity Meter, Model 4070
8.2 Conductivity probe
8.3 Automatic Temperature Compensation (ATC) probe
8.4 Clean sample containers
8.5 Squeeze-type wash bottle, 125 ml or larger
8.6 Deionized water
8.7 Calibration standard solution
8.8 Laboratory wipes - KimWipe or equivalent
8.9 Replacement batteries, types PP3, 6F12, or MN1640

9. Routine Preventative Maintenance.

It is necessary to keep the external surfaces clean and free from dust.

All conductivity probes should be thoroughly rinsed after use and stored in deionized water. Particular care should be taken to ensure that the electrical connections are free from dirt and debris. It is recommended that the instrument be checked and calibrated before going into the field. The symbol "BAT" will appear on the display if the batteries need replacing.

10. Reagents and Calibration Standards.

Potassium chloride standard solutions with a specific conductance closest to the values expected in the field should be used. The table below may be used for guidance:

SPECIFIC CONDUCTANCE OF KCl SOLUTIONS AT 25 DEGREES CENTIGRADE

Concentration	Specific Conductance	
mol/l	mg/l	umhos/cm
0.0001	7.456	14.94
0.0005	37.28	73.90
0.001	74.56	147.0
0.005	372.8	717.8
0.00702	523.4	1000
0.01	745.6	1413
0.02	1591.2	2767

NOTE: This table has been modified from Standard Methods for the Examination of Water and Wastewater (1980).

Standard solutions may be stored at 4°C for up to one week. Date of preparation can be noted on the container and on the Field Meter Instrument Calibration Log.

11. Calibration Procedures.

Cole Parmer Model 4070 Conductivity Meter

Two options for calibration of the Model 4070 are available in the field, depending on instrument accessory availability. If the pre-calibrated probe is available, this is the easiest calibration procedure to do in the field. However, if the probe is not available, calibration will have to be done daily before field use with a standard solution (commercially prepared):

Calibration with Pre-Calibrated Probe:

a. Connect a standard pre-calibrated probe to the unit.
b. Select the "Set K" position on the function switch.
c. Adjust the "Set K" control until the display indicates the value of the cell constant as marked on the probe being used.
d. The standard X 1.0 probe has a cell constant range from 0.80 to 1.20 and is calibrated to 2 decimal places. The display should be set to indicate this figure exactly.

   The standard X 10 probe has a cell constant range from 8.0 to 12.0 and is calibrated to 1 decimal place. The display should be set to indicate this figure shifted one place to the right.

   The standard X 0.1 probe has a cell constant range from 0.08 to 0.12 and is calibrated to 2 decimal places. The display should be set to indicate this figure shifted one place to the left.

d. Before using the 20 uS range, the probe should be thoroughly rinsed in deionized water, excess water shaken off and the outside of the probe body wiped dry. The display should then be set to zero, with the probe in free air, by using the "Zero 20 uS" control.

Calibration with a Standard Solution:

a. Select the "COND" range.
b. Immerse the conductivity cell and A.T.C. probe (if separate probe is being used) into the prepared standard.
c. Select the 2000 uS range if using a 1000 uS or 1413 uS standard or other suitable range if an alternative standard is being used.
d. Adjust the "Set K" control to give the exact readout of the standard solution selected on the display.
e. After carrying out the calibration with standard solutions as detailed above and with the probe still in the standard solution and the display set to the value of the standard solution, switch to the "Set K" range to give a direct readout of the cell constant.

f. If the readout cannot be set to the value of the standard solution with the "Set K" control, then the cell constant lies outside the "Set K' range of 0.80 to 1.20. In such cases, the display should be set to read 1.00 on the "Set K" position, the display reading on the range giving the best resolution should be noted and the cell constant calculated from the following formula:

$$K = \frac{\text{Conductivity of Standard Solution}}{\text{Display Reading}}$$

This figure should be noted and (with the cell constant set to 1.00 on the "Set K" position) the display reading should be multiplied by this figure to obtain the correct conductivity.

Note:

Ensure that the conductivity standard has not reached or gone over the expiration date marked on the container.

12. Sample Preparation.

If the sample contains a great deal of particulate matter which may interfere with readings, they may be filtered through a 4.5 m filter.

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).

13.2 Rinse the conductivity probe and the ATC probe thoroughly with deionized water, shake to remove internal droplets, and the outside should be wiped before immersing into sample.

13.3 Allow the readout on the instrument to settle (usually about one minute). Multiply the instrument readout by the correction factor determined during calibration. Record the corrected conductivity on the Well Purging and Sample Collection form.

13.4 Step 13.2 should be repeated after every sample to prevent cross-contamination.

13.5 On completion of sample measurement, the probes should be thoroughly rinsed in deionized water and for short term storage should be kept immersed in deionized water so that the plates remain wetted. For longer term storage, the probes should be thoroughly rinsed in deionized water, the outside of the probes wiped dry, and the probes stored dry. It should be noted that it may take some time for stability to be achieved when a dry probe is first used while the plate becomes re-wetted.

14. Data Deliverables.

Initial calibration of the instrument and continuing calibration check results will be recorded on the Field Meter Instrument Calibration Log form. Summary of sample analysis will be recorded on the Well Purging and Sample Collection form, including sample duplicates.

15. Quality Control Requirements.

The meter will be read to the nearest 10 umhos/cm within a range of 0 to 20,000 umhos/cm. Accuracy of measurements shall be ±5 percent of a standard. The meter will be calibrated at least once daily and after every 10 field samples. Field duplicates will be measured at a frequency of every 10 samples by thoroughly rinsing the probes in deionized water, waiting one full minute, and then immersing probes in the duplicate sample. Precision shall be a standard deviation of ±10 percent.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Cole Parmer Model 4070 Conductivity Meter.

17. Method Validation Data.

The parameter of specific conductance is being measured for field screening to select sampling locations, and method validation data is, therefore, not required.

12. Sample Preparation.

There is no sample preparation for this procedure other than allowing the electrode system and sample solution to reach thermal equilibrium (steady thermometer reading).

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).
13.2 Remove electrode system and ATC Probe from buffer solution and rinse them with distilled water.
13.3 Immerse the electrode system and ATC Probe into the sample solution and allow sufficient time for the electrode system and sample solution to reach thermal equilibrium.

Notes: Thermal equilibrium normally requires about 1 minute, but will vary depending upon temperature difference between electrode system and sample.

13.4 Read the pH value of sample from the digital display and record on the Well Purging and Sample Collection form. Remove electrode system and ATC probe from sample and rinse with distilled water. Repeat step 13.3 and 13.4 for remaining samples.
13.5 ON-OFF switch to OFF after last measurement.

14. Data Deliverables.

The pH accuracy will be assessed by performing two measurements on three standard buffer solutions. Each measurement will be within ±0.05% standard unit of the certified value for the buffer solutions. Precision will be assessed through replicate measurements on field samples. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit. The electrode will be withdrawn, rinsed with dionized water, and re-immersed between each replicate. Calibration and verification will be done in the field before the first replicate and after the last. The instrument used will be capable of providing measurements of 0.01 standard unit. The instrument will be calibrated at least once daily and every 10 samples and results recorded on the Field Meter Instrument Calibration Log. Field replicates will be done at a frequency of every 10 samples. This will be done in quadruplicate. All field sample measurements will be recorded on the Well Purging and Sample Collection form.

15. Quality Control Requirements.

Quadruplicate samples will be done every 10 samples by rinsing the electrode after the initial reading, waiting 1 full minute, and then measuring the next sample. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Fisher Accumet Model 955 Portable pH/mV Temperature Meter, Catalog No. 69348.

17. Method Validation Data.

The parameter of pH is being measured for field screening to select sampling locations and method validation data is, therefore, not required.

Standard Operating Procedure
for the
Measurement of Specific Conductance in the Field
Using the Cole Parmer Model 4070 Conductivity Meter

1. Parameter to be measured: Specific Conductance.

2. Range of Measurement: Range (a) 0 to 19.99 mS
(b) 0 to 1999 uS
(c) 0 to 199.9 uS
(d) -30.0 to ±150.0°C

Resolution (a) 0.01 mS
(b) 1 uS
(c) 0.1 uS
(d) 0.1°C

3. Sample Matrix.

This method is applicable to drinking, surface, saline, and groundwater samples; domestic and industrial wastes.

4. Principle, Scope, and Application.

The specific conductance of a sample is measured using a self-contained portable conductivity meter equipped with an Automatic Temperature Compensation (ATC) probe.

5. Interferences and Corrective Action.

5.1 Precipitation reactions and absorption of carbon dioxide from the air can affect the specific conductance. This can be avoided by taking the measurement as soon after sampling as possible.

5.2 Specific conductance is affected by temperature changes. The use of the ATC probe will eliminate this problem.

5.3 Any constituent of the sample which can coat the conductivity probe such as oil or grease, algae, or sedimentation can cause incorrect or sluggish response. Dried salts or particulate matter allowed to build up on the cell plates may cause the readings to be erroneous. It is important to rinse the cell carefully with deionized water.

5.4 Ensure that no air bubbles are trapped in the cell area between the plates. Failing to do so could cause a false reading.

6. Safety Precautions.

Common sense is the best safeguard against any potential hazards. Obviously, one must never pipette samples or standard solutions by mouth. Handle the probes carefully to avoid breakage. Since the meter will be measuring potentially hazardous material, the probes must never be placed in the mouth.

7. Sample Size, Collection, Preservation, and Handling.

Samples should be collected in clean glass or plastic containers. The volume should be such that the cell plates of the probe are completely immersed in the sample. Samples may be filtered through a 4.5 m filter before analysis if necessary. Specific conductance should be measured as soon after sampling as possible, however, if readings cannot be taken immediately, samples should be stored at 4°C and measured as soon as possible.

8. Apparatus and Material.

8.1 Cole Parmer Conductivity Meter, Model 4070
8.2 Conductivity probe
8.3 Automatic Temperature Compensation (ATC) probe
8.4 Clean sample containers
8.5 Squeeze-type wash bottle, 125 ml or larger
8.6 Deionized water
8.7 Calibration standard solution
8.8 Laboratory wipes - KimWipe or equivalent
8.9 Replacement batteries, types PP3, 6F12, or MN1640

9. Routine Preventative Maintenance.

It is necessary to keep the external surfaces clean and free from dust.

All conductivity probes should be thoroughly rinsed after use and stored in deionized water. Particular care should be taken to ensure that the electrical connections are free from dirt and debris. It is recommended that the instrument be checked and calibrated before going into the field. The symbol "BAT" will appear on the display if the batteries need replacing.

10. Reagents and Calibration Standards.

Potassium chloride standard solutions with a specific conductance closest to the values expected in the field should be used. The table below may be used for guidance:

SPECIFIC CONDUCTANCE OF KCl SOLUTIONS AT 25 DEGREES CENTIGRADE

Concentration	Specific Conductance	
mol/l	mg/l	umhos/cm
0.0001	7.456	14.94
0.0005	37.28	73.90
0.001	74.56	147.0
0.005	372.8	717.8
0.00702	523.4	1000
0.01	745.6	1413
0.02	1591.2	2767

NOTE: This table has been modified from Standard Methods for the Examination of Water and Wastewater (1980).

Standard solutions may be stored at 4°C for up to one week. Date of preparation can be noted on the container and on the Field Meter Instrument Calibration Log.

11. Calibration Procedures.

Cole Parmer Model 4070 Conductivity Meter

Two options for calibration of the Model 4070 are available in the field, depending on instrument accessory availability. If the pre-calibrated probe is available, this is the easiest calibration procedure to do in the field. However, if the probe is not available, calibration will have to be done daily before field use with a standard solution (commercially prepared):

Calibration with Pre-Calibrated Probe:

a. Connect a standard pre-calibrated probe to the unit.
b. Select the "Set K" position on the function switch.
c. Adjust the "Set K" control until the display indicates the value of the cell constant as marked on the probe being used.
d. The standard X 1.0 probe has a cell constant range from 0.80 to 1.20 and is calibrated to 2 decimal places. The display should be set to indicate this figure exactly.

   The standard X 10 probe has a cell constant range from 8.0 to 12.0 and is calibrated to 1 decimal place. The display should be set to indicate this figure shifted one place to the right.

   The standard X 0.1 probe has a cell constant range from 0.08 to 0.12 and is calibrated to 2 decimal places. The display should be set to indicate this figure shifted one place to the left.

d. Before using the 20 uS range, the probe should be thoroughly rinsed in deionized water, excess water shaken off and the outside of the probe body wiped dry. The display should then be set to zero, with the probe in free air, by using the "Zero 20 uS" control.

Calibration with a Standard Solution:

a. Select the "COND" range.
b. Immerse the conductivity cell and A.T.C. probe (if separate probe is being used) into the prepared standard.
c. Select the 2000 uS range if using a 1000 uS or 1413 uS standard or other suitable range if an alternative standard is being used.
d. Adjust the "Set K" control to give the exact readout of the standard solution selected on the display.
e. After carrying out the calibration with standard solutions as detailed above and with the probe still in the standard solution and the display set to the value of the standard solution, switch to the "Set K" range to give a direct readout of the cell constant.

f. If the readout cannot be set to the value of the standard solution with the "Set K" control, then the cell constant lies outside the "Set K' range of 0.80 to 1.20. In such cases, the display should be set to read 1.00 on the "Set K" position, the display reading on the range giving the best resolution should be noted and the cell constant calculated from the following formula:

$$K = \frac{\text{Conductivity of Standard Solution}}{\text{Display Reading}}$$

This figure should be noted and (with the cell constant set to 1.00 on the "Set K" position) the display reading should be multiplied by this figure to obtain the correct conductivity.

Note:

Ensure that the conductivity standard has not reached or gone over the expiration date marked on the container.

12. Sample Preparation.

If the sample contains a great deal of particulate matter which may interfere with readings, they may be filtered through a 4.5 m filter.

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).

13.2 Rinse the conductivity probe and the ATC probe thoroughly with deionized water, shake to remove internal droplets, and the outside should be wiped before immersing into sample.

13.3 Allow the readout on the instrument to settle (usually about one minute). Multiply the instrument readout by the correction factor determined during calibration. Record the corrected conductivity on the Well Purging and Sample Collection form.

13.4 Step 13.2 should be repeated after every sample to prevent cross-contamination.

13.5 On completion of sample measurement, the probes should be thoroughly rinsed in deionized water and for short term storage should be kept immersed in deionized water so that the plates remain wetted. For longer term storage, the probes should be thoroughly rinsed in deionized water, the outside of the probes wiped dry, and the probes stored dry. It should be noted that it may take some time for stability to be achieved when a dry probe is first used while the plate becomes re-wetted.

14. Data Deliverables.

Initial calibration of the instrument and continuing calibration check results will be recorded on the Field Meter Instrument Calibration Log form. Summary of sample analysis will be recorded on the Well Purging and Sample Collection form, including sample duplicates.

15. Quality Control Requirements.

The meter will be read to the nearest 10 umhos/cm within a range of 0 to 20,000 umhos/cm. Accuracy of measurements shall be ±5 percent of a standard. The meter will be calibrated at least once daily and after every 10 field samples. Field duplicates will be measured at a frequency of every 10 samples by thoroughly rinsing the probes in deionized water, waiting one full minute, and then immersing probes in the duplicate sample. Precision shall be a standard deviation of ±10 percent.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Cole Parmer Model 4070 Conductivity Meter.

17. Method Validation Data.

The parameter of specific conductance is being measured for field screening to select sampling locations, and method validation data is, therefore, not required.

Standard Operating Procedure
for the
Measurement of Turbidity in the Field
Using the LaMotte Model 2020 Turbidimeter

1. Parameter to be measured: Turbidity

2. Range of Measurement:
0.00-1100 Nephelometric Turbidity Units (NTUs)

3. Sample Matrix.

This method is applicable to drinking, surface, saline, and groundwater samples, and domestic and industrial wastes.

4. Principle, Scope, and Application.

The turbidity of a sample is measured by filling a 15 mL tube with water, capping the tube, and placing the tube inside the turbidimeter. The turbidity value of the sample, measured in nephelometric turbidity units (NTUs), is displayed on the meter readout. Groundwater turbidity measurements can be made in the field as an indication of completeness of well development and of the effectiveness of screen characteristics.

5. Interferences and Corrective Action

Any constituent of the sample which can adhere to the sample vial, such as oil or grease, algae, or sedimentation, can cause incorrect or sluggish response. The sample vials must be kept clean to ensure proper operation of the meter. Special care should be taken to avoid fingerprint marks on the sample vials.

6. Safety Precautions

Common sense is the best safeguard against any potential hazards. One must never pipette samples or standard solutions by mouth. Since the meter will be measuring potentially hazardous material, the probe must never be placed in the mouth.

7. Sample Size, Collection, Preservation, and Handling.

Samples should be collected in clean glass or plastic containers. The 15 mL sample vial should be filled and capped in accordance with the meter manufacturer's instructions. Turbidity should be measured as soon after sampling as possible. Care should be taken to avoid fingerprint marks on the glass vial.

8. Apparatus and Material.

8.1 LaMotte Co. Turbidimeter, Model 2020
8.2 Sample tubes
8.3 Calibration standards (1.0 and 10 NTU, 60 mL each)
8.4 AC Power Adapter

9. Routine Preventative Maintenance

The external surfaces should be kept clean and free of dust. The meter should be cleaned after each use and stored appropriately. The meter should be checked and calibrated before going into the field.

10. Reagents and Calibration Standards.

Turbidity calibration standards (1.0 and 10 NTU) are provided by the meter manufacturer.

11. Calibration Procedures.

See manufacturer's instructions.

12. Sample Preparation

See Section 7 above.

13. Analytical Measurement.

13.1 Calibrate the meter.
13.2 Fill a clean 15 mL tube with the water to be tested.
13.3 Insert the tube in the meter and close the meter lid.
13.4 Record the data value displayed on the meter readout.
13.5 Clean the sample vial prior to filling with another sample.

14. Data Deliverables.

Initial calibration of the meter and continuing calibration check results will be recorded on the Field Meter Instrument Calibration Log form. Summary of sample analyses will be recorded on the Well Purging and Sample Collection form.

15. Quality Control Requirements.

Accuracy: +/- 2% for readings below 100 NTU
+/- 3% for readings above 100 NTU

16. References.

Information for this SOP was obtained from the Instruction Manual for the LaMotte Co. Model 2020 Turbidimeter.

17. Method Validation Data.

Turbidity will be measured for recording of field parameters, and method validation data is not required.

APPENDIX B

Effective Date: July 1997
Version Number: 6
Initiated By:
Approved By:

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SOP No: 7.1

Title: Sample Chain-of-Custody Procedures

Scope: This Standard Operating Procedure describes the Chain-of-Custody procedures to be followed by Laboratory Personnel.

1.0 SAMPLE RECEIPT CHAIN-OF-CUSTODY

The appropriate Chain-of-Custody procedures must be observed for all samples received. Samples received from the Sample Management Office (SMO) must have a complete Chain-of-Custody (COC) record, since these samples result in data which must be legally defensible. Therefore, the following procedures must be followed upon the receipt of samples.

1.1 Sample receipt and inspection shall be performed as described in SOP 7.2, Sample Receipt, Inspection, Preservation and Storage Condition Requirements. The sample receipt shall be documented using the Sample Receipt Checklist, or for CLP samples CLP Form DC-1 (see SOP 7.2, Sample Receipt, Inspection, Preservation and Storage Condition Requirements).

1.2 After completing the sample inspection and documentation process and finding no discrepancies, the original form is retained and included in the respective project file. Upon receipt, the client's Chain-of-Custody Form is signed by Sample Custodians to document time and date. A copy is returned to the client or designated sample management agency.

1.3 Samples shall be logged into the Laboratory Information Management System (LIMS) as described in SOP 7.3 "Sample Logging and Record Keeping Procedures".

1.4 The Project Manager/Client Services Group shall be responsible for contacting the client (or SMO) to resolve any discrepancy or to report occurrences such as broken samples, improperly preserved samples, samples not listed on COC, insuffient sample volumes or inappropriate amounts or containers. The problem and the resolution shall be documented on the Sample Receipt Checklist Form.

2.0 LABORATORY CHAIN-OF-CUSTODY

Equally important to sample receipt Chain-of-Custody procedures is laboratory Chain-of-Custody documentation. Samples and sample extracts, digestates must be in custody of section supervisor or designated personnel at all times.

2.1 Samples are requested from Sample Control through the use of the Sample Request Form (Figure 1). These forms are available from Sample Control and are completed by the analyst requesting samples. The form requires that the person requesting the samples enter their name, the date, time the samples are needed, and the date of the request. This information is located at the top of the page. The samples requested are documented by entering the samples' GP Number and the analysis. The location block is completed by the analyst after a work order has been transmitted. Once custody of the samples has been transferred, the Sample Coordinator notes the date and time the sample request was completed and signs the form. The form is retained only for the purpose of review by the Sample Control Supervisor for use in assessing work load, and then may be discarded.

2.2 When a request for samples is received by Sample Control, the Sample Custodian shall first locate the samples requested as listed in the Sample Log Book. The LIMS Fraction Sheet (see SOP 7.3, Sample Logging and Record Keeping) lists all samples in each individual work order and the assigned locations. Transfers are documented on the COC form. All samples can be found at the assigned locations unless transferred to lab personnel. Transfers shall be documented on the in house Chain-of-Custody Form (Figure 2). The Chain-of-Custody document serves as an effective means in determining sample locations.

2.3 Once determining that samples are available for transfer, the sample custodian locates and removes the samples before placing on workbench. The identification of the samples is checked against the Sample Request Form, and the LIMS Chain-of-Custody Form. If the samples do not match the Sample Request Form or the LIMS Chain-of-Custody Form, the identity question must be resolved before any transfer can take place. If there are no problems, the samples are transferred to the analyst.

2.4 To transfer the samples to the laboratory the following information must be completed on the LIMS Chain-of-Custody Form.

- Fraction Id

  Enter the sample fraction Id designation for the samples being transferred. Since Chain-of-Custody Forms are work order specific only the two digit and one letter sample identifier need be entered.

- Released By

  Enter the name of the Sample Custodian releasing the samples.

- Date/Time

  Enter the date and time of the transaction.

- Transferred To

  Enter the name of the person the samples are being transferred to.

2.5 When samples are returned to Sample Control the change in custody must again be documented. The identification of the samples is checked versus the Chain-of-Custody to verify sample identity. The following information is completed on the same line previously used when the samples were initially logged out.

- Accepted By

  Enter the name of the Sample Custodian receiving the samples.

- Date/Time

  Enter the date and time of the transaction.

- Disposition

  Enter the disposition of the samples, i.e. returned to sample location. Empty sample containers are taken to the disposal area for proper discard.

2.6 Laboratory personnel accepting samples must take full responsibility for those samples. Samples must remain under the custody of that individual, and shall not be transferred to another chemist without documentation on the proper forms (Figures 2 & 3).

2.7 When sample disposal is approved, or when a sample is completely consumed, the information shall be noted on the LIMS Chain-of-Custody Form. Empty sample containers should be returned to Sample Control for documentation and disposal.

3.0 TRANSFER OF SAMPLE CUSTODY TO ANOTHER LABORATORY

3.1 When it becomes necessary to sub-contract sample analyses to another laboratory, custody of the sample(s) must be transferred to that laboratory in the form of a Chain-of-Custody for Subcontracted Analysis (Figures 4 and 5). The forms are available in the Sample Control office. Sample control will complete the information on the Chain-of-Custody regarding the name and address of the lab and the

sample information. The Sample Custodian/Coordinator must sign and date the form to release custody of the sample(s), and retain a copy of the form in the Chain-of-Custody record corresponding to the sample(s). The Chain-of-Custody will accompany the samples in the sealed container being shipped to the sub-contracted lab. The individual responsible for the custody of the sample(s) will sign and date the record, return the document to GP Environmental Services, addressed to the Sample Control office and/or project manager. The returned Chain-of-Custody shall be placed in the data package being sent to client.

Figure 1

SAMPLE REQUEST FORM

Requested By : _____ Date Requested : _____

Date Needed : _____ Time Needed : _____

GP Number	Analysis	Location	GP Number	Analysis	Location

Request Filled By : _____ Date/Time : _____

Figure 2

Date: 05/30/1997

Chain of Custody
GP Environmental Services, Inc.

Page 1

Order: 9704195 Received: 04/27/1997 Received by: _____

Samples: 5 # Containers: _____ Keep for: 90 days

Condition: _____

Sample Sign-Out				Sample Return		
Fraction	Released by	Date / Time	Released to	Accepted by	Date / Time	Disposition

SAMPLE EXTRACTION STORAGE AND CHAIN OF CUSTODY

Document Number: *GP291*

Project Number	GP Work orders	No of Samples	Parameter	Released By	Released To	Released Date	Sample Custody of	Date	Returned By	Date Retuned

Figure 3

Figure 4

Chain of Custody Form for Subcontracted Analyses

Page 1 of 1

GP Environmental Services, Inc.
202 Perry Parkway
Gaithersburg, MD 20877
(301) 926-6802
(301) 840-1209 (Fax)

GP W.O. No. 0000000

GP P.O. No.

Samples Transferred To:

Attn:

Phone:

GP Lab Sample ID	Field Sample ID	Date Sampled	Time Sampled	Sample Matrix	Analyses Required	Method	Type of Container	Preservative
0000000-01A	SAMPLE 1	05/28/97		WATER	SPARE FOR SUB C		1L PLASTIC	

Carrier:

Airbill No:

Report Due On: 05/29/97

Send Report Attn:

Perform Q.C. on Sample:

Condition Upon Receipt:

Comments:

Samples Relinquished By: Date: Time: Samples Received By: Date: Time:

Please complete this Chain-of-Custody form immediately upon receipt, retain a copy for subcontracting laboratory records and return the original to: GP Environmental Services, 202 Perry Parkway, Gaithersburg, Maryland 20877.

CHAIN OF CUSTODY FORM FOR SUBCONTRACTED ANALYSES

Page___of___

GP Environmental Services, Inc.
202 Perry Parkway
Gaithersburg, MD 20877
(301) 926-6802
(301) 840-1209 (Fax)

GP W.O. No._____

GP P.O. No._____

Samples Transferred To:
_____
_____
_____
Attn:_____
Phone:_____

GP Sample No.	Sample ID	Date Sampled	Time Sampled	Sample Matrix	Analyses Required	No. of Containers	Type of Container	Preser-vative	Comments

Figure 5

Carrier:_____ Airbill No:_____

Report Due On:_____ Send Report Attn:_____ Perform Q.C. on Sample:_____

Condition Upon Receipt:_____

Comments:_____

Samples Relinquished By:_____Date:_____Time:_____Samples Received By:_____Date:_____Time:_____

Please complete this Chain-of-Custody Form immediately upon receipt, retain a copy for subcontracting laboratory records and return the original to: GP Environmental Services, 202 Perry Parkway, Gaithersburg, Maryland 20877.

MISSION STATEMENT

It is the mission of Triangle Laboratories to become the leading organization in the world providing analytical chemistry services.

Beliefs

We believe that we must excel in relationships with our customers, our employees, and our investors while establishing leadership in our technology and operations management.

We believe that in all things and at all times our behavior must follow the highest ethical standards. This includes commitments made to customers, suppliers, employees, investors, and to one another.

We believe that to our customers, we must be the laboratory of choice. Our marketing program will always honestly inform. We will set the quality and timeliness standards in our markets. We will structure our company so that we have the flexibility and versatility required to be responsive to customer's needs. We will work until the customer is satisfied.

We believe that for our employees, we must be the employer of choice. Through the application of high ethical standards, maintenance of efficient operations and a respect for diversity, we will provide a work environment that enriches and builds people while giving them an opportunity to excel and enjoy the dignity, pride, and material rewards of being part of a winning team.

We believe that for our investors, we must commit to the development of long term value in their investment. This will be accomplished by taking those risks that have an appropriate probability of reward, controlling expenses to maintain high profitability and aggressively seeking opportunities to achieve growth through expansion of existing business and developing new business opportunities.

We commit ourselves to conducting research and development so that we are always a leader in technology, to apply the knowledge gained to maintain efficient operations and to service our customers needs in a timely manner while providing a reasonable profit for our investors.

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Section 1

INTRODUCTION

This manual is a description of the quality assurance program employed at Triangle Laboratories, Inc., referred to hereafter as Triangle Labs or TLI. It is intended to provide employees, accrediting agencies, and clients with the information needed to understand how an effective quality assurance system is maintained at Triangle Labs. The QA Manual is divided into fifteen sections and several appendices. The first three sections pertain to the manual itself. Sections 4 - 7 provide general descriptions of Triangle Labs, including its objectives, policies, facilities, organization, personnel, and services. The remaining sections describe specific quality assurance activities as practiced within different functions or work units. The order of sections 8 - 12 closely follows that of the production process at Triangle Labs. The appendices provide supplemental materials that support the descriptions in the QA Manual sections.

Written procedures for implementing the activities described in this manual are maintained as standard operating procedures (SOP's) and as department specific training procedures. The SOP's are made available to the operating staff through the widely distributed SOP Manuals. The training procedures are maintained by the department managers. The provisions of this manual are binding upon all laboratory personnel assigned responsibilities described herein. All laboratory personnel must adhere implicitly to the Standard Operating Procedures.

Section 2

AUTHORIZATION

The quality assurance system described in this Quality Assurance Manual has the absolute support of the management at Triangle Labs.

The provision of quality analytical services to our customers has given us an enviable reputation and has made us a leader in the industry. Assuring that we maintain this status in providing quality products to our customers is the responsibility of every member of the laboratory staff. It is hoped that everyone concerned will use this manual as a guide to quality improvement and to maintenance of our current standing as a quality-oriented laboratory.

Signature:	Date:
J. Ronald Hass President and Chief Executive Officer	11/17/97
Patty L. Ragsdale Quality Assurance Manager	11/17/97
Donald J. Harvan Vice-President	11/17/97
Phil Albro Technical Director	11/17/97

Section 3

MANAGEMENT OF THE QUALITY ASSURANCE MANUAL

The Quality Assurance Department is responsible for the publication and distribution of the Quality Assurance Manual. The manual is submitted to senior management for review and authorization annually. As major changes are implemented in the quality assurance system, the Quality Assurance Manual is revised and submitted to management for authorization. The assistance of laboratory management is essential for the publication of the QA Manual. Department specific information is supplied by the department supervisors for inclusion in the manual.

The authorization signatures found in Section 2 of the manual signify management review and approval of the Quality Assurance Manual. The authorization section must be kept current and reflect any organizational changes affecting the authorizing positions. The revision date for the authorization section must be the most recent of any section in the manual, indicating that all revisions have undergone management review.

Document control procedures are applied to the distribution of the Quality Assurance Manual. Controlled copies are serially numbered and are updated each time a section is revised. Controlled copies of the manual may be distributed to an individual or a department. Uncontrolled copies may be issued to persons or organizations outside of Triangle Labs. These copies are distinctly marked "uncontrolled" and are not subject to updates upon revision of the manual. A distribution list is maintained for all copies of the Quality Assurance Manual.

Upon revision, all text added or changed since the last issue of each section is marked with a vertical bar in the margin.

Section 4

OBJECTIVE AND POLICIES

Objective

The objective of the staff at Triangle Laboratories, Inc. is to provide products and services which satisy our clients' expectations and definitions of quality and which are legally defensible.

Policies

The management of Triangle Labs supports the following policies in order to achieve the objective and promote the overall quality assurance program:

- Standard operating procedures shall be implemented in order to determine client requirements and to clearly communicate these requirements within the laboratory.
- Organizational emphasis on quality improvement will take place through strong management commitment and leadership, employee empowerment and teamwork.
- A comprehensive quality control system shall be established and maintained in order to verify and assure continued precision and accuracy of analytical results.
- Adequate training on laboratory operations shall be available to all employees whose decisions may affect the quality of laboratory products.
- A comprehensive program of documentation shall be implemented to ensure maintenance of accountability and traceability throughout the analytical process.
- Measures shall be implemented to ensure that sample integrity is protected.
- Validation studies shall be performed for each analytical method, including extensive evaluations whenever major modifications have been implemented.

- The instrumentation, equipment, and materials used in the production process shall be controlled (i.e., purchased, verified, calibrated, maintained, monitored, and evaluated) to ensure that required standards are met.
- A comprehensive program for data reduction, validation, reporting, and archival shall be implemented.
- Preventive and corrective actions shall be taken to eliminate the causes of potential or actual nonconformance. Emphasis shall be placed on preventive measures.
- Measures shall be implemented in order to meet the requirements set forth by agencies from whom certifications and accreditations have been granted.

Section 5

LABORATORY DESCRIPTION

Triangle Laboratories, Inc.

The location, mailing address, and phone numbers for Triangle Laboratories, Inc. are:

Triangle Laboratories, Inc.
801 Capitola Drive
Durham, North Carolina 27713

P.O. Box 13485
Research Triangle Park, North Carolina 27709

(919) 544-5729
(919) 544-5491 (Facsimile)

Triangle Laboratories, Inc. is a privately held subchapter C Corporation registered and incorporated in the state of Delaware. Triangle Laboratories has been in business since 1984 and has established an unparalleled reputation for integrity and quality while undertaking the most challenging work in its industry. The company experienced rapid growth during the emergence of the environmental market. Recognizing the necessity of diversification even while the environmental business was in full swing, the company expanded internationally as well as moving into new markets. Triangle Laboratories currently serves two major market areas, environmental and pharmaceutical.

Facilities and Instrumentation

Triangle Laboratories, Inc. currently occupies more than 50,000 square feet. The facility is divided according to work function, including separate areas for sample receipt; sample, standard, and glassware preparation; sample and data storage; instrumentation; report generation, quality assurance; shipping; maintenance; and business/management offices.

Analytical instrumentation at Triangle Labs includes: high resolution gas chromatograph/high resolution mass spectrometers (HRGC/HRMS); high resolution gas chromatograph/low resolution mass spectrometers (HRGC/LRMS); high pressure liquid chromatograph/mass spectrometer/mass spectrometers (HPLC/MS/MS); high pressure liquid chromatograph (HPLC) with ultraviolet detector (UV); gas chromatographs (GC) with electron capture detectors (ECD) and flame ionization detectors(FID); AOX/TOX adsorption module and microcoulometric titration systems; ion chromatographs (IC); inductively coupled plasma atomic emission spectrophotometers (ICP) and atomic absorption spectrophotometers (AA).

Well maintained equipment is essential in assuring the timely delivery of complete, high quality analytical data to clients. This is facilitated through a program of regular maintenance for all equipment, equipment redundancy, an ample stock of spare parts, and an inventory of specialized test equipment to support rapid repair when unscheduled maintenance is required. Service technicians are available through contracts with local providers for most of the instruments. Procedures and schedules for preventive maintenance are available in several SOP's. All instrument maintenance, both preventative and corrective, is recorded in the dedicated maintenance logbook assigned to each instrument.

Environmental and Security Systems

Triangle Labs provides a secure environment for our employees, guests, clients, samples and analytical data.

Access

Standard procedures require that all exterior doors remain locked via keylock or combination lock unless manned. Visitors are required to sign the Visitor Log and must be accompanied by an employee of Triangle Labs.

The defined high security areas include all laboratories, data archives, computer system, data reduction offices, and quality assurance offices. Entry into these areas of the building are controlled by combination locks on the internal and external entry doors. Visitors must be accompanied by an employee of Triangle Labs at all times inside the high security area.

Several rules apply to protecting the combination lock codes. The combinations are changed periodically. New combinations are supplied to the active employees only by the employee's supervisor or the facility manager. When accompanied by visitors, employees obscure the punch lock combination from view.

Security

All doors are locked after hours and require a key for entry. The security alarm at Triangle Labs offers continuous monitoring for smoke, extreme fire related heat, cold room temperatures, motion, and door contacts. Panic buttons are located throughout the building which set off an audible alarm and call the central station when activated.

Archives

Limited access archive facilities are maintained that house all Triangle Labs copies of analytical reports, raw data, inactive logbooks, magnetic tapes and other data which facilitate traceability of analytical results. Materials housed in the archives are packaged to reduce potential damage from fire and water.

Chemical Storage and Disposal

All chemicals are stored in appropriate cabinets and are properly disposed of when necessary. All flammable solvents are kept in OSHA and NFPA approved cabinets. Acids are stored in OSHA approved acid cabinets. An authorized waste carrier is contracted to pick up lab waste monthly and dispose of it, usually by incineration, meeting all regulatory requirements. Post-analysis disposition of samples is dependent upon client requests. Remaining sample material may be returned to

the client, safely discarded, or archived for a specific period of time.

Environmental Control

The working and storage environments are maintained in a safe and appropriate manner. Heating, ventilation and air-conditioning systems satisfy the needs of personnel, equipment and supplies. Lighting, noise and other environmental factors are also considered and kept at appropriate levels. Safety measures which protect personnel and property from injury or illness include the following: fume hoods, fire extinguishers and blankets, alarm systems, safety training, protective clothing, emergency showers, eyewashes and spill control kits. Triangle Laboratories has a contract with Duke University which provides an occupational health program for all employees.

Accreditations, Certifications, Licenses and Registrations

Triangle Laboratories, Inc. has received approval from several state and national agencies. The American Association for Laboratory Accreditation has conferred accreditation upon Triangle Labs for technical competence in environmental testing. The laboratory has been validated by the United States Army Corps of Engineers, and while not currently under contract, Triangle Labs has performed organic analyses under the United States Environmental Protection Agency (USEPA) Contract Laboratory Program. TLI is registered under current Food and Drug Administration (FDA) regulations to engage in the testing of drugs; has received registration under the provisions of the Clinical Laboratory Improvement Amendments of 1988 (CLIA) to perform high complexity testing (dioxin and PCB's) of human samples; has been licensed, and has been provisionally certified by several USEPA regions to analyze drinking water samples for dioxin.

Section 6

ORGANIZATION AND PERSONNEL

Organization

Responsibility and Authority

At Triangle Laboratories, the management structure is best illustrated by referring to the Organizational Chart in Appendix 1A. Responsibilities and authority of key personnel found on the charts will be summarized later in this section. Brief resumes of key Triangle Labs personnel may be found in the company's Statement of Qualifications.

Verification Resources and Personnel

Verification activities include inspection and monitoring of process and product quality and auditing of the quality system, processes and products. Provision is made for personnel to be trained and have responsibility for these activities.

Production personnel, under the direct supervision of area managers, are responsible for the inspection and monitoring of in-process and final products. Audits of the quality system and products are performed by personnel independent of those having direct responsibility for the work being performed. Quality system audits are carried out by Quality Assurance Department personnel, while data audits (audits of the final product) are carried out by employees in both Client Services and Quality Assurance.

Effective verification activities are achieved by the provision of adequate resources to personnel. These resources include adequate training, time for verification activities, knowledge about requirements, documented procedures, access to quality records, and adequate supplies and equipment necessary to perform verification.

Management Representative for Quality Assurance

The Quality Assurance Manager reports directly to the President, functions independently of production, and has the authority to implement and maintain the quality system. The management of Triangle Labs presents a strong commitment towards the important role of quality assurance in its organization. The Quality Assurance Manager and other members of the Quality Assurance Department interact frequently with personnel at all levels throughout the organization.

Management Review

A formal management review of the quality system occurs annually. The purpose of this review is to ensure that the quality system remains effective, meets the quality objectives and policies stated in Section 4 of this manual, and satisfies the requirements of state, national, and international certifications held by Triangle Labs. Records of management reviews shall be maintained in the

Quality Assurance Department.

Personnel

Job Descriptions of Key Technical Personnel

While not all-inclusive of assigned duties, the following are brief descriptions of the chief technical personnel at Triangle Labs.

President/Chief Executive Officer: management of administrative, business, quality assurance, personnel and production activities, through direct supervision of the Production Management Team, the Quality Assurance Manager; and the Technical Director, minimum qualifications - education: Ph.D. Chemistry, experience: 10 years analytical chemistry.

Quality Assurance Manager: coordination and management of the Quality Assurance Department; reports directly to the President; responsible for overseeing all quality aspects of the laboratory; specific elements to be maintained are: the Standard Operating Procedures, Quality Assurance Manual; coordination of internal and external audits, performance samples and laboratory certification data; minimum qualifications - education: B.S. Chemistry or equivalent, experience: 5 years in scientific field.

Production Management Team: comprised of the three Production Area Managers. The team functions as a single entity which is responsible for developing production plans to meet commitments made to clients, identifying and resolving issues which impede success, and promptly reporting to the president any issues which cannot be resolved with available resources.

Production Area Managers: management of a defined production area, instrumentation, reporting and/or sample preparation; minimum qualifications - education: B.S. Physical Science, experience: 5 years general analytical chemistry, 2 years supervisory.

Recruitment Policy

The Personnel Department of Triangle Labs uses several methods of recruitment. Current employees are offered the earliest opportunity to apply for openings within the facility by posting available positions on the bulletin boards one week before outside sources are considered for candidates. Then, announcements are made in local newspapers, placement agencies (temporary and permanent), colleges and the Employment Security Commission offices. The recruitment process consists of collecting applications and resumes, distributing them to the appropriate supervisors, scheduling interviews as requested by supervisors and having candidates meet with relevant staff and a representative from the Personnel Department. The references of promising candidates are investigated prior to making job offers.

Training

Training is provided for new employees and as continuing education for veteran employees, both at the Triangle Labs facility and off-site.

On-Site Training: Training goes on at different levels throughout the facilities. Numerous manuals, texts, videos, SOP's, journals, analytical protocols and in-house instructors are available to trainees. On-the-job training related directly to the position is done by area managers or other qualified staff. Typically, a trainee goes through a stepwise method to learn procedures pertaining to such areas as analytical methodology, report generation or quality assurance activities: he is given an SOP to read, he observes the trainer performing the procedure, he assists the trainer in performing the procedure several times, he performs the procedure without assistance but with the trainer's frequent inspection of his work, and finally, he may perform the procedure without supervision. The Quality Assurance Manual is available to all employees whose activities have a direct impact on product quality. Cross training, supervisory training and other related training takes place on a scheduled basis and is documented for training files.

Off-Site Training: This type of training takes place on an as-needed basis. Recommendations and suggestions about promising educational programs come from all levels of staff. Completed studies are documented and updated regularly in the training files. Courses may be taken at local colleges and universities. Workshops and seminars are often made available by instrument manufacturers, software companies and national associations specializing in analytical chemistry or laboratory quality assurance.

Training Records Maintenance

Résumés, education and experience records, job descriptions and training records are maintained by the personnel department: Résumés are put in a uniform format upon hire. These résumés are updated on an annual basis or as needed. Additional education and experience is updated with the résumés. There is a job description for each position existing within the company. Active training records are kept on file in the work areas. Employees are responsible for maintaining their own training records. These training files contain records for any pertinent on- or off-site educational experiences, orientation records, SOP competence records or self help courses, such as "Smoke Stoppers" or Stress Management.

Safety and Health Policies

All personnel undertake a one day orientation upon initial employment and on-the-job intensive training concerning health and safety issues. Triangle Labs complies with the OSHA requirement that safety and health training takes place on an annual basis, with a careful introduction to new principles. We have contracted with Duke University Medical Center Occupational Health Services to provide us with recommendations for the improvement of the safety and health practices at Triangle Labs and periodic medical examinations for all employees. Triangle Labs' policy with respect to health and safety issues is presented in detail in several documents, with which employees are provided.

Section 7

ANALYTICAL SERVICES

Triangle Labs has assembled an international staff of unparalleled expertise in analytical sciences with particular specialization in mass spectrometry and the analysis of complex biological matrices. The skills of the staff are routinely applied to environmental samples, including of air, water, solid and tissue matrices, and to biological samples associated with studies supporting the research efforts of the pharmaceutical industry.

Pharmaceutical Services

Triangle Labs serves the research pharmaceutical industry by providing analytical results for drugs of interest in a variety of biomatrices. This work is typically associated with pharmacokinetic Phase 1 through Phase IV studies for reporting to the Food and Drug Administration (FDA).

GC/MS and LC/MS/MS methods are typically employed for these analyses. High resolution mass spectrometers and alternate ionization methods are frequently utilized to achieve low detection limits. The staff is also experienced in assays, both GC and LC based, for chiral compounds.

Environmental Services

Triangle Labs provides environmental analytical services which include the preparation and analysis of a wide variety of sample matrices for such analytical categories as:

Volatile and Semivolatile Organic Compounds, including Polychlorinated Biphenyls, by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry

Pesticides and Herbicides by High Resolution Gas Chromatography

Polychlorinated Dibenzo-*p*-Dioxins, Polychloro-dibenzofurans, Polychlorinated Biphenyls, and Polynuclear Aromatic Hydrocarbons by High Resolution Gas Chromatography/ High Resolution Mass Spectrometry

Polychlorinated Dibenzo-*p*-Dioxins and Polychloro-dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry

Adsorbable Organic Halides and Total Organic Halides by Adsorption and Microcoulometric Titration

Inorganics by Ion Chromatography, Atomic Absorption Spectrophotometry, and

Inductively Coupled Plasma-Atomic Emission Spectrophotometry

Triangle Labs is experienced in the analysis of many matrices, including air, aqueous, plant and animal tissues, soils, and other solids. Air matrices currently analyzed include Modified Method 5 (MM5) samples and Volatile Organic Sampling Trains (VOST). Several auxiliary services are also offered, such as the provision and preparation of sampling containers (e.g., XAD traps, VOST tubes, and bottles).

Analytical Methodology and Target Compounds

Triangle Labs utilizes a variety of published and in-house analytical methods. In some cases minor modifications of methodology may be employed. Such modifications are validated prior to implementation in the laboratory. Target Compound Lists (TCL's) are chosen from the analytical methods. Published methodology utilized for each category of analytical services is listed below:

Volatile Organic Compounds (VOA) - Methods 8240, 8260 and 1624

Semivolatile Organic Compounds (SVOA) - Methods 8270

Pesticides - Methods 8081

Polychlorinated Biphenyls (PCB's) - Modified Method 680 and 8081

Polychlorinated Dibenzo-*p*-Dioxins (PCDD's) and Polychlorodibenzofurans (PCDF's) - Methods 8290, 23, 1613, 8280, 613 and NCASI 551

Adsorbable Organic Halides (AOX)/Total Organic Halides (TOX) - Methods DIN 38409, DIN 38414, EPA 9020, EPA 1650, PTS-RH: 012/90, SCAN-W 9:89, ISO/DIS 9562, and APHA 5320B

Inorganics - Ion Chromatography by Methods 7D, 26, 26A, 218.6, 300.0, and 9057; Trace Metals analyses by Methods 200.7, 6010, 7020, 7040, 7041, 7060, 7080, 7091, 7131, 7140, 7200, 7210, 7380, 7420, 7421, 7450, 7460, 7470, 7471, 7481, 7520, 7610, 7740, 7760, 7770, 7840, 7841, and 7870

Additional information about analytical services and methodology can be found elsewhere in this manual, and in the Analytical Services Guide. Selected analytical methods are summarized in Appendices 2 and 3 of this manual.

Triangle Labs has developed in-house methods for the analyses for Polynuclear Aromatic Hydrocarbons (PAH's) and Polychlorinated Biphenyls (PCB's by High Resolution Gas Chromatography/High Resolution Mass Spectrometry. These methods are proprietary and utilize state-of-the-art technologies.

Contract Review

For all analytical services to be provided by Triangle Labs, contract review is accomplished through the generation of a written quote or contract. Written quotes are utilized for short-term contracts, usually consisting of one analytical project. Written contracts are utilized for long-term contracts consisting of multiple analytical projects. Sales and Client Services personnel are responsible for implementing and documenting contract review. Client requirements, including special needs that are not normally provided by Triangle Labs, are defined and documented in the written quote or contract. Project scientists, who each have expertise in specific analytical services, are consulted to ensure special requirements can be met by the laboratory. If it is decided that the special requirements cannot be met, this is discussed with the client, and a counterproposal may be offered. Information about the capacity of the lab is made available to Sales and Client Services personnel on a regular basis. This practice allows the sales staff to make informed decisions regarding contracted delivery times.

Subcontracted Analyses

In dealing with any analyses that Triangle Labs cannot perform, there are established procedures for subcontracting. Depending on the nature of the client's requests for analyses, two courses of action may be followed. The client may be referred directly to another laboratory, if known; or work may be subcontracted by TLI to another laboratory. The latter usually takes place when Triangle Labs is able to perform part of the requested analyses. When the subcontracted analysis is one that Triangle Labs has been certified to perform, the subcontract lab must have a quality assurance system in place that is consistent with Triangle's system. Incoming samples which will be subcontracted are subjected to normal sample receipt procedures by the sample custodian. The samples are prepared and shipped to the subcontract laboratory. Results are received at Triangle Labs, a copy is sent to the client, and the original is archived. Triangle Labs invoices the client for the subcontracted work.

Section 8

LABORATORY MATERIALS—PURCHASING AND HANDLING

Purchasing, Receiving, Inspection, Inventory and Storage of Laboratory Materials

Practices utilized for the purchase, receipt, inspection, inventory, and storage of laboratory materials are described in several SOP's. A completed purchase requisition form provides a clear description of the product ordered. This includes, where applicable, a precise identification and reference to any specifications that must be met. Purchases are pre-approved by department heads. The purchasing department orders the material, from an approved supplier whenever possible. Upon receipt of the goods, receiving personnel examine them for damage before signing the bill of lading. Within two days, items and quantities in all shipments are compared with what was ordered and this information is communicated to purchasing and accounts payable. All stocked items are stored in the warehouse and a monthly inventory is performed. Non-stocked inventory is forwarded to the requisitioning person. Reagent materials are assigned expiration dates and placed on shelves so that the older materials will be used first.

Sample Container Cleaning, Storage, Preparation and Shipping

While Triangle Labs does not perform sampling, sampling kits may be provided upon client request. The vials, jars, and bottles contained in the kits are purchased and must be QC class, precleaned, with a certificate of analysis. The certificates of analysis are maintained by TLI. Since kits are assembled only upon clients' requests, no "ready for shipping" kits are stored. Precleaned glassware is stored in small quantities in house. Sampling materials, such as XAD traps, PUFs and VOST tubes, are also provided to or owned by the client. These are prepared, stored and handled as detailed in several SOP's.

All glass containers are wrapped in sheets of bubble wrap to prevent breakage. The containers are placed in plastic coolers with non-frozen ice packs and Chain-of-Custody forms, seals and labels enclosed in a ziplock bag. The kit is filled with additional packing material and sealed with tape for shipping.

Glassware Cleaning

All glassware used for the preparation of samples is cleaned as described in written standard operating procedures. These procedures include pre-rinses and soapy water washes. The pre-rinse may be solvent, water or acid solution depending on the analysis for which the glassware will be used. Basins and brushes are kept segregated so that cross contamination is minimized. Glassware used for high concentration analyses is kept segregated from glassware used for low concentration analyses, as is the glassware used for volatile, extractable organic compound and metals analyses. Glassware used for the analysis of extractable organic compounds, including dioxins and furans, is subjected to a solvent soak and rinses with several solvents. All clean

glassware is covered with aluminum foil and transferred to a proper storage location, taking care that the glassware is not intermixed with other types of glassware. In the Inorganic area, glassware is cleaned by a washing procedure that exceeds EPA guidelines. This glassware is washed with detergent, followed by acid soaks and multiple rinses with deionized water. The clean glassware is air-dried and stored in plastic bags.

Vendor Qualification

The process for qualification of vendors and the maintenance of an approved vendor list is detailed in the SOPs. Vendors subject to qualification are those who provide laboratory supplies, chemicals, and calibration services which directly impact on the quality of our product. Placement on the approved vendor list is based on the vendor's ability to meet one or more qualification factors which cover the purchased product. These factors include but are not limited to:

1. the vendor's quality system or product meets an applicable state, national, or international standard, based on third party certification

2. an acceptable quality assurance plan/survey, or on-site audit;

3. the vendor provides quality inspection documentation with each shipment or batch lot of product;

4. the vendor passes comprehensive inspections of three consecutive product shipments;

A vendor may be provisionally approved until qualification factor(s) are met, but in-house inspection of each batch lot of material is required. Previously approved vendors may be disqualified due to unacceptable performance.

Client Verification

When required by contract, the client or a representative may verify that purchased products conform to contract specifications. This verification may take place at the vendor's premises or at Triangle Labs. Client verification shall not be used as evidence of effective control of quality by the vendor and shall not absolve Triangle Labs of responsibility to provide an acceptable product.

Section 9

ANALYTICAL STANDARDS

During the analytical process, it is possible to obtain a variety of measurements. These include such measurements as volume, weight, concentration, pH, and temperature, to name just a few. The laboratory must implement practices that facilitate the traceability of these measurements to recognized standards of measurement.

Chemical Standards

The procurement, preparation, handling and storage of chemical standards is critical to the analytical process. It is through these chemical standards that reported analyte measurements in samples are traceable to reference values. Only the highest quality chemicals are used as reference materials at Triangle Labs. Whenever possible, standard solutions will be traceable to national standards, such as NIST, EPA or A2LA certified reference materials. Numerous written procedures describe the management of these analytical standards. These procedures are written to ensure consistency with the requirements of analytical methods and current certifications and accreditations.

Sources of Standards, Traceability and Verification

Triangle Laboratories purchases standards from approved suppliers of chemical standards. Occasionally, clients supply standards specifically for use in the preparation and analysis of their samples. Prior to using these standards, an agreement must be reached with the client about the handling and disposition of their standards. Information about these standards and any client requirements are recorded in the pertinent standards logbook. The chemist receiving a chemical standard shipment verifies that the information on the standard label is consistent with that on the supplier paperwork. Information about the standard is recorded in a standards logbook. Traceability of standard solutions is facilitated by the use of codes that unambiguously identify the supplier, materials and all derived preparations. Non-certified standard materials are verified against certified reference standards, when the latter are available. When certified reference standards are not available, second source verification is required.

Types of Standards

Analytical methodologies define a variety of standard solutions which are used by the laboratory. Included among them are: surrogate spikes, matrix spikes, internal standards, QC check standards, recovery standards, and calibration solutions. The composition and concentration of these solutions must conform to method specifications.

Standards are categorized at Triangle Labs according to the following definitions:

Primary Standard A neat standard received from a supplier.

Stock Standard	A solution of a primary standard at a high concentration, used to prepare secondary standards. These may be prepared in-house or received from a supplier.
Secondary Standard	A solution of one or more stock standards, with each analyte prepared at a selected concentration, to be used as a beginning mixture for preparation of calibration or spike solutions. These may be prepared in-house or received from a supplier.
Working Standard	A solution that will be used without dilution for instrument calibration or sample fortification. These may be prepared in-house from secondary standards, or purchased from a supplier,

Preparation of Standards

The preparation of any standard solution is performed by an experienced chemist (usually the Standards Preparation Chemist), and is documented in the appropriate standards logbook. New standard solutions are prepared as needed. The manner of preparation for a standard solution depends upon the required amount and concentration and its intended application. Several SOPs are utilized to assure the correct preparation and documentation of standard solutions.

All standards are assigned an expiration date. The supplier's assigned expiration date, if provided, is used for neat or primary standards. Otherwise, the expiration date is assigned based upon the supplier's date of preparation and the known stability of the analyte. (Some analytes are known to be highly volatile or to easily degrade or react.) When applicable, assigned expiration dates meet the requirements of analytical methods. A standard mixture is assigned an expiration date no later than that of the oldest components. The expiration date is only a guideline. Standards are removed from production prior to the assigned expiration date if deterioration is observed visually or analytically or if the integrity of the material can no longer be assured.

Analyte or standard components common to calibration solutions and associated sample fortification solutions may be of the same primary source or an independent source. Some methodologies require that primary standards of the same supplier batch or lot number be used for both. Certain spiked QC samples must be prepared from reference material that is independent of the associated calibration standards. New standards are prepared as necessary to meet these requirements.

Inventory and Storage

Documentation for all standards is carefully recorded in relevant standards logbooks and/or computer inventory system. The manner of storage for a

standard is determined by its type and expiration date or shelf life. All light sensitive standards are stored in amber vials or bottles. Environmental organic standards are kept in designated refrigerators/freezers. Pharmaceutical standards are stored according to the conditions specified in the associated protocol, validation report or stability report. Analytical standards are never stored together with samples or extracts.

Measurement Equipment

All equipment used for measurement and testing shall meet the specific requirements of pertinent analytical methods and applicable certification agencies. This includes small equipment, such as thermometers, analytical balances, pH meters, autopipetors, and volumetric glassware; as well as large equipment, such as gas chromatographs and mass spectrometers.

Written procedures for the operation of measurement equipment, large or small, shall contain the information described below, where applicable. In addition, Section 11 on "Instrumental Analysis" of this manual contains more specific information about the calibration and operation of large measurement equipment.

- What equipment the procedure is to be performed on, including equipment type
- How the equipment is to be calibrated and used for measurement
- What measurements are to be made
- Acceptance criteria for the calibrations, including the accuracy and precision required
- Corrective action for failed acceptance criteria, including assessment of previous calibration results
- Basis used for calibration (e.g., national standards of measurement, such as NIST, ASTM, and A2LA; participation in EPA and state performance evaluations; round-robin studies with other laboratories)
- Frequency at which the equipment will be calibrated, adjusted and checked
- What records will be maintained to document the calibration and use of measurement equipment
- How the calibration status for equipment is determined (e.g., a sticker or logbook entry)

- What environmental conditions are necessary before measurement equipment may be calibrated or used for measurement
- What adjustments to measurement equipment, including software, cannot be made due to possible invalidation of the calibration setting
- How measurement equipment is to be handled, preserved, and stored in order to maintain accuracy and fitness for use

Section 10

SAMPLE RECEIPT, HANDLING AND PREPARATION

Sample Receipt and Chain-of-Custody

The Sample Custodian or a designated assistant receives deliveries of all samples. A unique project number is assigned to each shipment of samples received from a client, and the first in-house records for the new project, including an internal Chain-of-Custody, are initiated. When samples are hand delivered by a customer, the individual's name is recorded on the internal Chain-of-Custody. The shipping containers, their contents, and accompanying client documentation are examined by the Sample Custodian. Information about the presence and condition of custody seals and the state of preservation of the samples is noted on the internal Chain-of-Custody. Any discrepancies in documentation or problems with sample condition are also noted and brought to the attention of the client, who may provide clarification or further instructions. The Sample Custodian assigns an internal sample ID to each sample, which is labelled on the sample container. The following information pertinent to each sample is recorded on the internal Chain-of-Custody: internal sample ID, client sample ID, sample matrix and storage location. The original internal Chain-of-Custody is placed in storage with the samples. The sample receipt and handling SOP's describe procedures for sample receipt and log-in, chain-of custody, along with those for handling sample shipment containers provided by clients.

Sample Preservation and Security

Samples are stored in a manner which ensures their integrity and security. Samples are stored at temperatures which meet specifications of the methodology and client. Depending on the nature of the sample and the requirements of the method, samples may be stored in a freezer at -70° C or at -20° C, in a refrigerator or cooler at 4° C, or in a cabinet at room temperature. Required preservation techniques may be found in Appendix 4 for most methods employed at Triangle Labs. Quality Assurance Project Plans (QAPP's) and protocols often give specific preservation requirements that must be observed. Addition of chemical preservative to sample containers normally takes place at the time of sample collection. Sample storage facilities at Triangle Labs are located within laboratory areas which are secured by locked doors. Internal chain-of-custody procedures and documentation pertaining to sample possession, removal from storage and transfer are outlined in written procedures. Care is taken to ensure that cross-contamination does not occur during sample storage. Temperatures of cold storage areas are monitored and recorded at least twice a day, and corrective action is taken as necessary. Walk-in coolers housing environmental samples and freezers used for pharmaceutical samples and standards are monitored electronically 24 hours a day. Further details about sample storage and preservation may be found in the sample receipt and handling SOP's.

Sample Preparation Procedures

Samples are prepared in a way that is method and matrix specific. Most environmental samples must be prepared within a method-specified time after sampling. These preparation holding times are complied with to the extent possible. Samples are occasionally received near or beyond the expiration of these holding times. For most methods employed at Triangle Labs, holding times may be found in Appendix 5. Applicable Quality Assurance Project Plans (QAPP's) and protocols must be consulted for project-specific holding time requirements. Many primary extracts require clean-up procedures before they may be injected into a GC or GC/MS analytical system. All sample preparation procedures employed at Triangle Labs are covered by appropriate SOP's.

Sample, Extract, and Digestate Archival and Disposal

The Sample Custodian and other authorized personnel are responsible for the archiving and disposal of raw samples, extracts, and digestates. Raw and prepared samples may not to be archived or disposed of until all of the designated analyses are complete and resultant analytical data are sent to clients. Samples in cold storage are retained there until at least 30 days after receipt. Archive samples are placed in boxes, labelled with the project numbers, and retained in a secured sample archive area for a specific length of time, prior to disposal. Written procedures describe routine archival and disposal practices. Clients are informed about these procedures and are given an opportunity to request exceptions to these routine practices. There is a storage fee for the retention of samples in cold storage or archive longer than the time established by routine practices.

Sample Return to the Client

When a client has requested the return of samples, the Sample Custodian prepares and ships the samples according to written procedures. Protection of the samples during delivery is ensured by the implementation of special packaging procedures. Packages are delivered by a commercial carrier whose procedures for protecting the samples are not within the control of Triangle Labs. Clients are informed that a commercial carrier will deliver their samples.

Sample Loss, Damage, or Unsuitability

It is possible for samples or sample containers to be lost, damaged or determined to be unsuitable, for whatever reason, after initial receipt at Triangle Labs. Whenever this happens, the event is recorded in the sample handling documentation by the observer. The problem is brought to the attention of a Project Scientist, who reports it to the client. Plans for disposition of the affected sample(s) or containers are agreed upon with the client, carried out, and recorded in the project records.

Section 11

INSTRUMENTATION AND EQUIPMENT

Instrumental analysis consists of setting up proper instrument operating conditions, executing acceptable calibrations and other instrument performance tests, analyzing prepared samples, and collecting data from the analyses. Instrumental analysis procedures, frequencies and acceptance criteria are described in several SOP's, the contents of which are derived from methods. A description of data collection and reduction at Triangle Labs is given in Section 12.

Instrument Operating Conditions

The published analytical methods normally define the optimum instrument operating conditions (e.g., temperature programs, column conditions, flow rates). Where applicable, these specifications will be followed, unless otherwise indicated for a project.

Calibration Procedures and Frequencies

Equipment used for inspection, measuring and testing must meet all specific requirements for proper measurement capability as identified in the pertinent analytical method and applicable certification agency. This includes small equipment and instruments as well as large analytical instruments such as gas chromatographs and mass spectrometers. Calibration procedures and frequencies specific to types of equipment are briefly described below.

The instrumental performance requirements of the published methods will be followed unless otherwise specified for a project. Other performance tests may also be executed to further demonstrate proper functioning of instrumentation.

Small equipment

Thermometers Laboratory thermometers are routinely checked for accuracy against certified, NIST-traceable thermometers. These calibrations are performed annually for mercury or alcohol in glass thermometers, and quarterly for metal thermometers. Infrared thermometer calibrations are verified daily. Correction factors derived from the annual and quarterly calibrations are applied to temperature readings where applicable. NIST-traceable thermometers are professionally calibrated and re-certified annually.

Balances Calibration checks are performed for each day of use for each balance. The calibration consists of a minimum of two weights which encompass the weight the balance will be used to measure. Calibration weight measurements must meet the acceptance criteria listed in the associated balance calibration log book. Each balance is serviced and calibrated by a certified, professional semiannually. The accuracy of the calibration weights are verified annually.

Volumetric Glassware

All volumetric glassware used at Triangle Laboratories, Inc. must be type "class A". The calibration of each piece of new volumetric glassware is verified gravimetrically prior to the initial production use. Volumetic glassware is never heated or placed in an oven.

Automatic Pipettes

Delivery volumes for the automatic pipettes are checked gravimetrically monthly. Each pipette is checked throughout the volume range of use. Acceptance criteria for continued use is 2% RSD and 97.5 - 102.4% recovery. Pipettes which fail to meet these criteria are tagged and removed from service until repaired such that the criteria is met.

pH Meters

pH meters are calibrated prior to use each day. The meter is calibrated using a single buffer solution at mid-range and the pH of two other solutions (at low and high range) is measured and recorded to verify the accuracy over the range of the meter.

Conductivity Meters

A five point calibration curve using potassium chloride (KCl) solutions is analyzed annually. A single KCl standard solution is used as a check standard each day the meter is used. Acceptance criteria is ±20% of the true value.

Gas Chromatography/Mass Spectrometry (GC/MS) and Liquid Chromatography/Mass Spectrometry (LC/MS/MS)

Tuning and Mass Calibration

For high resolution, selected ion monitoring analyses, the high resolution mass spectrometer is tuned to give the required static resolving power, which is checked by using an oscilloscope. This measurement is confirmed by the use of a data system. The instrument is then mass calibrated using perfluorokerosene (PFK) or perfluorotributlyamine (PFTBA). Mass calibration is adjusted automatically to within ± 5 parts-per-million (ppm) approximately once per second during the course of all quantitative analyses.

The mass calibration of a quadrupole mass spectrometer is checked daily through the use of the perfluorotributylamine reference compound (FC-43/PFTBA). The instrument is adjusted to give specified peak ratios for this compound, consistent with the type of analysis to be performed. The GC/MS is hardware tuned prior to performing the initial and continuing calibrations. Results must meet the peak ratio specifications of the analytical methods. For volatiles analyses, 50 ng of bromofluorobenzene (BFB) is used, and for semivolatiles analyses, 50 ng of decafluorotriphenylphosphine (DFTPP) is used.

Initial Calibration

For environmental samples, the mass spectrometer response is typically calibrated by analyzing a set of five or more initial calibration solutions, as appropriate for each GC/MS method. Typically each solution is analyzed once,

unless the method requires multiple analyses. The relative response factor for each analyte (target compounds, surrogate / internal / alternate standards) is calculated using the expression in Formula 11-1. The mean relative response factor for each analyte is then obtained using the expression in Formula 11-2. Integrated ion currents are utilized for these expressions. An acceptable calibration must meet the method specified criteria for percent relative standard deviations (% RSD) of the mean relative response factors, calculated for each analyte. Failure to meet the criteria will result in corrective action (e.g., locating the source of the problem and adjusting the instrument tuning parameters) before repeating the rejected analysis. Triangle Labs does not analyze any samples unless the performance criteria for calibrations are satisfied.

For pharmaceutical samples, the calibration curve normally consists of a minimum of five standard concentrations analyzed at the beginning and end of the analytical sequence, or are dispersed throughout the analytical run depending on the client's requirements. All standards are used for the regression, with exclusion criteria defined in each method SOP.

Continuing Calibration

For environmental analyses, the initial calibration is verified through the analysis of a continuing calibration standard every 12 hours. The concentration of continuing calibration standard is dependent on the requirements of the specific method. The relative response factors for all analytes of interest are calculated and verified against the initial calibration mean relative response factors. The percent difference (%D) for each analyte is calculated using the expression in Figure 11-3. An acceptable continuing calibration run must have measured percent differences for the analytes within method specified ranges. Should any criteria for an acceptable calibration not be met, either instrument maintenance is performed such that a new continuing calibration analysis meets all criteria or a new initial calibration will be established before any samples can be analyzed. No samples may be analyzed unless acceptance criteria have been met.

For pharmaceutical analyses, the calibration is verified through the analysis of quality control samples which are interspersed throughout the analytical sequence. The quality control samples are matrix spikes which contain known levels of analyte and are extracted with the samples.

Formula 11-1

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where

RRF = *the relative response factor for the analyte*

A_{is} = *integrated area or ion current of the internal standard*

A_s = *integrated area or ion current of the analyte*
C_{is} = *amount of the internal standard*
C_s = *amount of the analyte*

Formula 11-2

$$\overline{RRF} = \frac{1}{n}\sum_{i}^{n}\frac{A_s C_{is}}{A_{is} C_s}$$

where: $\overline{RRF}$ = *the mean value of the relative response factors for the analyte*
n = *the total number of data points derived from the initial calibration*
A_{is}, A_s, C_{is} *and* C_s *have the same meaning as in formula 11-1.*

Formula 11-3

$$\%D = \frac{\overline{RRF} - RRF_{cc}}{\overline{RRF}} \times 100$$

where:
$\overline{RRF}$ = *mean relative response factor for the analyte in the initial calibration*
RRF_{cc} = *relative response factor for the analyte from the continuing calibration*

Gas Chromatography/Electron Capture Detector (GC/ECD)

Initial Calibration

Internal standard calibration is utilized for the analysis of pesticides, PCBs and herbicides by GC/ECD. The method-specified number of calibration standards are be used. Each solution is analyzed once and the analyte relative response factors are calculated using the expression in Formula 11-1. The mean relative response factor for each analyte is then obtained by using the expression in formula 11-2. Integrated areas are utilized for these expressions. For multiple response pesticides/PCB's, quantitation consists of an average of the quantitated values for five selected peaks, if possible. The percent relative standard deviation (% RSD) must be less than ±20% in order to use the mean relative response factor for quantitation. If it is greater than ±20%, one more attempt is made to meet criteria. If the second attempt is unsuccessful, the

analyst takes corrective action, such as instrument maintenance, and begins the sequence again.

Atomic Absorption Spectrophotometry (AA)

An initial calibration is performed daily with freshly prepared working standards. A four-point calibration curve is acquired which must have a correlation coefficient of 0.995 or better. The initial calibration is verified every 10 samples or 2 hours, whichever is more frequent. The continuing calibration is required to be within 10% or 20%, depending on the analytical method utilized. Continuing calibration blanks are run at the same frequency. Analysis of samples cannot begin until an initial calibration verification has been performed and is found to be within 10% of the true value.

Inductively Coupled Plasma Emission Spectrophotometry (ICP)

Initial calibration is performed every 8 hours and continuing calibrations are performed every 10 samples or 2 hours, whichever is more frequent. Analysis of samples cannot begin until an initial calibration verification has been performed and is found to be within 10% of the true value. The continuing calibration is required to meet the criteria of the analytical method.

Ion Chromatography (IC)

The ion chromatograph is typically calibrated by analyzing a set of five or more initial calibration solutions, with concentrations of analytes appropriate to the analytical methods. Procedures for verifying the calibration curve are method specific.

AOX/TOX Instrumentation

Instrumentation for the determination of AOX/TOX consists of a column adsorption module, titration cell and combustion/microcoulometric system. Several system performance tests are conducted and must meet acceptance criteria prior to sample analysis. The following performance tests are typically conducted, with slight variations between the different analytical methods. Granular activated carbon utilized in the column adsorption module is tested for purity. The titration cell is tested and adjusted based on the results of an injection of sodium chloride solution. Calibration of the combustion/microcoulometric system is accomplished through the analysis of 2,4,6-trichlorophenol. Verification of system performance and calibration is performed during sample testing according to specifications in the analytical methods.

Sample Analysis Procedures

Techniques for quantitative analysis of samples are specific to the analytical methods and sample matrices. Samples may either be subjected to a series of preparation steps prior to instrumental analysis, or they may be ready for analysis upon arrival at Triangle Labs. Most samples must be analyzed within a defined period of time following their collection, receipt at the lab and/or preparation. These analysis holding times are complied with to the extent possible (samples are

occasionally received near or beyond the expiration date of holding time). Holding times for most methods employed at Triangle Labs may be found in Appendix 4.

After sample analysis is completed and the data is processed, the analyst reviews the resultant data. If established acceptance criteria are not met, corrective action is taken to resolve problems. Once all the samples in a project have been analyzed and the data have met the criteria, the project documentation (instructions, raw data, reports, etc.) is sent to the next stage for preparation of the final report.

Section 12

DATA HANDLING AND SOFTWARE MANAGEMENT

Data Collection and Reduction

Quality assurance principles are applied in the acquisition of raw data related to chemical measurements. Raw data is "primary data" which will be used to generate "secondary" data (the final analytical report). Data can be acquired manually or electronically. Manually acquired data is hand written on data sheets and in logbooks. Electronically acquired data is acquired from an instrument and instrument/computer interface. Specific definitions and data requirements are detailed in the Raw Data SOP.

Manually Acquired Data

Manually acquired data is recorded on data sheets or in notebooks. The data must be recorded immediately by the analyst in permanent ink. Each entry must be signed and dated immediately after entry. Corrections must not obscure any original entries and are made by canceling with one line through the original. Each correction must be dated and initialed by the person who made the correction and a reason for the correction must be stated. Data sheets are standardized, preprinted forms which are subject to document control. Data sheets may be bound into a book or may be used as loose sheets depending on the application. Notebooks are bound, consecutively numbered, and subject to a controlled distribution and archival system.

Electronic Data

Electronically produced data may consist of chromatograms, spectra, data printouts, and raw quantitation reports). The first accepted hard copy report constitutes the raw data for each sample and calibration. Acceptance is signified by the dated signature of the analyst(s),. The accepted hard copy report must contain the full sample ID or calibration name, file name, as well as date and time of acquisition. In the case of inorganic data, all replicate and dilution data is included in the documentation. Any alterations to the raw data hard copies and computer files must be fully documented and clearly attributable to the person making such alterations (e.g., manual integrations are hard-copied for inclusion in the raw data file, with area changes fully documented on the data printouts). No ambiguity in data system printouts as to what peak on a chromatogram corresponds to an analyte of interest is allowed. Computer-collected data is reduced to hard copy as soon as possible. The signed and dated hard-copies of the data files are retained in the project file and are maintained for a minimum of 10 years. The electronic files are safeguarded by a system of disk storage and backup disks to protect loss of data and programs. Software used for data acquisition and quantitation reports is tested according to written procedures to assure that no "bugs" are present.

There are several different means of data collection, review and reduction, which are dependent upon specific methodology and instrumentation. Data review and reduction of pharmaceutical data normally consists of data acquisition via a dedicated computer with further reduction and data reporting utilizing validated spreadsheets. Regression and sample calculations are verified independently for each pharmaceutical data set. Data review and reduction of environmental analyses normally follow the guidelines of relevant EPA reference methods to the extent possible. For HRGC/HRMS analyses, established procedures consist of data acquisition and reduction on a Digital Micro VAX and VAX 3100 and further reduction and data reporting using dBase software on a PC. For HRGC/LRMS analyses, established procedures consist of data acquisition and reduction using PC-based software or a PDP-11/24 system followed by further data reduction and reporting using dBase software. For HRGC analyses, established procedures consist of data acquisition and reduction using PC-based software followed by further data reduction and reporting using dBase software. For AOX/TOX analyses, manual data acquisition from instrument panel readings is followed by data reduction and reporting using spreadsheet software.

All GC, GC/MS, and inorganic data go through several levels of review and inspection, starting with an initial examination in the Instrumentation area, followed by a thorough review in the Report Preparation/Data Review area. After preparation of a report, an independent review is performed by a Chemist other than the one who prepared the report. At each stage of the analytical process, data are reviewed for completeness, adherence to protocol requirements, and credibility. Results are fully validated, possible compromises of data quality are evaluated, and deviations from protocol requirements are documented. To the greatest extent possible, computer programs are utilized for data reduction. Where manual data procedures are required, data review is performed according to standard operating procedures. This ensures that the results are as independent of the chemist performing the duties as possible. Corrective actions are implemented at the earliest possible opportunity.

Data Validation

The tests performed by Triangle Labs typically involve the performance of complex chemical analyses by a number of chemists. For this reason data validation and coordination are very important. At the conclusion of the analyses, data are checked against the original shipping information and analytical request to be sure that the required analyses have been performed on all samples.

The validity of the data are verified through the analysis of blank samples, duplicate samples and matrix spikes. The blank sample results demonstrate the absence of laboratory contamination of the samples. Duplicate analyses give a measure of analytical precision. The analysis of matrix spike samples permits a measure of accuracy. Data for these QC samples are reviewed as soon as possible after analysis. For example, in the inorganic area, a data quality checklist is used by the instrument operator at the time of analysis, to verify that all calibration verifications are within tolerance, and that other QC indicators such as spike recoveries and blanks, are acceptable for a project.

Data Reporting

The data are reported as components identified and the quantities present. The final report includes example calculations and descriptions of the equipment and procedures utilized. Complete data packages of all raw sample and calibration data are be prepared and archived. These are furnished to the client upon request. Sample flagging procedures for HRGC/HRMS analyses are summarized in the final report.. While sample flagging is not done directly on most HRGC/LRMS analytical reports, problematic results are discussed in the case narrative which accompanies each data package. Several standard report formats are used in the inorganic area, tailored to the data structure for the specific project type (e.g., TCLP, Multi-Metals Train or CLP).

Data Package Delivery

Data packages are prepared for delivery by the Shipping and Archive department according to their SOP's. Unless otherwise requested by the client, a copy of the data package is shipped, while the original is retained in a secured archive facility. Reports are fully paginated prior to copying. The data packages are packed to meet the requirements of the commercial carrier chosen for delivery. Packages are delivered by a commercial carrier whose procedures for protecting the data packages are not within the control of Triangle Labs. Should the shipped data package be lost or damaged during delivery, a copy can be quickly prepared as a replacement. Clients are made aware that a commercial carrier will deliver their data packages.

Corrections and Additions to Documentation

The policy for handling additions/corrections of reports already issued is as follows. The Project Scientist requests an addition/correction in writing to the appropriate data review/report preparation personnel, who make the requested change in a timely manner and internally verify the change. An authorized Chemist reviews and approves the addition/correction, and the Data Package Assembly Department mails or faxes the new report, which is then stored with the original data package for a minimum of ten years. In all cases, revised pages are clearly noted as such, as are additional pages added to the report.

Software Management

Triangle Labs has begun a formal validation program of its computer systems. Ultimately, the validation program is intended to be of a level such that all computer systems will meet the scope of any computer system audit. The validation approach is three pronged. First, new software is developed according to appropriate internal validation guidelines. Second, a validation committee has been appointed to oversee specific validation efforts of existing systems. Finally, systems are kept validated through a system of change controls. This includes the *Computer Systems Services Request* (CSSR) forms which employees use to make known to the MIS department, desired changes to software and hardware. CSSR forms include personnel sign-off for each step of the change process; and depending on the nature of the change, specify increasingly stringent required levels of authorization. Change controls also include software version control; changes to existing software are announced, uniquely labeled, documented, and old versions are archived for future reference.

The goals of the software development methodology, existing system validations, and the change control system are to ensure that the software systems perform the required functions accurately, that the users understand how to use the system, and that auditors can assure themselves of the validity of the analytical methods utilized. This in turn insures the ability to deliver accurate analyses in a timely fashion.

Section 13

DOCUMENTATION FOR QUALITY ASSURANCE

Objectives of Documentation

The objectives of documentation for quality assurance are: to provide a standardized, written program of policies, procedures and instructions; to demonstrate that adequate quality assurance and quality control procedures have been implemented; to demonstrate that accountability of the data is maintained; and to ensure traceability of analytical results is facilitated.

Document Control

The laboratory maintains control over the possession and distribution of all documents that directly impact the quality of a product or service. It is the responsibility of area supervisors to ensure that document control files are created and maintained for all applicable documents originating in their areas. This includes, but is not limited to, documents such as the Quality Assurance Manual, Standard Operating Procedures (SOP's), Work Area Guidelines (WAGs), Quality Assurance Project Plans (QAPP's), Analytical Services Guide, client instructions, and product sheets. It also includes standard forms, such as laboratory bench sheets, project communication forms, and corrective action reports.

A written procedure describes document control practices. Full or limited document control is applied, depending upon the purpose of the document. Those publications which document the quality assurance system at Triangle Labs, specifically the QA Manual and Standard Operating Procedures, are subject to full document control practices. Limited document control procedures are employed for other relevant documents, such as forms, flow charts, and price lists. The procedure for limited document control allows for the retention of a previous version for historical information and purposes. Such historical copies are clearly marked as such and can only be used as reference material.

Every document is assigned a unique identification (usually a title, file ID and creation/revision date) which must be present on each page of the document. This unique identification is entered on a master list of documents, along with a distribution list for each document to ensure that pertinent documents are made available wherever they are essential. A master set of current documents is maintained along with the master list.

Full document control, as applied to the QA Manual and Standard Operating Procedures, also includes the following. The status of each document, active/current or inactive/obsolete is indicated on the master list. Each document and any subsequent revisions must be reviewed and approved by authorized personnel prior to issue. Personnel authorized to review and approve a document are to have access to all necessary information on which to base their review and approval. Obsolete documents are to be retrieved from distribution points and replaced with current versions. The nature of changes in documents shall be identified within the document.

Standard Operating Procedures (SOP's)

Standard Operating Procedures (SOP's) are controlled documents in which instructions for every repetitive or standard operations performed by the laboratory are detailed. The author of an SOP should be the person most familiar with the topic being addressed. The standard format for writing SOP's is fully described in the SOP on SOPs. Each SOP is reviewed by senior level staff and authorized by management prior to distribution.

It is important that SOP's receive evaluation and input by laboratory supervisors and key technical personnel. The content of each SOPs must conform to applicable requirements of analytical methods and certification agencies, and be consistent with the Good Laboratory Practice standards. Within these constraints, the content of an SOP may be customized to meet the needs of a particular area of the laboratory. The performance of laboratory operations is subject to audit for compliance with written SOP's. If an SOP is impractical, hard to follow, or no longer meets laboratory needs, it must be modified or replaced.

The need for new or revised SOP's can be determined when a new method is implemented, when the scope of the existing method is extended or when some activities are being performed without adequate SOP's. Such a need can be identified by the analyst involved in the production or by someone from management. Also, the QA Department may identify the need and request new or revised SOP's, usually as a corrective action for deficiencies found during an internal inspection. SOP's are created to provide a clear, concise, description of the procedure with explanatory information to enable a person with the appropriate background to perform the procedure. Revisions are made to SOP's as necessary to reflect changes in procedures.

While area managers are responsible for the operating SOPs, the administrative staff assists with the typing on an as-needed basis. Once technical approval is obtained for a new or revised SOP, the SOP is reviewed by the Quality Assurance Department for compliance with all requirements. The Quality Assurance Department also maintains a database of SOP distribution and version status, as well as maintaining the original copies of each active SOP and the historical files of each out-dated version. The administrative staff distributes copies of the authorized SOPs to area SOP coordinators according to the distribution plan contained in the SOP database. The area SOP coordinator is responsible for discarding copies of obsolete SOPs upon receipt of revisions. Area managers are responsible for training staff in all applicable new or revised SOPs.

Work Area Guidelines

Work Area Guidelines (WAGs) are training documents which entail step-by-step instructions for specific tasks. WAGs are supplements to the SOPs and as such contain additional detail and guidance for handling unusual occurrences. The WAGs are comprised almost entirely of proprietary information and are restricted to use by TLI employees. These documents cannot be distributed to clients or other non-employees.

Quality Records

Quality records must be maintained to prove that the quality assurance system is being effectively applied. At Triangle Labs, specific procedures for the identification, collection, indexing, filing, storage, maintenance, and disposition of various quality records are described in several SOP's.

All quality records must be recorded in permanent (indelible) ink, legible, attributable to those personnel who wrote them, and protected so they may not be adversely affected by an unsuitable environment. They are stored and maintained in a manner that facilitates rapid retrieval for a period of at least ten years after completion. With the exception of internal audit reports, project specific quality records are available for evaluation by the client or his representative during the archive period of ten years. In fact, certain quality records, as specified by SOP or contract, are delivered to the client with the final product.

Project specific quality records are maintained to prove that adequate quality control procedures are being implemented, accountability of the project data is maintained, and traceability of analytical results is facilitated. Accountability means that reported data reflect the sample as it was received, that sample mix-up was avoided, and the sample was properly preserved after receipt. Traceability means that reported data may be reconstructed at a later date. Through proper documentation, a laboratory is able to demonstrate or prove to clients or government agencies that the quality of the data is what the laboratory says it is. Records must contain sufficient information to permit the reconstruction of calibrations, sample preparations and sample analyses.

Quality records that are maintained at Triangle Labs include, but are not limited to, the following.

- records for sample receipt, preparation and handling
- field sample and quality control sample analysis data
- project communication tracking forms
- inspection reports for receiving, in-process and final product
- subcontractor records
- vendor qualification records
- logbooks: run logs, maintenance logs, temperature logs, balance logs, etc.
- method validation records: MDL studies, initial precision and accuracy demonstrations
- recovery data for samples, blanks and spiked samples (maintained in a database)
- system and data audit reports
- corrective action reports
- QA reports to management

Many of these quality records are discussed at length in other sections of this manual. Laboratory notebooks (or "logbooks") are utilized throughout Triangle Labs for many different purposes. All logbooks are maintained according to written procedures. New logbooks are issued by a system of signing them out in a designated logbook. Information that must be documented, both in the new logbook and the sign-out logbook, includes the assigned owner, the date issued, and the name and subject of the logbook. Logbooks must be maintained in accordance with the raw data SOP. Logbooks are kept to document all monitoring, maintenance and calibration of analytical instrumentation, and such laboratory equipment as balances, refrigerators and ovens. Software and hardware records for computers are also kept in logbooks. Logbooks specific to a piece of equipment are kept near that equipment to ensure that the work is recorded concurrently. Logbooks used for personal notes and telephone logs are distributed and tracked in the same manner as laboratory notebooks. Upon completion, all distributed notebooks are stored in the Archive Room for a minimum of ten years.

Archive

The Archive Room is locked at all times and only trained, designated staff have access. All other personnel may enter the room only in the presence of a trained Archivist and must sign and date a logbook in the Archive Room. Any materials removed from the Archive Room must be signed out by the Archivist.

All magnetic and hard copies of data, calibrations, equipment maintenance records, calculations, records of original observations, final test results and any other miscellaneous quality records directly associated with sample analyses are stored in a secured facility for a minimum ten (10) years after completion of a project. They may be stored in the Archive Room or at a secure, off-site storage facility. When completed or no longer in use, logbooks are also archived.

Section 14

QUALITY ASSURANCE

Through a formal quality assurance system, Triangle Laboratories, Inc. is able to prove that products and services meet specific quality standards. These quality standards are defined to meet the needs and requirements of our clients, the analytical methods utilized, government agencies, and senior management of Triangle Labs.

Quality assurance is a very broad and multifaceted concept. It is composed of quality control and quality assessment. Quality control is the most important component of quality assurance. The need for quality assessment would be negligible if the laboratory always achieved perfect quality control.

> *Quality control* is a system of activities applied at each stage of the production process. Its purpose is to assure that products meet defined quality standards. This system includes the following: employee education, training, and experience; documentation (e.g., instructions, document control, records); instrument calibration and maintenance; laboratory accommodations; and inspection.
>
> *Quality assessment* is a system of activities employed to assure that quality control takes place at each stage of the production process. This system includes the following: system, data, and performance audits; reference materials; statistical evaluations; retests; and measurement bias investigation (when measurements may be operator-, instrument-, or methodology-dependent).

The success of a quality assurance system is dependent upon acknowledgment by all personnel of their responsibility for the system. The management of the laboratory is ultimately accountable for product quality, but no one person or group (e.g., the QA Department) is responsible for the greater part of quality assurance program activities. Details of the program may be found throughout this QA manual. The remainder of Section 14 will be limited to a discussion of the Quality Assurance Department, and the major activities performed and/or administered by this group.

The Quality Assurance Department

At Triangle Labs, the QA Department monitors the quality assurance system, as it is implemented throughout the laboratory, and reports the results of its observations to senior management. The Quality Assurance Manager reports directly to the President and the QA Department has no direct responsibility for productivity in the laboratory. The objective of this independence is to eliminate all conflicts of interest in the performance of QA duties. Major activities performed and/or administered by the QA Department are summarized below. Each activity is discussed in greater detail elsewhere in the QA manual, as indicated.

- Performance of internal audits and coordination of external audits (see this section)

- Administration of a system for formal Corrective Action Reports (see this section and Section 15)
- Performance of Quality Assurance Unit (QAU) duties required for GLP-regulated studies (see this section)
- Administration of the system for document control, with emphasis on the maintenance of Standard Operating Procedures (see Section 13)
- Performance of statistical evaluations for selected quality indicators, and maintenance of quality records (e.g., control charts, summary reports) generated to document selected statistical evaluations performed throughout the laboratory (see Section 15)
- Publication of the QA Manual and other documents that describe the quality assurance system at Triangle Labs (see Section 3)

Audits and Inspections

There are several different types of audits. These may be internal, in which the laboratory reviews and examines itself, or external, in which the laboratory is audited by outside organizations, such as accrediting or regulatory agencies and clients.

Internal System Audits

A system audit is an on-site inspection and review of the quality assurance system as it is employed in the laboratory. During an audit, verification may be sought that: adequate written instructions are available for use; that analytical practices performed in the laboratory are consistent with SOP's; that adequate quality control practices are applied during production; that corrective actions are applied as necessary; that deviations from approved protocols are occurring only with proper authorization and documentation; that SOP's, quality records, analytical records, magnetic tape, etc., are properly maintained; and that personnel training records are satisfactory and current.

Internal system audits are implemented by the Quality Assurance Department to assess the functioning of one or more department(s) of the laboratory. These audits consist of real time inspections of the analytical process, comparing the daily operation to the applicable SOPs and policies. Formal inspection reports are issued detailing the extent of the inspection and any non-conformance issues noted. The production staff is required to correct all noted deficiencies and a second acceptable inspection is required for acceptance of the corrections.

Inspection reports may be routed to management at any point in the process depending on the severity of the infraction. Major infractions are reported to management immediately while minor infractions are normally communicated in a summary report dealing with several inspections. The original of each completed inspection report, with management notification dates, is kept on file in the QA files.

External System Audits Representatives of clients, government agencies, and accrediting agencies frequently perform system audits of Triangle Labs. These audits are usually announced inspections, but sometimes are conducted without forewarning. QA Department personnel usually accompany such audit teams through the lab. The auditors receive a brief overview of company objectives, activities, and facilities. Interviews with essential supervisory and technical staff are arranged, along with retrieval of any documentation pertinent to the audit. Auditors typically provide an account of their findings shortly after the audit. This account is evaluated by QA personnel and reported to management, along with recommendations for actions in response to any cited deficiencies.

Data Audits Data audits are performed by technical personnel (in Client Services or the QA Department) on a random sampling of the data reports produced at Triangle Labs. It is a goal to perform a comprehensive evaluation of a representative sampling of data reports. A data report is carefully evaluated for technical, clerical and administrative accuracy. Primary emphasis is placed on the ability of the data report to meet customer requirements. Data audits are utilized for several purposes, including: identification of opportunities for process improvement, evaluation of the efficiency of the system, detection of inadequate execution of quality control procedures, early warning of potential system deficiencies, corrective action recommendations, and reports to upper level management.

Performance Audits A performance audit is the analysis of a fortified blank sample, for the purpose of evaluating laboratory or analyst performance. There are several examples of performance audits, which may be of internal or external origin. Performance Evaluation (PE) samples have analyte concentrations unknown to Triangle Labs, and are submitted by external organizations. PE's may be analyzed as part of multi-laboratory round robin studies, in conjunction with accreditation programs, or as blind check samples submitted by clients. Internal performance audits are fortified blanks with known analyte concentrations, the values of which may or may be known to the analyst. Examples of internal performance audits include initial precision and accuracy studies, QC check samples, laboratory control samples, and blind samples. The results of performance audits are utilized for several purposes other than the evaluation of laboratory performance, including: to fulfill accreditation requirements, to serve as analyst proficiency tests, and to facilitate laboratory improvement efforts.

Non-Conformance Reports

All instances of failure to comply with acceptance criteria are documented in a non-conformance report (NCR). Each report contains a description of the "failure", details of the resulting investigation, and the determined impact on the associated sample(s). Each NCR must be accepted by a member of the quality assurance staff. Original NCRs are maintained as part of the QA records and a copy of the NCR is included in the raw data file of the associated samples. A non-conformance issue may be caused by a particular sample independent of the analytical process or it may have been caused by a faulty analytical process with minimal adverse impact on the particular samples. The staff at Triangle strives to identify both types of situations and deal with them accordingly.

Corrective Action Reports

All major non-routine problems, deficiencies, or irregularities must be reported to management. A formal Corrective Action Report (CAR) system, administered by the QA Department, is in place at Triangle Labs. The QA Department issues CAR forms, monitors the progress of corrective actions, maintains completed documentation, and provides reports to senior management on the status of formal corrective action activities. CAR's may be originated by anyone responsible for the quality of a product. A completed form is sent to an appropriate person or group to whom responsibility for corrective action is assigned. One person is designated the Corrective Action Analyst. This person records the corrective action plans, implementations and follow-up actions completed by the responsible person(s). During the corrective action process, several measures may be taken. These include: determination of the root cause through careful analysis of processes, specifications, quality records, customer complaints, etc., using statistical process control when applicable; implementation of measures that prevent recurrence of the problem; implementation of process controls to ensure that effective corrective action is taken; application of remedial actions to products affected by the identified problem; and revision of documentation for procedures that have undergone change as a result of corrective action.

Certification and Accreditation

Triangle Labs has been granted numerous certifications and accreditations, based upon compliance with standards set forth by the granting agencies. These credentials have enabled Triangle Labs to expand and retain a substantial client base. More information about specific credentials can be found in Section 5, page 3. The nature of the quality assurance program implemented at Triangle Labs is profoundly affected by requirements of certification agencies. The administrative staff is responsible for the administration application and renewal activities associated with the various certification programs, while the QA Department is responsible for the coordination of the technical and quality issues associated with the certification programs. The QA Department is directly responsible for the coordination of:

- On-site audits by outside agencies
- Analysis of blind performance evaluation (PE) samples
- Responses to deficiencies cited in audit reports and performance evaluation results.
- Dissemination of requirements and status of certifications to relevant laboratory personnel.

GLP Regulated Studies

The Good Laboratory Practices (GLP's) are a set of regulations decreed by the United States Environmental Protection Agency (EPA) and the United States Food and Drug Administration (FDA). Compliance with these regulations is required for certain projects ("studies") completed at Triangle Labs. The GLP's define some specific responsibilities for the Quality Assurance Department. Briefly summarized, these QAU duties include the following:

- Maintenance of a copy of the master schedule sheet for all studies

- Maintenance of copies of all protocols pertaining to all studies
- Inspection of each study at adequate intervals
- Preparation of written status reports on each study with reports to management and the study director
- Determination that no deviations from approved protocols or SOP's were made without proper authorization and documentation
- Review of the final study report
- Preparation of a signed statement of the inspections performed and the dates each was reported to management for inclusion in the final study report

Section 15

QUALITY CONTROL

At Triangle Labs, quality control is achieved through the application of a many practices. Quality control activities commence before production is initiated, and are assimilated at each stage of the production process. The purpose of these activities is to assure that all required standards of quality are met. Quality control activities are described in many sections of this manual. The remainder of this section will describe a subset of quality control activities that may be considered a discrete process, summarized as follows:

> Prior to the initiation of production activities, required quality standards are defined. These are derived from several sources, including: requirements of the analytical methods, needs stated by the clients, and standards established within Triangle Labs.
>
> During production, verification activities are performed to determine that defined quality standards have been met. Also, preventive measures are applied to avoid the possibility of nonconformity.
>
> When defined quality standards have not been met (nonconformities), corrective actions are applied and verified to determine that the results meet requirements.

Data Quality Objectives

Data are produced for clients at Triangle Labs. Defined quality standards for these data may be expressed as data quality objectives (DQO's). These are established prior to sample preparation and analysis. Quality assurance indicators common to all DQO's include, but are not limited to: accuracy, precision, completeness, representativeness, and comparability. Examination of the QA indicators is performed to demonstrate that the data are scientifically valid, legally defensible and that they adequately meet established DQO's. The QA indicators may be summarized as follows:

Accuracy — A quantitative measure of the relationship of reported data compared to the "true" or expected values. This measurement may be accomplished by evaluation of the recoveries of analytes spiked into samples. Specific accuracy measurement activities include surrogate spikes, matrix spikes and Quality Control Check Samples. .

Precision — A quantitative measure of the reproducibility of measurements made under controlled conditions. This measurement may be accomplished by comparison of recoveries of analytes in replicate samples or injections. These analytes may be spiked or native to the duplicate samples. Specific precision measurement activities include blind field replicates, lab replicates, matrix spike replicates and replicate injections

Completeness — A qualitative measure of the amount of valid data obtained from the analytical process compared to the amount that was expected to be obtained. Valid data must meet all data quality objectives for precision and accuracy.

Representativeness — A qualitative measure of the degree to which data represents the characteristics of the population from which samples were collected. This is usually dependent upon sampling techniques not controlled by the analytical laboratory, however, there is representativeness of subsamples prepared within the laboratory from collected samples. Parent samples must be subjected to thorough homogenization prior to subsampling.

Comparability A qualitative measure of the confidence with which one set of data can be compared to another. Characteristics that make comparison possible include standardized report format, consistency of units (e.g., mg/L, ppm), and standardized sample preparation and analysis.

Quality Control Samples and Spikes

Analytical performance is monitored through quality control samples and spikes, such as laboratory method blanks, surrogate spikes, quality control check samples, matrix spikes, matrix spike duplicates, duplicate samples and duplicate injections. Many of these quality control measures, as applied at Triangle Labs, are summarized below.

Laboratory Method Blank A laboratory method blank consists of a sample that is processed in a manner identical to that of a regular sample, except that the matrix is replaced with distilled water for aqueous matrices, sodium sulfate for solid matrices, XAD-2 resin for MM-5 and PUF filter for PUF air sampling cartridges. The laboratory method blank sample is fortified and prepared along with the field samples, at a frequency of one laboratory method blank per batch of 20 (or less) field samples of a given matrix type. The laboratory method blank serves to demonstrate a contamination free environment in the laboratory.

Surrogate Standards For certain methods, all samples, including the laboratory method blank, are spiked with a set of specific surrogate standards to monitor accuracy of the analytical determination for each particular sample. QC criteria for surrogate recoveries are method and matrix specific. Typically, laboratory QC criteria are established upon acquisition of a sufficient number of data points (20 or more) and used for evaluation of sets of data via control charts, while method specified limits are utilized for individual samples.

Quality Control Check Sample A quality control check sample consists of a blank matrix sample which is fortified not only with appropriate internal and/or surrogate standards, but also with target analytes. QC check samples are analyzed at a frequency dependent on the method. They serve as an estimation of system precision and accuracy. Results of QC check samples are monitored on control charts, with QC requirements for recoveries being established as they are for surrogate recoveries.

Matrix Spike Sample A matrix spike (MS) sample consists of a field sample, identified by the client, that is split into two parts and processed in a manner identical to that of the rest of the field samples. However, in addition to the regular fortification with the standards (internal, surrogate and/or alternate), the chemist will add a set of the target analytes to one part of the chosen sample before the preparation. The fortification levels for the target analytes are defined by the analytical method or the client's request. At the request of the client, one such sample will be prepared for every batch of 20 samples (or less) for a given matrix. To be able to run matrix spikes, the client must provide Triangle Labs with extra sample amounts.

The analytical report for the matrix spike will contain a tabulation of the analyte concentrations as expected and as measured, along with the calculated percent recoveries based on the expected concentrations. The percent recoveries actually represent a measurement of the method accuracy for that particular sample and matrix. Accuracy is established and updated for a particular analyte and method. In the absence of observable quantitative interferences, the MS sample showing accuracies falling outside the QC limits must be reanalyzed unless the matrix spike duplicate (MSD), which was processed along with the MS, shows similar deviations as a result of a "matrix effect." This type of corrective action can only be implemented if the sample selected for the MS (and MSD) was proven to be free of the target analytes, or did not contain high concentrations that significantly exceed the MS fortification level of these analytes. "Matrix effect" is further substantiated by acceptable recoveries in a QC check sample processed along with the field samples. Matrix

spike recoveries, and the possible effects on data quality when accuracies fall outside the QC limits, are discussed in the Case Narrative.

Matrix Spike Duplicate Sample

The matrix spike duplicate (MSD) sample is commonly prepared (at the Client's request) in conjunction with the matrix spike (MS) sample. The analytical report will summarize the data from the MS and MSD analyses in a format allowing determination of the precision of the analyses. As for the matrix spike sample, the client must provide Triangle Labs with extra sample amounts.

Duplicate Sample

A duplicate sample (DUP) consists of a set of two identical samples obtained during a single sampling session. At the client's request one such sample per batch of 20 samples (or as specified by the client) per matrix type will be analyzed, provided the client supplies Triangle Labs with the necessary samples.

The analytical report for the duplicate analyses will contain a tabulation of the results showing the precision as relative percent difference (RPD). Precision exceeding any specified target values will necessitate a non-conformance report and an evaluation of the associated data. The influence of the sampling procedure will be included in the data evaluation.

The RPD is calculated as:

$$RPD = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100$$

where:

RPD = the relative percent difference

X_i(i=1,2) = the analyte concentration in the original sample (1) and the duplicate sample (2)

Duplicate Injection

Upon client request, a duplicate injection of a single sample extract will be performed. In the absence of observable interferences, the RPD is expected to be within ± 30% or the injections will be repeated after identification of the cause of the poor precision. Field samples analyzed during a suspected out-of-control situation will be reinjected as well.

Statistical Evaluation

Statistical evaluations can be made of selected analytical quality indicators, including spike recoveries, calibration responses, contamination levels, and method detection limits. Production units monitor levels of compliance with many criteria on a "real time" basis. Control charts are used to identify shifts in the analytical process. All identified performance shifts are investigated and causes of adverse shifts are eliminated. Causes of positive shifts are also identified and incorporated in SOPs and staff training as applicable. In-house QC criteria may be determined through historical trend analysis of data collected on QC charts. Statistical evaluations can be performed by both the QA department and production units.

QC Inspection

Quality control inspections are built into the production process. These inspections consist of peer review at each step of the process the ensure compliance with process and product specifications. Acceptance criteria are included in the production SOP's. Written documentation of the analytical process is maintained

beginning with sample receipt and preparation, through instrument calibration, sample analysis, data review and report preparation. This documentation is reviewed for completeness, compliance with written procedures and consistence with client documentation.

Written records of all QC inspections are required indicating the date, inspector and results of the inspection. Detected nonconformances must be recorded during the inspection. Corrective action must be taken and documented whenever nonconformance is detected. The identity of the inspection authority responsible for releasing the product is documented in the inspection records. Until required inspections are performed on the intermediate and final product, it is not permitted to progress further along the production process, except by special, documented, client request.

In-process Inspection and Testing

Each department is responsible for a segment of the production process and for all in-process inspection and testing that takes place within the department. In-process inspection is accomplished through 100% screening for all areas. Each client sample that goes through the analytical process is unique and can be considered a separate lot.

Final Inspection and Testing

The last stage of the production process is the preparation of a final data. This requires a thorough review of all records generated for a client sample set since its receipt, including inspection records and any client documentation that may have originated before sample receipt. A Report Preparation Chemist performs this function during the preparation of the data package. This inspection serves as both an in-process and final inspection of the product. In addition, a second chemist performs another final QC inspection of the data package and quality records. As in any other part of the process, any nonconformances found during these inspections must be documented and corrected before the data package is released. Approval of the data package for release to the client is indicated by the signatures of the Report Preparation and QC Chemists on the case narrative.

Nonconformity

Each field sample that is incorporated into the analytical process is unique. Laboratory procedures are designed to introduce as much standardization as possible. Whenever conformance to standards is uncertain, the product is reviewed to determine the nature and cause of nonconformance. If it is judged to be nonconforming due to the unique nature of a sample, there may be little recourse other than to simply inform the client.

Each case of failure to comply with written acceptance criteria must be recorded in a non-conformance report (NCR). The failure must be recorded by the person who detected or observed it. All investigative efforts are recorded on the NCR with an evaluation of the impact the non-conformance had on the associated samples. Impact on the analytical process is also noted. Recommendations for corrective action are made. A copy of the NCR is kept with the project data. The original NCR is submitted to the QA Department for review and acceptance. Data cannot be reported until all associated NCRs have been accepted by the QA Department

Rework and reanalysis is subject to the same inspection procedures as the initial work. Nonconformity, its review, and its disposition must be documented in the quality records as prescribed by the written procedures.

Corrective and Preventive Action

Appropriate actions must be taken to prevent or correct nonconformities in products and problems in analytical systems. When actions result in permanent procedural changes, pertinent documentation (e.g., SOP's) must also be modified to reflect these changes. Cost-effective preventive measures are applied whenever possible. In specific cases, the cost of applying preventive measures would exceed the cost of

applying routine corrective actions. Because every client sample possesses unique and unknown properties, some predisposition to unpredictable, unpreventable nonconformities exists.

Corrective Action

Specific corrective actions are of two types: routine corrective actions applied to solve minor or commonplace problems, and formal corrective actions taken to eliminate major or non-routine problems.

Routine corrective actions are usually made by the chemists, technicians or instrument operators who detect minor problems or product nonconformances. These actions are taken in response to observed non-conformance issues are recorded on the associated NCRs.

There are three procedures for conducting formal corrective actions. The first is corrective action in response to a system audit report from the Quality Assurance Unit. This procedure is more thoroughly described in Section 14, page 2. The second procedure is the formal Corrective Action Report, which may be initiated by anyone who detects a significant quality problem. This procedure is also administered by the Quality Assurance Unit. Further information about it can be found in Section 14, page 3. The third practice is described in a written procedure on "Problem Sample Communication." It is initiated in response to client complaints about specific projects.

Preventive Action

Preventive actions are implemented as part of standard operating procedures, process improvement efforts and corrective actions. When circumstances inherent to a procedure are known to have a high potential for error, the SOP must define measures to prevent the error from occurring. Preventive actions are an integral part of corrective actions, because resultant changes in procedures often prevent recurrence of problems.

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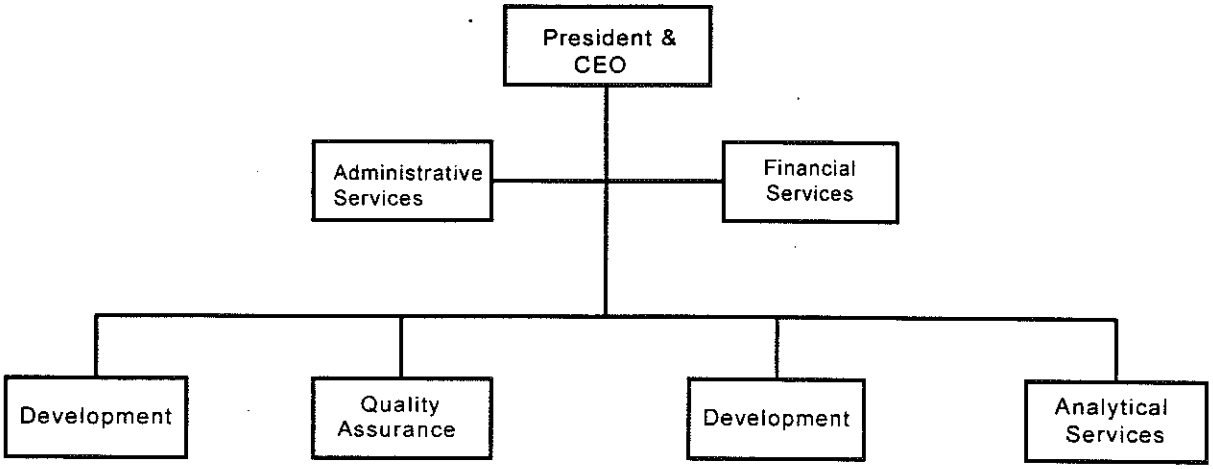

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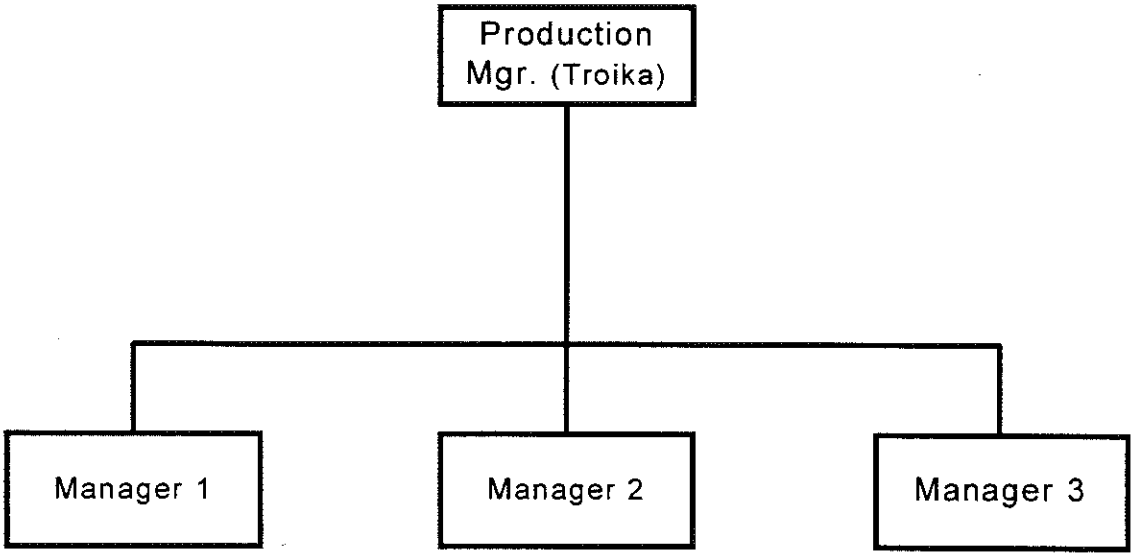

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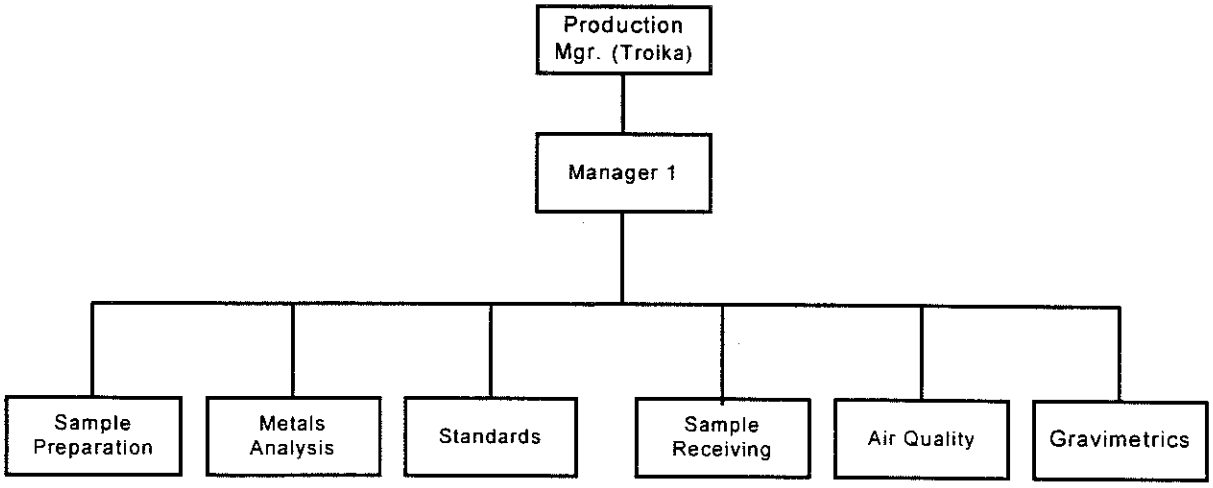

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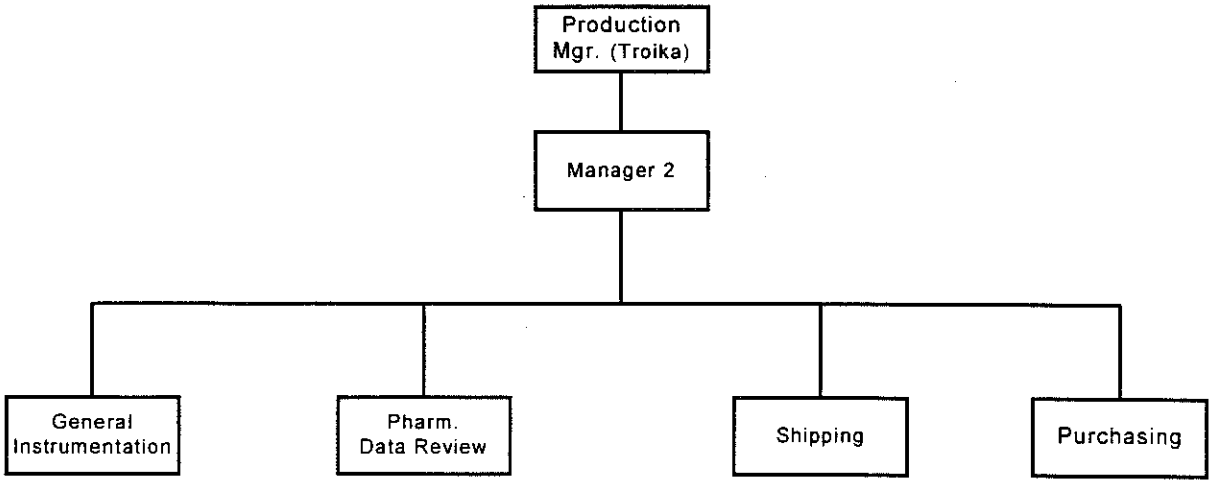

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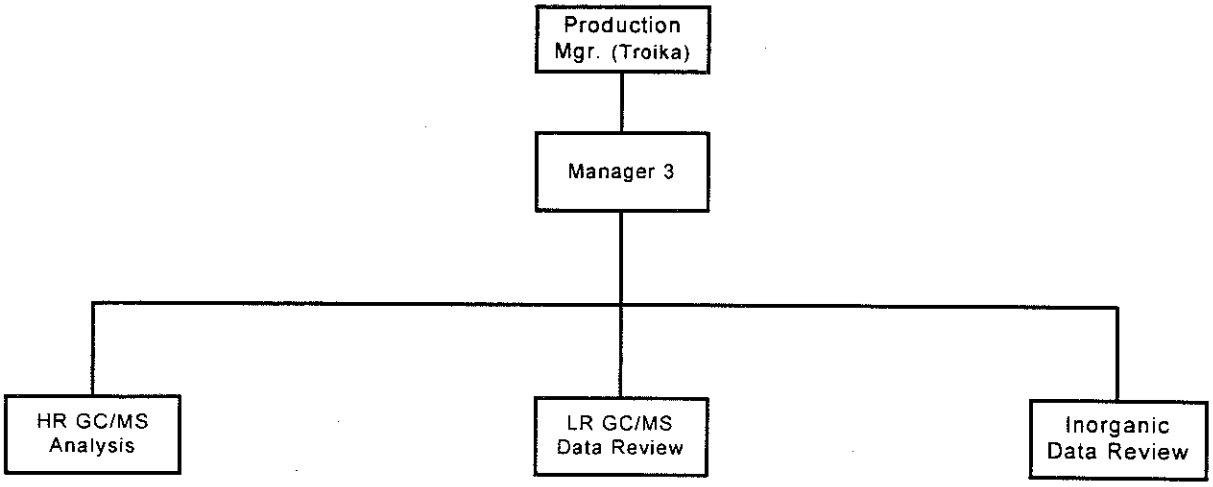

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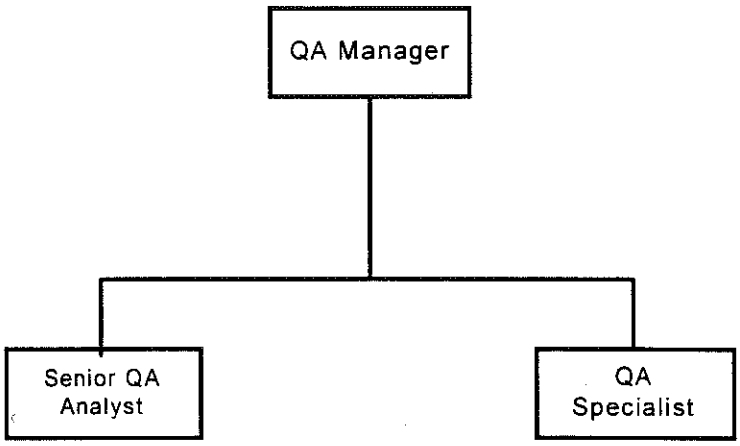

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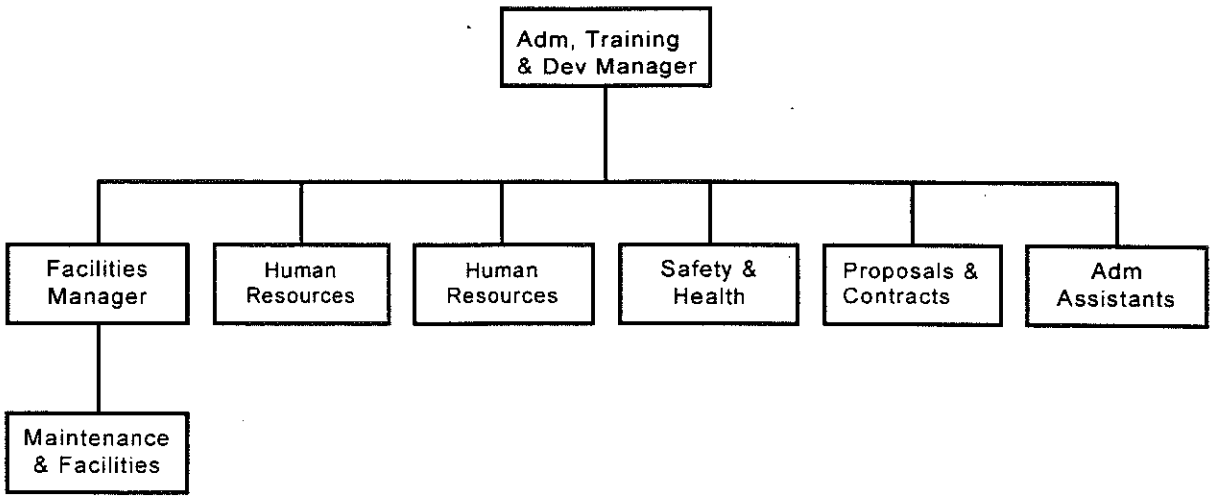

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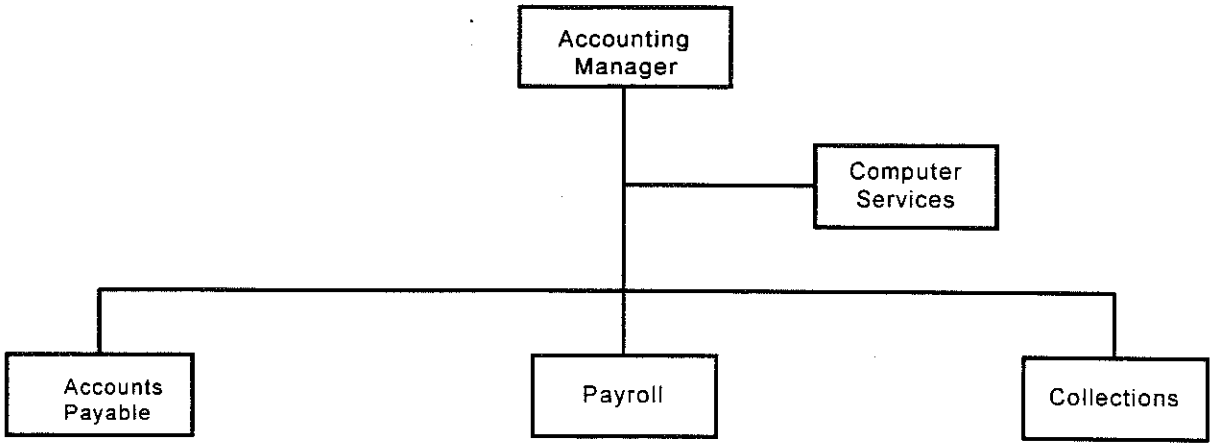

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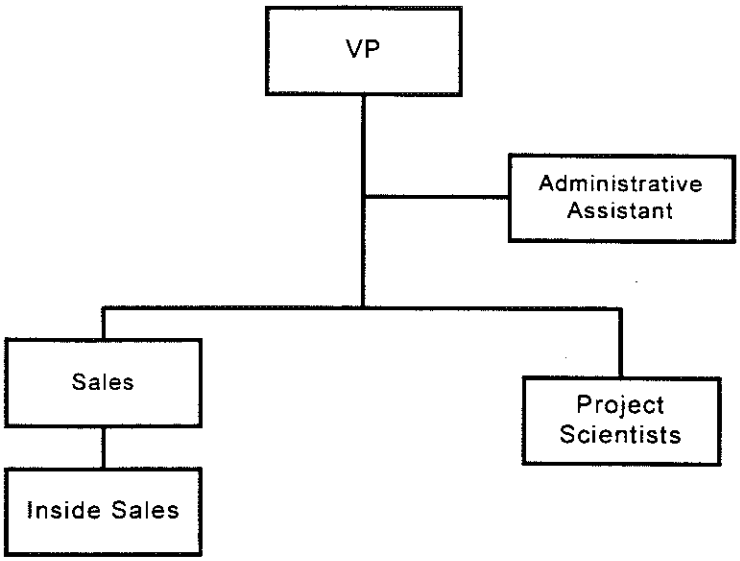

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Appendix 2A

VOLATILE COMPOUNDS

Analytes are displayed with the associated internal standard (underlined).

SW-846 Method 8240, Table 2

Bromochloromethane
Acetone
Bromomethane
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
Iodomethane
Methylene chloride
Trichlorofluoromethane
Vinyl chloride
1,2-Dichloroethane-d_4 (surrogate)

1,4-Difluorobenzene
Benzene
Bromodichloromethane
Bromoform
2-Butanone
Carbon Tetrachloride
Chlorodibromomethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
4-Methyl-2-pentanone
Styrene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
o-Xylene
m-/p-Xylene

Chlorobenzene-d_5
Chlorobenzene
Ethylbenzene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Bromofluorobenzene (surrogate)
Toluene-d_6 (surrogate)

Non-target compounds known as tentatively identified compounds (TIC's) are identified by a computer generated searcch of the National Institute of Standards and Technology (NIST) Mass Spectral Library.

Appendix 2B

SEMIVOLATILE COMPOUNDS

Analytes are displayed with the associated internal standard (underlined).

SW-846 Method 8270, Table 2

1,4-Dichlorobenzene-d_4
Benzyl alcohol
Bis(2-Chloroethyl)ethene
Bis(2-Chloroisopropyl)ether
2-Chlorophenol
1,4-Dibromobenzene (surr)
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
Hexachlorophenol
2-Methylphenol
4-Methylphenol
N-Nitroso-di-n-propylamine
Phenol
Phenol-d_5 (surr)
2-Fluorophenol (surr)

Naphthalene-d_6
Benzoic acid
4-Chloroaniline
Bis(2-Chloroethoxy)methane
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylphenol
Naphthalene
Nitrobenzene
2-Nitrophenol
1,2,4-Trichlorobenzene
1,2,5-Trichlorobenzene-d_3 (surrogate)
Nitrobenzene-d_5 (surr)
Acenaphthene-d_{10}
Acenaphthene
Acenaphthylene
2-Chloronaphthalene
4-Chloorophenyl phenyl ether
Dibenzofuran
Diethylphthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
Hezachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2-Fluorobiphenyl (surr)
2,4,6-Tribromophenol (surrogate)

Phenanthrene-d_{10}
Anthracene
Anthracene-d_{10} (surr)
4-Bromophenyl phenyl ether
Di-n-butylphthalate
4,6-Dinitro-2-methylphenol
Fluorene
Hexachlorobenzene
N-Nitrosodiphenylamine
Pentachlorophenol
Phenanthrene
Chrysene-d_{12}
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butylbenzylphthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Pyrene-d_{10}

Perylene-d_{12}
Terphenyl-d_{14} (surr)
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Di-n-octylphthalate
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene

Non-target compounds known as tentatively identified compounds (TIC's) are identified by a computer generated searcch of the National Institute of Standards and Technology (NIST) Mass Spectral Library

Appendix 2C

DIOXIN/FURAN COMPOUNDS

Table 1- Method 551 Target Analytes

Specific Isomers	Total Isomers
2,3,7,8-TCDD	Total TCDD (22 isomers)
2,3,7,8-TCDF	Total TCDF (38 isomers)

Table 2- Methods 8280, 8290, 23, 1613

Specific Isomers	Total Isomers	
2,3,7,8-TCDD	Total TCDD	(22 isomers)
1,2,3,7,8-PeCDD	Total PeCDD	(14 isomers)
1,2,3,4,7,8-HxCDD	Total HxCDD	(10 isomers)
1,2,3,6,7,8-HxCDD	Total HpCDD	(2 isomers)
1,2,3,4,6,7,8-HpCDD		
OCDD	Total TCDF	(38 isomers)
	Total PeCDF	(28 isomers)
2,3,7,8-TCDF	Total HxCDF	(16 isomers)
1,2,3,7,8-PeCDF	Total HpCDF	(4 isomers)
2,3,4,7,8-PeCDF		
1,2,3,4,7,8-HxCDF		
1,2,3,6,7,8-HxCDF		
2,3,4,6,7,8-HxCDF		
1,2,3,7,8,9-HxCDF		
1,2,3,4,6,7,8-HpCDF		
1,2,3,4,7,8,9-HpCDF		
OCDF		

Appendix 2D

PESTICIDE COMPOUNDS

Method 8081

Aldrin
α-BHC
β-BHC
δ -BHC
γ -BHC (Lindane)
Chlordane (technical)[a]
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
Methoxychlor
Toxaphene
Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
Tetrachloro-meta-xylene (TCMX) - surrogate
Decachlorobiphenyl (DCBP) - surrogate

Appendix 3A

GC/MS ANALYTICAL METHODS: VOLATILES

Matrices	VOST tubes, solids, water
Compounds	See Appendix 2A
Initial Calibration	5 point minimum, SPCC compounds RF > 0.300 (Bromoform RF > 0.250), CCC compounds RSD <30%
Continuing Calibration	mid-level standard analyzed at the beginning of every 12 hours of analysis time, SPCC compounds RF > 0.300 (Bromoform > 0.250), CCC compounds %D < 25% from initial calibration average
Internal Standards	Bromochloromethane 1,4-Dichlorobenzene Chlorobenzene-d_5
Standard Solution Lifetime	Stock Solutions (>1000 ppm): gases in methanol 2 months liquids in methanol 6 months Dilutions (<1000 ppm): in methanol 2 weeks in water 1 week
Holding Time	14 days from sample collection
Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes at 20 µg/L. Results must meet all method criteria.
QC Check Sample	Blank matrix spiked with equivalent of 20 µg/L all analytes. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.

Appendix 3B

GC/MS ANALYTICAL METHODS: SEMIVOLATILES

Matrices	solid waste, soil, water, and air	
Compounds	See Appendix 2B	
Initial Calibration	5 point minimum, SPCC compounds RF > 0.050, CCC compounds RSD <30%	
Continuing Calibration	mid-level standard analyzed at the beginning of every 12 hours of analysis time, SPCC compounds RF > 0.050, CCC compounds %D < 30% from initial calibration average	
Internal Standards	1,4-Dichlorobenzene-d_4 Naphthalene-d_8 Acenaphthalene-d_{10}	Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	Nitrobenzene-d_5 2-Fluorobiphenyl Terphenyl-d_{14} Phenol-d_5 2-Fluorophenol	2,4,6-Tribromophenol pyrene-d_{10} 1,3,5-Trichlrobenzene-d_3 1,4-Dibromobenzene-d_4 Anthracene-d_{10}
Standard Solution Lifetime	Stock Solutions 1 year	
Holding Time	Extraction: water 7 days from sample collection soils 14 days from sample collection Analysis: 40 days from extraction	
Validation	Initial performance analysis (water): four (4) 1 L samples composed of reagent water spikes with all analytes at 100 µg/L, extracted and analyzed. Results must meet all method criteria.	
QC Check Sample	Blank matrix spiked with equivalent of 100 µg/L all analytes. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.	

Appendix 3C

GC/MS ANALYTICAL METHODS: DIOXIN/FURAN

	Methods 8290 & 23	Method 1613	Method 551
Matrices	water, soil, sludge, tissue, pulp, paper, ash, MM5, PUF (Method 23- MM5 only)		
Compounds	See Appendix 2C, Table 2	See Appendix 2C, Table 2	See Appendix 2C, Table 1
Initial Calibration	5 points- 20/25% RSD (Method 23- 25/30% RSD)	5 points- 20/25% RSD	5 points- 20/25% RSD
Continuing Calibration	mid-level standard every 12 hours, 20/25% RPD (Method 23- 25/30% RPD)	Mid-level standard every 12 hours, 20/25% RPD	Mid-level standard at the beginning of every 12 hours and 4th point at the end of injection sequence, 20/25% RPD
Internal Standards	$^{13}C_{12}$-2,3,7,8-TCDD $^{13}C_{12}$-2,3,7,8-TCDF $^{13}C_{12}$-1,2,3,7,8-PeCDD $^{13}C_{12}$-1,2,3,7,8-PeCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-1,2,3,4,6,7,8-OCDD	same as Method 8290 plus: $^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,7,8,9-HxCDF $^{13}C_{12}$-2,3,4,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	same as Method 8290
Surrogate Standards	$^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF $^{37}Cl_4$-2,3,7,8-TCDD	$^{37}Cl_4$-2,3,7,8-TCDD	same as Method 8290
Standard Solution Lifetime	Based on concentration- ≥10 µg/mL: 15 years, or according to supplier specifications <10 µg/mL: 1 year		
Holding Time	8290 Extract within 30 days of collection; analyze within 45 days of extraction 23 Analyze within 60 days of collection	Water - 1 year at 0-4° C. Solids - 1 year at <-10 ° C.	

Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes: tetra at 200 pg/L, penta - hepta at 1000 pg/L, and octa at 2000 pg/L.
QC Check Sample	Blank matrix spiked in the same manner as the validation series. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater. (Only 1 per day or once per 20 samples Method 1613)

Appendix 3D

GC/MS ANALYTICAL METHODS: PESTICIDES/PCBs

Matrices	groundwater, soil, non water-miscible waste
Compounds	See Appendix 2D
Initial Calibration	5 point minimum, RSD ≤20%, use average RF
Continuing Calibration	mid-level standard every 10 samples, ≤15% D
Internal Standards	Decafluorobiphenyl 2,4,5,6-Tetrachloro-meta-xylene
Standard Solution Lifetime	Stock Solutions (≥1000 ppm): According to supplier specifications Working Solutions (<100 ppm): 6 months
Holding Time	Extraction: water 7 days from sample collection soils 14 days from sample collection Analysis: 40 days from extraction
Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes at equivalent of 10 and 2 μg/L. Results must meet all method criteria.
QC Check Sample	Blank matrix spiked with all analytes, equivalent of 10 and 2 μg/L. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.

Appendix 4

CONTAINERS, PRESERVATIVES AND HOLDING TIMES

Parameter	Matrix	Holding time	Recommended Volume	Preservative[d]
Volatile[a] organics	Water	14 days from collection	two 40 mL glass vials with Teflon lined septa, no headspace present	4 drops conc. HCl 4°C
	Soil	14 days from collection	20 g, glass vials with teflon septa, no headspace present	Cool, 4°C
Extractable[b] organics	Water	7 days from collection 40 days from extraction	2.0 L in glass bottles	Cool, 4°C, $Na_2S_2O_3$ if residual chlorine (80 mg/L)
	Soil	14 days from collection 40 days from extraction	100 g in glass jar	Cool, 4°C
AOX/TOX	Water	≥3 days but <6 months after collection	250 mL in glass bottle	HNO3 to pH <2, $Na_2S_2O_3$ if residual chlorine present (20 mg/ 250 mL)
	Soil	≥3 days but <6 months after collection	50 g in glass jar	none
Dioxin	Water	method specific, see Appendix 3C	2.0 L in glass bottles	Cool, 4°C 1613 - $Na_2S_2O_3$ if residual chlorine (80 mg/L)
	Soil	method specific, see Appendix 3C	100 g in glass jar	Cool, 4°C
Metals	Water	28 days Hg 6 months all other metals	0.5 L in glass or plastic	HNO3 to pH <2
	Soil	28 days Hg 6 months all other metals	50 g in glass jar	none

[a]For SW-846: Free chlorine must be removed prior to addition of HCl by exact addition of $Na_2S_2O_3$. Adjust pH <2 for purgeable aromatic hydrocarbons with H_2SO_4, HCl or solid $NaHSO_4$. Adjust pH to 4-5 for acrolein and acrylonitrile.

[b]For SW-846: Preserve phenols, benzidines, nitrosamines, nitroaromatics and cyclic ketones, PAHs, haloethers, chlorinated hydrocarbons and pesticides with 0.008% $Na_2S_2O_3$. Nitrosamines, Nitroaromatics, cyclic ketones and PAHs should be stored in the dark. Pesticides pH=5-9.

[c]For CLP: Dissolved metals require filtration before pH adjustment.

[d]Preservation temperatures are approximate with an acceptable range of ±20C.

APPENDIX C

Chemical Waste Management

Vickery, Ohio

ENSR

Evaluation of Impacts of an Acidic Material Spill on Aquatic Communities in Little Raccoon and Raccoon Creeks

ENSR Consulting and Engineering

August 1993

Document Number 1413-013-600

1413-013-600

EVALUATION OF IMPACTS OF AN ACIDIC MATERIAL SPILL ON AQUATIC COMMUNITIES IN LITTLE RACCOON AND RACCOON CREEKS

Prepared for

CHEMICAL WASTE MANAGEMENT
Vickery, Ohio

Prepared by

ENSR CONSULTING AND ENGINEERING
Fort Collins, Colorado

August 1993

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1.0 INTRODUCTION

Chemical Waste Management's Vickery Facility in Vickery, Ohio, reported a release of acidic waste into Meyer's Ditch on April 22, 1993. The release was detected at about 10:50 a.m., when a flange on a low-pressure pipeline to one of the wells was discovered to be leaking acidic material onto the ground and into an adjacent intermittent drainage ditch (Meyer's Ditch). The exact volume of waste released from the pipeline is unknown, although it was considered to be small, since a routine inspection of the line on Thursday morning (April 22) indicated no leakage. After discovering the leak, immediate actions were taken to shut off the flow and contain the acid material. On-site activities consisted of pumping the water out of Meyer's Ditch. All cleanup activities were approved by the Ohio Environmental Protection Agency (Ohio EPA). Silt screens also were established in Meyer's Ditch downstream of the facility boundary, and two downstream receiving waters, Little Raccoon and Raccoon Creeks. Initial measurements in Meyer's Ditch on April 22 indicated a low pH. As the material moved downstream, the pH increased due to dilution from the larger volume of water. By April 23 the pH had returned to about 7 in Meyer's Ditch. The release of the acidic material is believed to have caused an orange/red precipitate in the streams, possibly as a result of metals becoming insoluble in the higher pH waters of Little Raccoon Creek. The presence of orange/red water was used to track the progress of the material in Little Raccoon and Raccoon Creeks. It is believed by April 24, the material had progressed to Lake Erie. An orange precipitate was evident on the stream bottom and banks in Meyer's Ditch and Little Raccoon Creek. The orange precipitate was not obvious in Raccoon Creek.

The Raccoon Creek drainage that received the acidic material is a low-gradient, low-order stream system that drains into Lake Erie. Meyer's Ditch, which first received the acidic material, is a small, intermittent stream. The acidic material traveled about 1.5 miles in Meyer's Ditch and entered Little Raccoon Creek, which is a small, perennial stream. From its confluence with Meyer's Ditch, Little Raccoon Creek traverses about 3 miles and empties into Raccoon Creek, which is a medium-sized perennial stream that drains into Lake Erie. The approximate distance from the confluence of Little Raccoon and Raccoon Creeks to Lake Erie is about 2 miles.

The purpose of this report is to describe studies that were used to evaluate the impacts of the acidic material on aquatic communities in Little Raccoon and Raccoon Creeks. The types of studies conducted for this assessment included water and sediment chemical analyses, water and sediment toxicity, fish kill counts, and benthic macroinvertebrate and fish population surveys. The report is divided into Methods (Chapter 2.0), Results (Chapter 3.0), Discussion (Chapter 4.0),

Conclusions (Chapter 5.0), and References (Chapter 6.0). In designing the studies, guidance documents (Ohio EPA 1987) regarding methods for determining biological criteria for the Ohio water bodies were reviewed. Where applicable, sampling methods and data analyses proposed for fish and macroinvertebrate studies in this plan followed the Ohio EPA (1987) biological procedures.

2.0 METHODS

2.1 Sampling Locations

Six sampling locations were selected for the chemistry and biological surveys conducted in Meyer's Ditch, Little Raccoon Creek, and Raccoon Creek (Figure 2-1). As described in Section 2.2, the types of analyses and surveys conducted at these locations varied. The approximate locations of the sampling sites are shown in Figure 2-1 and described below:

- M-1 is located in Meyer's Ditch approximately 75 yards upstream of the confluence with Little Raccoon Creek.

- US-1 is located in Little Raccoon Creek about 20 yards upstream of the confluence of Meyer's Ditch and Little Raccoon Creek. Because this site is upstream, and not influenced by inputs from Meyer's Ditch, data from this location served as a reference to data resulting from the downstream locations.

- Three locations in Little Raccoon Creek (DS-1, DS-1A, and DS-2) were sampled downstream of Meyer's Ditch. DS-1 is located immediately downstream of the confluence with Meyer's Ditch, while DS-1A is positioned about midway between the confluences with Meyer's Ditch and Raccoon Creek. DS-2 is located about 50 feet upstream of the confluence of Little Raccoon and Raccoon Creeks.

- DS-3 is in Raccoon Creek approximately 1 mile downstream of its confluence with Little Raccoon Creek. This location was the farthest downstream point that could be reached by land on April 23, and it was near the estimated downstream location of the reddish precipitate reported to be caused by the acidic material spill.

A summary of width, depth, and substrate characteristics at these six sampling locations is provided in Table 2-1.

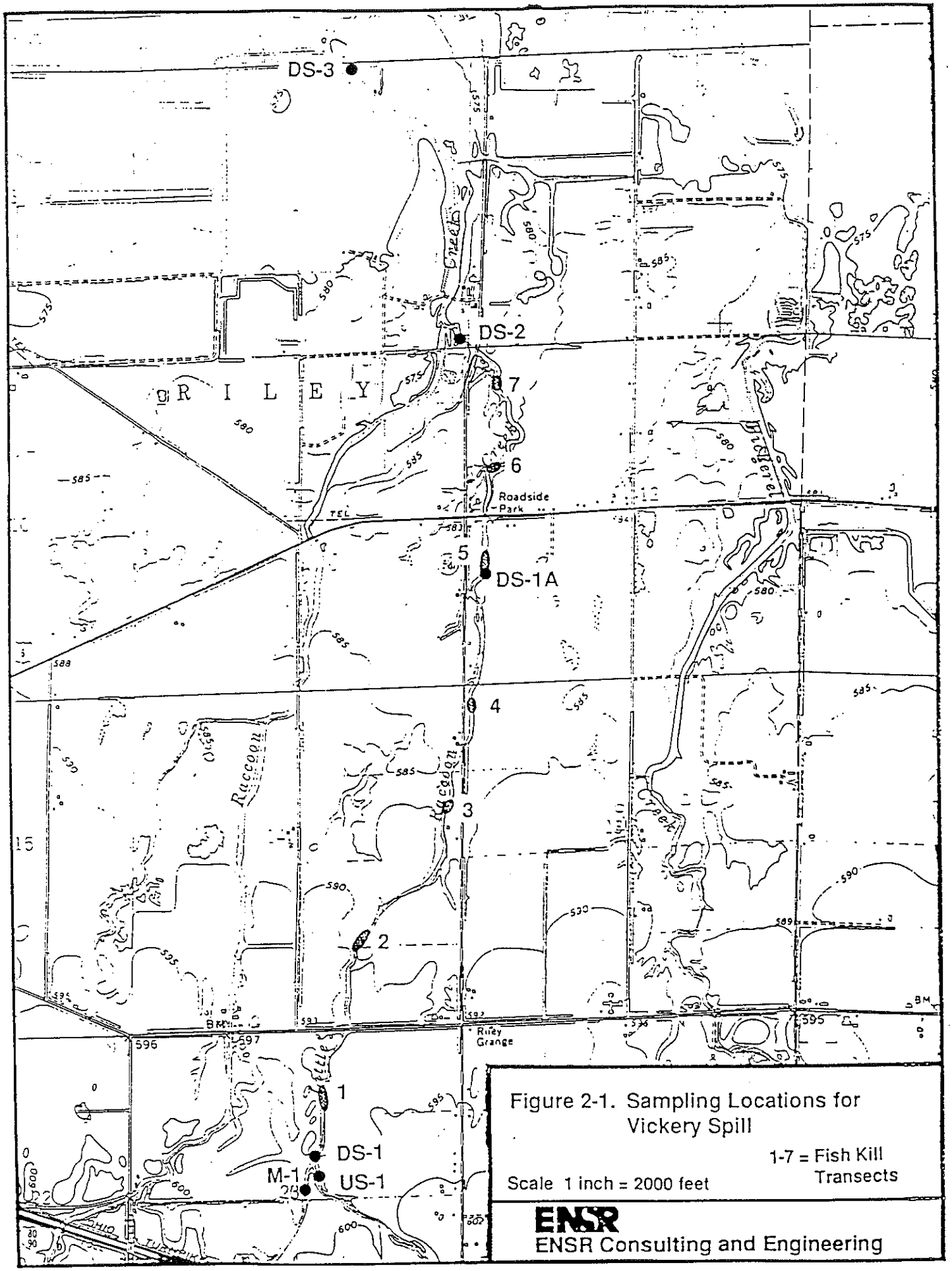

Figure 2-1. Sampling Locations for Vickery Spill

1-7 = Fish Kill Transects

Scale 1 inch = 2000 feet

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Table 2-1

Description of Sampling Locations on April 24, 1993, for the Acidic Material Leak Near the Vickery, Ohio, Facility

Location Designation	Stream Name	Width (ft)[1]	Depth (ft)[1]	Dominant Substrate
US-1	Little Raccoon Creek	4 - 6	<0.1 - 1	Silt and clay with some sand
DS-1	Little Raccoon Creek	4 - 6	<0.1 - 1.5	Silt and sand
DS-1A	Little Raccoon Creek	4 - 10	<0.1 - 3	Clay and detritus
DS-2	Little Raccoon Creek	18 - 25	0.5 - 4	Clay and detritus
DS-3	Raccoon Creek	40 - 50	2 - 6	Clay and silt
M-1	Meyer's Ditch	3 - 4	<0.1 - 0.2	Silt and clay

[1]Width and depth fluctuated during the three sampling periods.

2.2 Types of Analyses and Surveys

The types of analyses and surveys conducted for the acidic material leak assessment included water and sediment chemistry, water and sediment toxicity, fish kill survey, benthic macroinvertebrate sampling, and fish population sampling. The initial studies consisted of water and sediment chemistry, collection of water for toxicity testing, and a fish kill survey. These studies were conducted on April 23 and 24, 1993, which was within 48 hours following the detection of the pipeline leak. Subsequent collections and biological surveys were conducted on April 29, May 13, and June 2 and 3, 1993, as indicated in Table 2-2. The types of analyses and surveys conducted at the six sampling locations also are listed in Table 2-2. The April 29 analyses (water and sediment chemistry and collection of water for toxicity testing) were included to determine the effects of a heavy rain event on April 25 and 26, 1993.

2.3 Chemistry

Water samples for analytical chemistry (metals) were collected in clean, high-density polyethylene containers (Eagle-Picher®). The containers were rinsed with stream water and then filled. The samples were kept on ice (at or near 4°C) until arrival at the laboratory (Aquatech, Marion, Ohio). At the laboratory the samples were filtered through a 0.45 µm filter to obtain samples for dissolved measurements. Water samples from the first sampling effort (April 23 to 24) were not analyzed for total metals (prior to filtration); samples collected during the second and third sampling efforts were analyzed for dissolved and total metals. Analysis was completed using EPA method 200.7/6010 (Inductively Coupled Plasma Emission - ICP). Samples were analyzed for 22 metals (see Chapter 3.0, Results).

Sediment samples were collected by scooping material from the stream bottom by hand with heavy, rubber gloves. At each site the gloves were thoroughly cleaned with site water, prior to collection of the sample. Samples were placed in wide-mouth, high-density polyethylene jars or Ziploc® bags. Sediment samples were kept on ice (at or near 4°C) until analysis at the laboratory (Aquatech, Marion, Ohio). Sediment samples were analyzed for the same metals as the water samples, also using ICP, following digestion. All analytical samples were labeled with the site designation, stream name, date, and type of sample.

Duplicate water and sediment samples were collected. Data were analyzed by determining the mean value of each parameter. If a metal concentration for one duplicate was below the method detection limit, but the other duplicate had a detectable concentration, then the below detection duplicate was assigned a value of 1/2 the detection limit.

Tabl ?

Samples Collected and Analyses Performed at Selected Sites
Near the Vickery, Ohio, Facility

Site	Dates	Water Chemistry	Sediment Chemistry	Water Toxicity	Sediment Toxicity	Fish Kill Survey[1]	Benthic Population Survey	Fish Population Survey
US-1	April 23-24	X	X	X		X		
US-1	April 29-30	X	X					
US-1	May 13			X				
US-1	June 2-3	X	X		X		X	X
DS-1	April 23-24	X	X	X		X		
DS-1	April 29-30	X	X					
DS-1	May 17			X				
DS-1	June 2-3	X	X		X		X	X
DS-1A	June 2-3	X	X				X	X
DS-2	April 23-24	X	X	X		X		
DS-2	April 29-30	X	X					
DS-2	May 13			X				
DS-2	June 2-3	X	X				X	X
DS-3	April 23-24	X	X	X		X		
DS-3	April 29-30	X	X					
DS-3	May 13			X				
DS-3	June 2-3	X	X		X			
M-1	April 23-24		X			X		
M-1	April 29-30	X	X					

[1] Fish kill surveys were actually completed by counting dead fish in several sections of the impacted creeks.

2.4 Biological

The health of aquatic ecosystems, either under normal conditions or following an acute impact, is typically assessed using analytical chemistry and toxicity tests. These aspects of this study have been addressed in Sections 2.3 and 2.5. The Ohio EPA recommends targeted sampling of both the fish and benthic macroinvertebrate communities (Ohio EPA 1987). Fish and macroinvertebrates inhabit receiving waters continuously and are a reflection of the chemical, physical, and biological history of the receiving waters. The Biological Criteria documents (Volumes 1 through 3) are designed to examine the continuous conditions of a water body, and do not specifically address impacts of an unanticipated spill (Ohio EPA 1987). Therefore, some methodologies suggested are not applicable to the Vickery spill (e.g., use of artificial substrates for the collection of benthic macroinvertebrates).

2.4.1 Fish Kill Survey

Fish kill surveys were conducted in Meyer's Ditch, Little Raccoon Creek, and Raccoon Creek on April 23 and 24. The method used to count dead fish varied depending on the size and length of the three streams, as well as access restrictions. Since Meyer's Ditch was relatively small and the length affected by the leak was about 1.5 miles, the lower 1 mile of this stream was walked on April 22 and examined for dead fish. In contrast, Raccoon Creek was surveyed by boat because the stream was quite deep and shoreline access was limited. The entire shoreline area was surveyed for dead fish along both banks from its confluence with Little Raccoon Creek and Lake Erie.

The counting method used in Little Raccoon Creek was a transect procedure recommended for narrow streams by the American Fisheries Society (1982). The procedure involved dividing the 3-mile study area in Little Raccoon Creek into 0.5-mile sections. Initial measurements on-site estimated the Little Raccoon segment to be about 3.5 miles. Subsequent, more accurate measurements indicated the segment was 3.0 miles. Therefore, all dead fish were counted in one 100-yard segment within each 0.5-mile section in the upper 2.5 miles of Little Raccoon Creek; and two segments in the lower portion of the creek (just upstream of its confluence with Raccoon Creek). The initial 100-yard segment was randomly selected in the downstream portion of the stream. Subsequent 100-yard segments were selected at approximate 0.5-mile intervals. The exact location of the segments also depended on landowner's permission. In total, seven 100-yard segments were counted for dead fish (numbered 1 through 7 in Figure 2-1). All dead fish within each 100-yard segment were counted on April 24 by walking the streambanks. The numbers and length of fish were recorded in a field notebook. The total fish counts for the

seven, 100-yard segments were expanded to the entire 3.0 miles in Little Raccoon Creek by the following formula:

$$E = (1{,}760 \text{ yards/mile})\ T/L$$

Where: E = expansion factor
T = total length affected by leak (3.0 miles)
L = sum of the lengths of the counting segments (700 yards).

The expansion factor was multiplied by the counts for each species to estimate the total number of dead fish for the 3.0 miles in Little Raccoon Creek.

On the initial day of the leak and during the fish kill counts, dead fish were collected and frozen for potential use in tissue analyses. The fish are being held at ENSR's laboratory in Fort Collins.

2.4.2 Benthic Macroinvertebrates

Benthic macroinvertebrates are those organisms living in or on the substrate of a lake or, in this case, a stream. These organisms can be insects (e.g., midge larvae) or other invertebrates (e.g., crayfish or worms). In order to assess the impacts on the benthic community, quantitative samples were obtained from the four sites in Little Raccoon Creek within approximately 5 weeks of the material leak. These sites included US-1, DS-1, DS-1A, and DS-2.

At each site, four replicate samples were collected using a petite Ponar dredge (grab). The grab samples were placed into a bucket with a brass grid in the bottom; large rocks or other debris were checked for organisms and removed. Excess sediment was rinsed out of the bottom of the bucket. All captured organisms and remaining debris were placed in a wide-mouth jar and preserved with 5 to 10 percent buffered formalin.

In the laboratory, all samples were picked and sorted, and organisms placed in 70 percent isopropanol. Identification and enumeration of macroinvertebrates were performed by Mr. Henry Zimmerman, a taxonomist located in Fort Collins, Colorado. Organisms will be identified to the Lowest Practical Taxon (LPT). Community parameters calculated for this study include: density ($\#/m^2$), number of taxa, Shannon diversity, and Shannon evenness (Shannon diversity and evenness were calculated using the natural log). In addition to these parameters, the Invertebrate Community Index (ICI) also was computed according to Ohio EPA (1987). Statistical analyses were performed on densities, number of taxa, Shannon diversity, and evenness at the

upstream and downstream locations using analysis of variance and Tukey's multiple range test (α = 0.05).

2.4.3 Fish Population Survey

A fish survey was conducted on June 2, 1993, to determine the relative impact of the leak on fish composition and relative abundance. Since most of the dead fish were observed in Little Raccoon Creek, this stream was emphasized in the survey. Four sample locations were surveyed in Little Raccoon Creek, which included upstream of the confluence with Meyer's Ditch (reference site, US-1), downstream of the confluence with Meyer's Ditch (DS-1), upstream of the Route 6 Bridge (DS-1A), and about 100 feet upstream with the confluence with Raccoon Creek (DS-2). The survey was conducted using a backpack electroshocker (Smith-Root) in a 100-foot section at each location. A two-pass removal method was used to estimate fish numbers at each location (Seber and LeCren 1967). Equal effort was used for each pass at each site.

The following equation was used for estimating populations of the most abundant species (or taxonomic groups, i.e., minnows) and total fish at each site:

$$N = \frac{U_1}{1-(U_2/U_1)}$$

Where: N = population estimate;
U_1 = number of fish removed on the first pass; and
U_2 = number of fish removed on the second pass.

For comparative purposes, abundance data were expressed as a consistent density measure (e.g., fish per acre [ac]). The estimated probability of capture (p) on each pass was calculated for estimated populations using the following equation:

$$p = 1-(U_2/U_1)$$

Probability of capture values in this study varied depending upon the sampling location. Sampling at US-1 showed a probability of capture of 1, while values at the other locations were 0.67 at DS-1, 0.73 at DS-1A, and 0.72 at DS-2. Probability of capture values less than 0.80 indicate that, because of lower sampling efficiency, the population estimate is of lower accuracy.

Three biologists electrofished the stream by walking slowly upstream and collecting any stunned fish. All fish were identified and enumerated; non-minnow species, such as white sucker or green sunfish, were measured for total length in millimeters and weighed in grams. All fish were examined externally for evidence of disease or parasites. All fish were returned to the stream after field processing. The number and percent composition of fish were presented for each location. To allow useful comparisons to the reference site, the effort at each site was the same, especially in terms of the length of the sampling.

In conjunction with the fish sampling, a general characterization of macrohabitat features was made at the four sampling locations following the Ohio EPA's (1987) Qualitative Habitat Evaluation Index (QHEI) procedure. The QHEI requires data on substrate, instream cover, channel morphology, riparian zone and bank erosion, pool or riffle quality, and riffle/run depth. The reason for including the QHEI with the fish survey was to document whether habitat characteristics are contributing to possible differences in fish communities at the four sampling locations.

2.5 Toxicity Testing

2.5.1 Water

Samples for toxicity testing were collected in new, 2.5-gallon cubitainers (two from each site), which were rinsed with site water before being filled. The cubitainers were labeled appropriately and kept on ice at or near 4°C until arrival at ENSR Consulting and Engineering's Fort Collins Environmental Toxicology Laboratory (FCETL) in Fort Collins, Colorado. Upon arrival, the samples were logged in and stored at 4°C until initiation of toxicity testing. For each of the four samples, chronic tests were performed using the water flea (*Ceriodaphnia dubia*) and the fathead minnow (*Pimephales promelas*). The tests were conducted using standard U.S. Environmental Protection Agency (EPA) (1989) methods.

Due to a shipping error, water from site DS-1 was not collected on May 13 for the second round of toxicity testing along with water from the other sites. Water from this site was collected on May 17 and shipped to the FCETL.

At the end of the testing period (7 days for *Pimephales promelas* and 5 to 8 days for *Ceriodaphnia dubia*, depending on organism reproductive performance), data were analyzed using appropriate parametric or nonparametric statistical methods ($\alpha = 0.05$) depending on whether the data met normality and variance assumptions ($\alpha = 0.01$). Parameters calculated include: 48-hour LC_{50}, NOEC, and IC_{25}. The 48-hour LC_{50} is an acute endpoint that measures

the Lethal Concentration at which 50 percent of organisms die after 48 hours. The NOEC is the No Observable Effect Concentration, and is the concentration at which there is no significant difference from the control at the end of a chronic test. Finally, the IC_{25} is the Impact Concentration representing the concentration at which there is a 25 percent reduction in organism performance at the end of a chronic test.

2.5.2 Sediment

To determine if sediments downstream of Meyer's Ditch display significantly greater toxicity than upstream sediments, toxicity tests were performed using the amphipod, *Hyalella azteca*. Sediments were collected at US-1, DS-1, and DS-2 in clean, 4-liter jars to correspond with the biotic sampling (on June 3). The sediment samples were labeled appropriately, placed on ice, and shipped to the FCETL in Fort Collins, Colorado. Testing was conducted on 100 percent stream sediment and a reference sediment using the American Society of Testing and Materials (ASTM) standard methods (1992). The endpoints examined were organism survival and significant difference from the reference sediment (a clean, laboratory sediment) and upstream control sediment (US-1).

3.0 RESULTS

3.1 Chemistry

3.1.1 Water

Several parameters were not detected in the water samples in either their total or dissolved forms: aluminum, barium, calcium, iron, potassium, magnesium, manganese, sodium, and zinc (Table 3-1). The lack of detectable levels of metals, however, may be due more to the method detection limit than to the actual absence of the material in the water. The method detection limit for several metals using ICP is higher than what could be detected using other techniques and, in fact, is higher than levels that may produce toxic responses. For example; the detection limit for selenium was 70 μg/L using ICP. However, the EPA acute and chronic criteria (EPA 1991) for the protection of aquatic life are 20 and 5 μg/L, respectively. Therefore, selenium could still be present in the water column at toxic levels, but not be detected using ICP. High levels of some metals in the sediment (see Section 3.1.2) support this possibility. Discussion, however, will be limited to those materials that were detected in the water column. In some cases, total concentrations were higher than dissolved forms; for most parameters, however, there was little difference between dissolved and total forms, indicating that much of the material was bioavailable. Because it is the dissolved form that is bioavailable and thus potentially toxic, discussion will be further limited to dissolved concentrations.

For several metals the EPA chronic and acute criteria were calculated and compared to measured concentrations. Since metal toxicity is often related to the hardness of the water, with toxicity decreasing with increasing hardness, it was necessary to calculate site-specific metal criteria for manganese, lead, and zinc. Samples collected on April 23 showed hardness values ranging from 382 to 452 mg/L as $CaCO_3$. Samples collected on May 13 showed higher hardness values, ranging up to 680 mg/L. These values were similar to what was measured by Chemical Waste Management . Since hardness of the stream water at the time of the spill was probably closer to the April values, criteria were calculated using a hardness of 400 mg/L as $CaCO_3$ to represent an average of the various measurements.

Zinc. Zinc was one of only two metals measured at very high concentrations during the first sampling period (Figure 3-1). The measured concentration at DS-2 was nearly 3 mg/L dissolved zinc, and the concentration at DS-3 was nearly 2 mg/L. There were also detectable levels of zinc at both US-1 and DS-1, although these levels were below both the acute and chronic criteria.

Table 3-1

Mean Concentrations (ppm) of All Analytes

Station	Date	Matrix	Form	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg
US1	Apr 23	Water	Diss	0	0	0	0.04	0	117	0	0	0	0	0	0
US1	Apr 29	Water	Diss	0	0.08	0	0.035	0	128.5	0	0	0	0	0	0
US1	Jun 03	Water	Diss	0	0.19	0	0.049	0	214.5	0	0	0	0	0.142	0
US1	Apr 29	Water	Total	0	0.735	0	0.04	0	135	0	0	0	0	0.51	0
US1	Jun 03	Water	Total	0	0.435	0	0.054	0	227.5	0	0	0	0	0.332	0
US1	Apr 23	Sediment	Total	0	8400	92	64.5	0.45	12935	0.7	13	10	15.5	19450	0
US1	Apr 29	Sediment	Total	0	6250	0	56	0.325	11500	0	13.5	10	14	17500	0
US1	Jun 03	Sediment	Total	0	6055	15	62.5	0.45	6400	0	13.5	9.5	12.5	15350	0
DS1	Apr 23	Water	Diss	0	0	0	0.03	0	109	0	0	0	0	0	0
DS1	Apr 29	Water	Diss	0	0	0	0.03	0	124.5	0	0	0	0	0	0
DS1	Jun 03	Water	Diss	0	0.195	0	0.048	0	211.5	0	0	0.007	0	0.193	0
DS1	Apr 29	Water	Total	0	0.745	0	0.04	0	137	0	0	0	0	0.525	0
DS1	Jun 03	Water	Total	0	0.455	0	0.052	0	218	0	0	0	0	0.365	0
DS1	Apr 23	Sediment	Total	0	6745	120	70	0.55	7200	0	12	26.5	17.5	21100	0
DS1	Apr 29	Sediment	Total	0	10850	0	145	0.7	8800	0.525	32	21	23.5	28850	0.04
DS1	Jun 03	Sediment	Total	0	10575	37	162.5	0.85	13950	0.275	30.5	15	75	36300	0.035
DS1A	Jun 03	Water	Diss	0	0.345	0	0.053	0	210	0	0	0	0	0.408	0
DS1A	Jun 03	Water	Total	0	0.515	0	0.072	0	254	0	0	0	0	0.495	0
DS1A	Jun 03	Sediment	Total	0	13450	20	75	0.8	34050	0	11	71	23	21250	0.095
DS2	Apr 23	Water	Diss	0	0	0	0.035	0	104.5	0	0	0	0	0	0
DS2	Apr 29	Water	Diss	0	0.12	0	0.05	0	108	0	0	0	0	0	0
DS2	Jun 03	Water	Diss	0	0.37	0	0.041	0	183.5	0	0	0	0	0.466	0
DS2	Apr 29	Water	Total	0	2.745	0	0.05	0	99.3	0	0	0	0	3.235	0
DS2	Jun 03	Water	Total	0	1.015	0	0.046	0	193	0	0	0	0	0.859	0
DS2	Apr 23	Sediment	Total	0	17350	174	111	1.05	6350	0	16.5	20	21.5	32300	0
DS2	Apr 29	Sediment	Total	0	12500	10	89	0.85	10400	0	19.5	23.5	21.5	31150	0.085
DS2	Jun 03	Sediment	Total	0	17550	28.75	103	1.15	10265	0	18.5	24.5	26	32150	0.145

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3- (continued)

Station	Date	Matrix	Form	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg
DS3	Apr 23	Water	Diss	0	0	0	0.04	0	117.5	0	0	0	0	0	0
DS3	Apr 29	Water	Diss	0	0.075	0	0.04	0	120	0	0	0	0	0	0
DS3	Jun 03	Water	Diss	0	0.58	0	0.062	0	203	0	0	0	0	0.781	0
DS3	Apr 29	Water	Total	0	1.905	0	0.04	0	111	0	0	0	0	2.465	0
DS3	Jun 03	Water	Total	0	1.06	0	0.057	0	171.5	0	0	0	0	1.365	0
DS3	Apr 29	Sediment	Total	0	8400	0	51	0	39500	0	10	13	16.5	19050	0.05
DS3	Jun 03	Sediment	Total	0	10635	22	59	0.55	40650	0	10	15	20.5	20600	0.08
M1	Apr 29	Water	Diss	0	0.08	0	0.03	0	86.3	0	0	0	0	0	0
M1	Apr 29	Water	Total	0	0.99	0	0.04	0	88.95	0	0	0	0	0.765	0
M1	Apr 23	Sediment	Total	0	12600	137	132	0.85	8500	0	30.5	18	22.5	30450	0
M1	Apr 29	Sediment	Total	0	10200	0	125	0.7	7300	0	27.5	33.5	23.5	25300	0

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3-1 (Continued)

Station	Date	Matrix	Form	K	Mg	Mn	Na	Ni	Pb	Se	Sb	Tl	V	Zn
US1	Apr 23	Water	Diss	3.4	29.2	0.04	24.25	0	0	0	0	0	0	0.037
US1	Apr 29	Water	Diss	3.35	33.05	0.05	22.65	0	0.06	0	0	0	0	0.02
US1	Jun 03	Water	Diss	5.9	35.85	0.093	27.7	0	0	0	0	0	0	0.026
US1	Apr 29	Water	Total	3.5	34.7	0.06	23.55	0	0	0	0	0	0	0
US1	Jun 03	Water	Total	6	37.45	0.101	28.55	0	0	0	0	0	0	0
US1	Apr 23	Sediment	Total	795	5360	680	126.5	21.5	13	65.5	0	0	17	47.5
US1	Apr 29	Sediment	Total	700	3850	745	145	21	15	0	0	0	16	45
US1	Jun 03	Sediment	Total	821.5	2755	915.5	146.5	22.5	15	15	0	0	20	46
DS1	Apr 23	Water	Diss	3.1	29.05	0.06	24.75	0	0	0	0	0	0	0.07
DS1	Apr 29	Water	Diss	3.2	31.7	0.05	21.75	0	0.065	0	0	0	0	0.012
DS1	Jun 03	Water	Diss	5.85	35.65	0.098	27.55	0	0	0	0	0	0	0
DS1	Apr 29	Water	Total	3.8	35.3	0.06	23.8	0	0	0	0	0	0	0
DS1	Jun 03	Water	Total	6.05	36.35	0.102	28	0	0	0	0	0	0	0
DS1	Apr 23	Sediment	Total	965	4550	553.5	135	24.5	12.5	69.5	0	0	19	71.5
DS1	Apr 29	Sediment	Total	1200	4850	1900	165	44.5	35.5	0	0	0	28	95.5
DS1	Jun 03	Sediment	Total	1257	5085	2220	167.5	40	19.5	8	0	0	35	71
DS1A	Jun 03	Water	Diss	5.1	38.35	0.105	40.35	0	0	0	0	0	0	0.009
DS1A	Jun 03	Water	Total	5.05	47.8	0.138	37.4	0	0	0	0	0	0	0
DS1A	Jun 03	Sediment	Total	2400	6575	362	378.5	24	11.5	0	0	0	31	180
DS2	Apr 23	Water	Diss	3.45	27.65	0.56	26.15	0.1	0	0	0	0	0	3
DS2	Apr 29	Water	Diss	3.4	31.1	0.135	23.3	0	0.035	0	0	0	0	0.012
DS2	Jun 03	Water	Diss	5.45	31.75	0.084	46.45	0	0	0	0	0	0	0
DS2	Apr 29	Water	Total	3.45	29.25	0.155	22.25	0	0	0	0	0	0	0.03
DS2	Jun 03	Water	Total	6.1	33.25	0.092	48.45	0	0	0	0	0	0	0
DS2	Apr 23	Sediment	Total	1305	5150	330	173	31	17	109	0	0	28	80
DS2	Apr 29	Sediment	Total	1400	5700	395	310	37	25	10	8.5	10	25	116.5
DS2	Jun 03	Sediment	Total	2310	6690	388.5	250.5	36	21	8.225	0	0	42.5	109.5

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3-1 (Continued)

Station	Date	Matrix	Form[1]	K	Mg	Mn	Na	Ni	Pb	Se	Sb	Tl	V	Zn
DS3	Apr 23	Water	Diss	4.1	25.85	0.315	30.95	0.065	0	0	0	0	0	2.01
DS3	Apr 29	Water	Diss	3.6	27.35	0.07	30	0	0.03	0	0	0	0	0
DS3	Jun 03	Water	Diss	6.4	36.9	0.151	54.65	0	0	0	0	0	0	0
DS3	Apr 29	Water	Total	4	25.45	0.095	28.65	0	0	0	0	0	0	0.025
DS3	Jun 03	Water	Total	5.8	30.8	0.132	47.1	0	0	0	0	0	0	0.01
DS3	Apr 29	Sediment	Total	955	8000	215	335	23	12.5	0	0	0	14.5	116
DS3	Jun 03	Sediment	Total	1300	11835	240	225	23	10	4	0	0	24	63.5
M1	Apr 29	Water	Diss	1.95	34.85	0.01	23.4	0	0.195	0	0	0	0	0.012
M1	Apr 29	Water	Total	2.3	36.05	0.11	23.8	0	0	0	0	0	0	0.1
M1	Apr 23	Sediment	Total	1145	5700	1860	164	40.5	24.5	99.5	0	0	31	102
M1	Apr 29	Sediment	Total	990	4800	1650	245	42	29.5	0	0	0	24.5	135

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

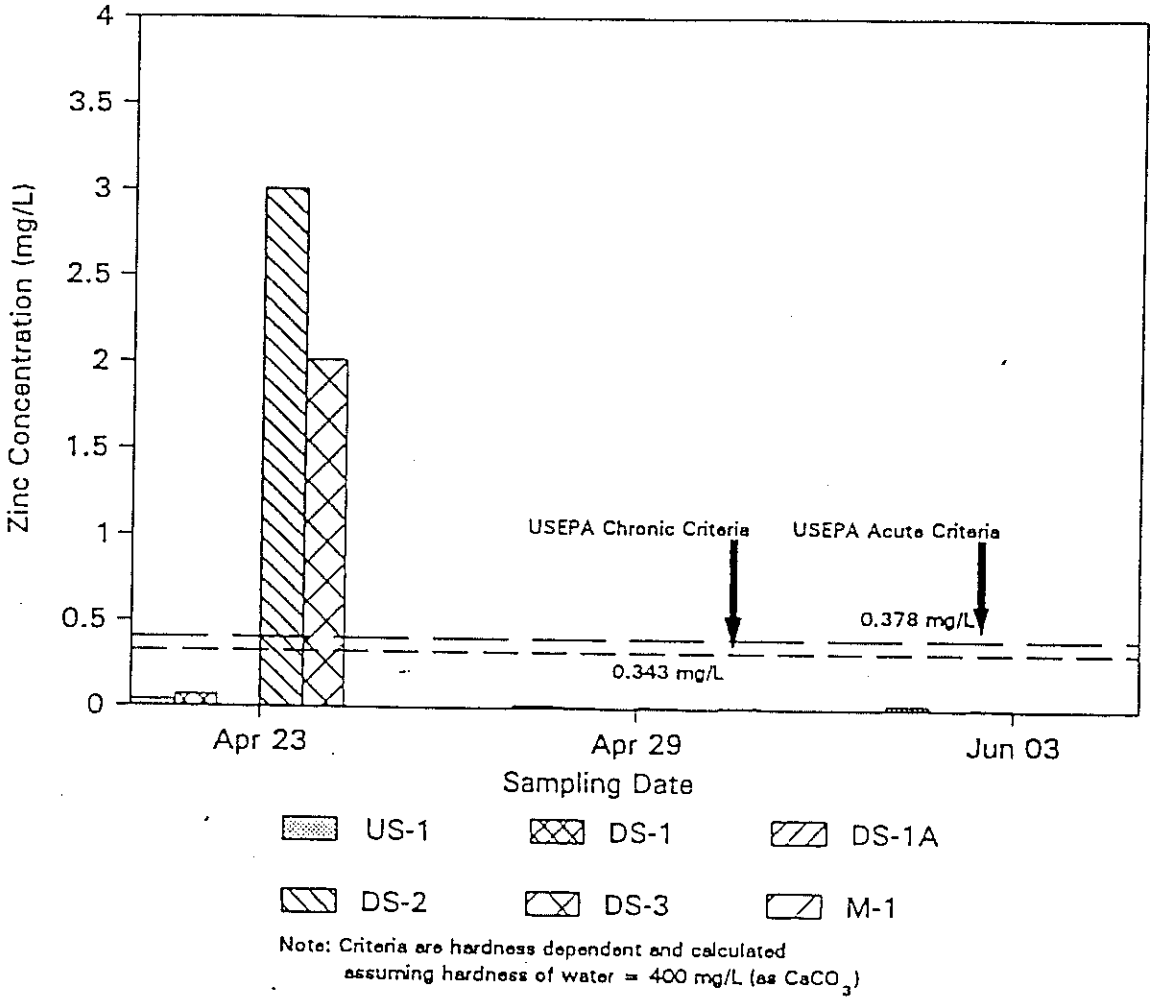


Figure 3-1. Mean concentration of dissolved zinc in water samples collected at six sites on three dates following the spill.

Samples collected during the second and third sampling rounds showed very low or undetectable levels of zinc.

Manganese. Like zinc, manganese concentrations in water samples collected on April 23 were much higher at DS-2 and DS-3 compared to concentrations at US-1 or DS-1 (Figure 3-2). Also, like zinc, the concentrations decreased dramatically during the second and third sampling rounds. Despite these elevated levels of manganese, the concentrations were still below the estimated criteria (acute = 2.5 mg/L; chronic = 2.1 mg/L). These criteria were calculated at ENSR using EPA methods.

Lead. Lead was the only metal measured that showed higher dissolved concentrations in samples collected during the second sampling period (April 29) (Figure 3-3). The level in the water samples collected at M-1 was in excess of 0.19 mg/L, which was well above the EPA chronic criterion of 0.0185 mg/L at a hardness of 400 mg/L. While lead concentrations at DS-1, DS-2, and DS-3 were also high, so was the dissolved lead concentration measured at US-1. Therefore, some of the lead may be coming from another source.

Aluminum. Aluminum was highest during the third sampling period (Figure 3-4), with the highest levels being found at DS-3. Concentrations at US-1 were measurable, although lower than at the other sites. Aluminum was undetectable during the first sampling period. No measured concentrations, however, were above the EPA acute and chronic criteria (for pH between 6.5 and 9.0) of 1.496 and 0.748 mg/L.

For other metals that were detected in the water column samples, concentrations were often higher in the third sampling period (e.g., iron, magnesium, sodium). This may be due to the low water conditions that resulted in a concentrating effect on ions. For most of the materials, concentrations at US-1, the upstream reference site, were neither consistently higher nor lower than at the downstream sites.

3.1.2 Sediment

Nearly all metals for which analysis was performed were detected in sediments (Table 3-1). Silver was not detected, and cadmium, antimony, and titanium were detected in only a few samples. Several metals were present at higher concentrations at the downstream sites than at the upstream reference site (US-1). Those include zinc (Figure 3-5), vanadium (Figure 3-6), and nickel (Figure 3-7). The concentration of lead at US-1 was slightly higher than at DS-1 in samples collected on April 23, but concentrations were higher at DS-2, and even higher at M-1

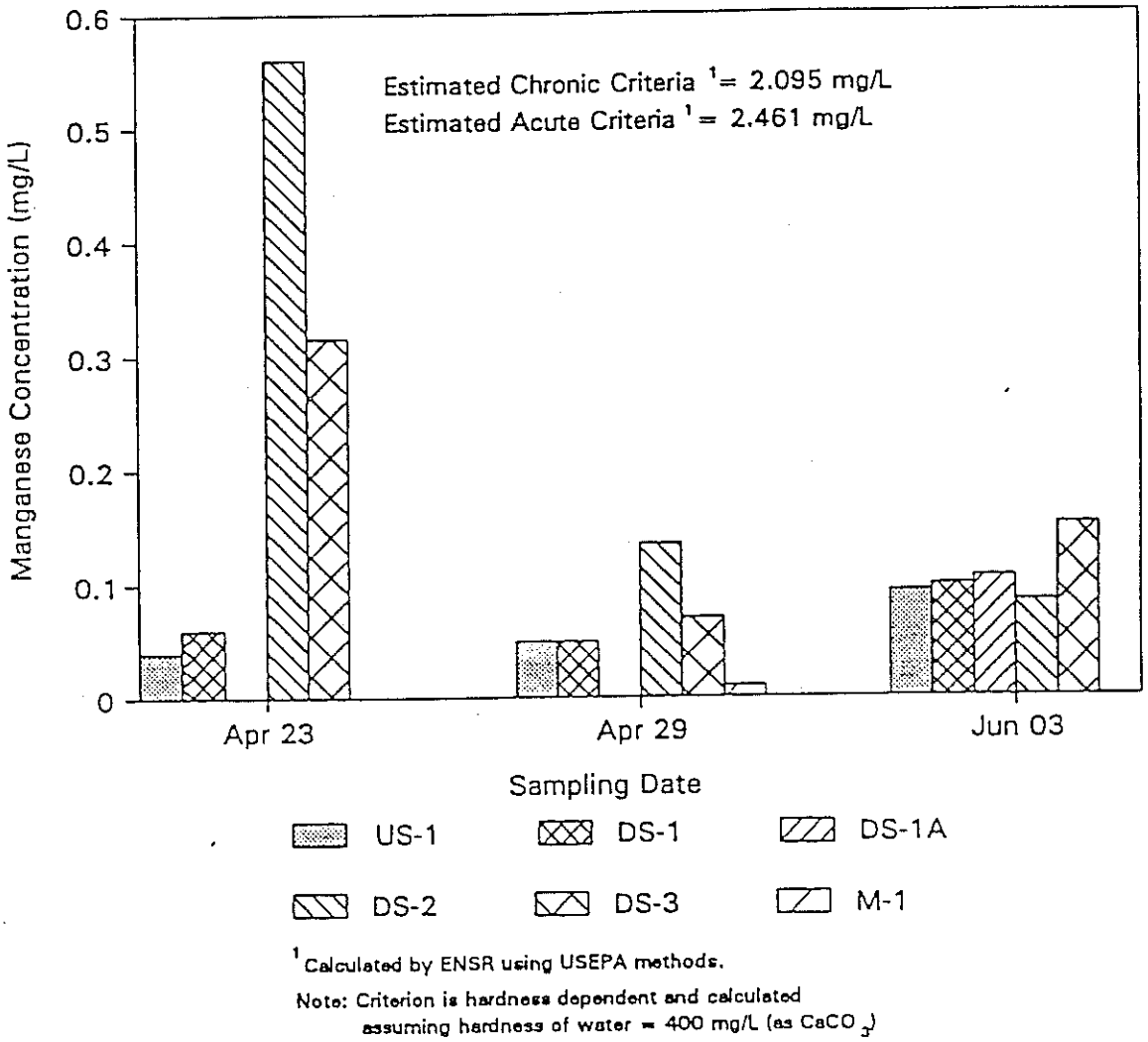
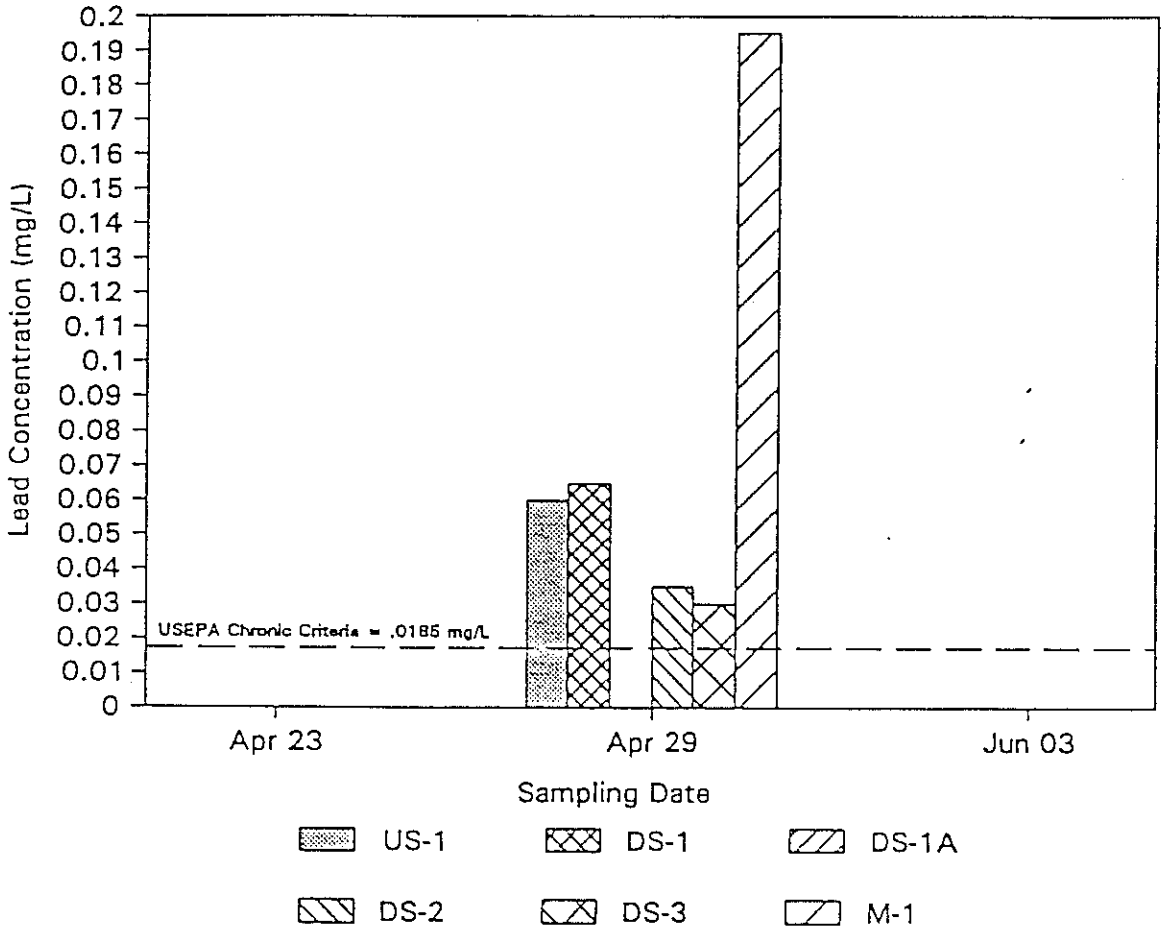


Figure 3-2. Mean concentration of dissolved manganese in water samples collected at six sites on three dates following the spill.



Note: Criterion is hardness dependent and calculated assuming hardness of water = 400 mg/L (as $CaCO_3$)

Figure 3-3. Mean concentration of dissolved lead in water samples collected at six sites on three dates following the spill.

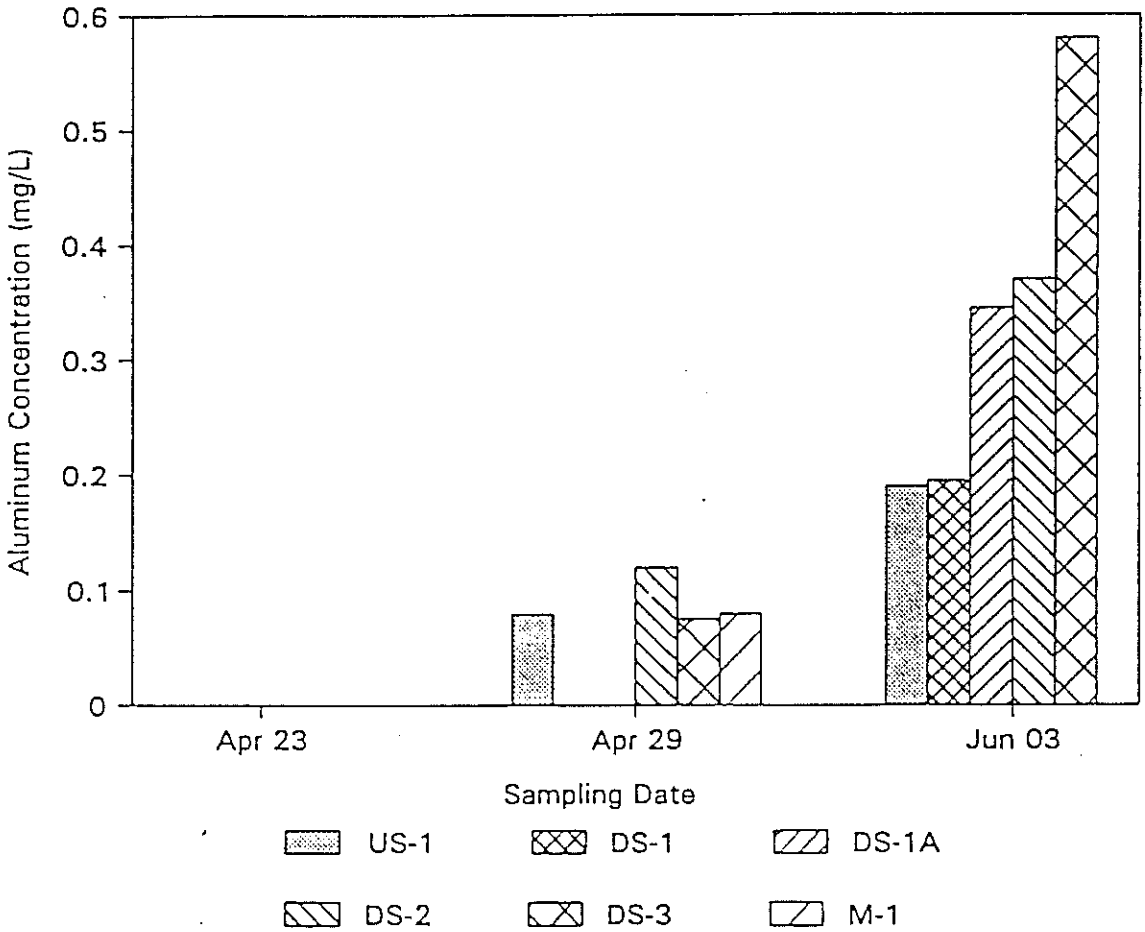


Figure 3-4. Mean concentration of dissolved aluminum in water samples collected at six sites on three dates following the spill.

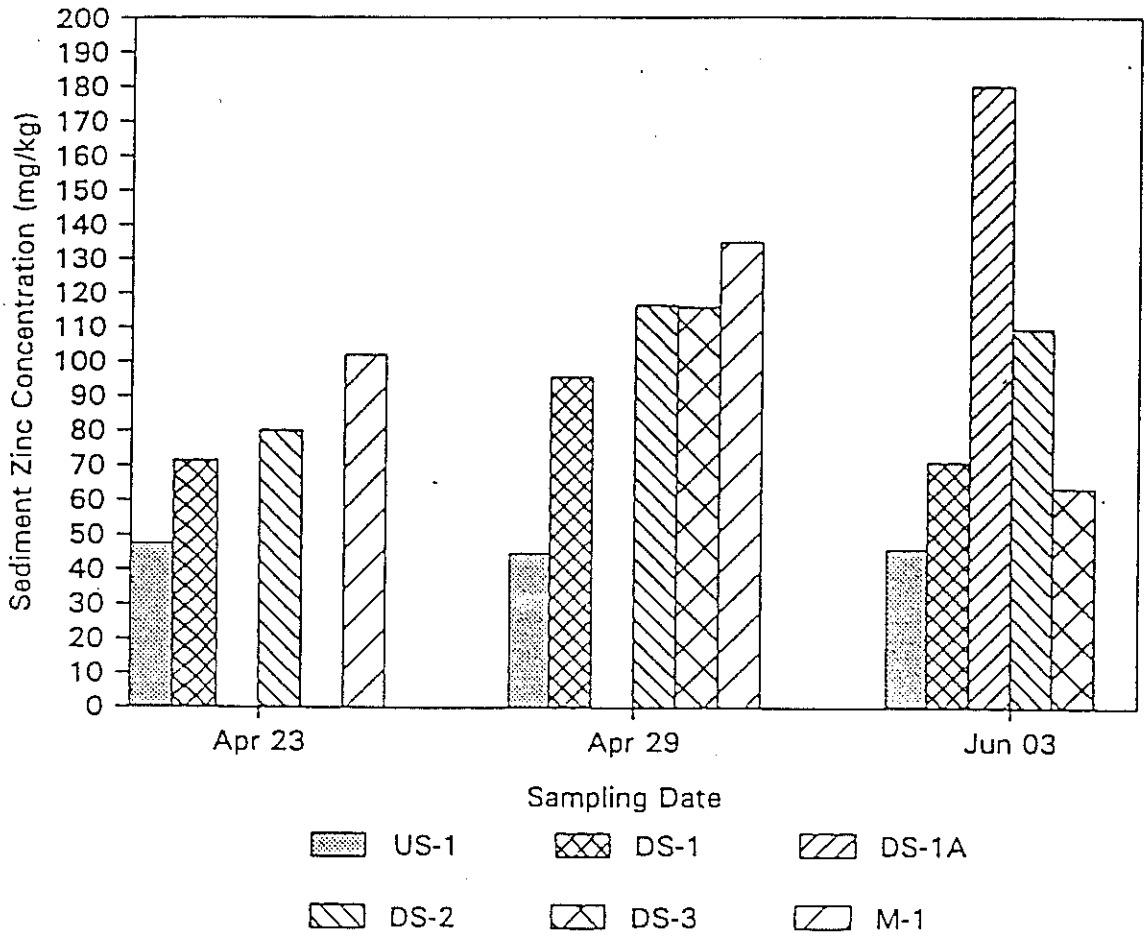


Figure 3-5. Mean concentration of zinc in sediment samples collected at six sites on three dates following the spill.

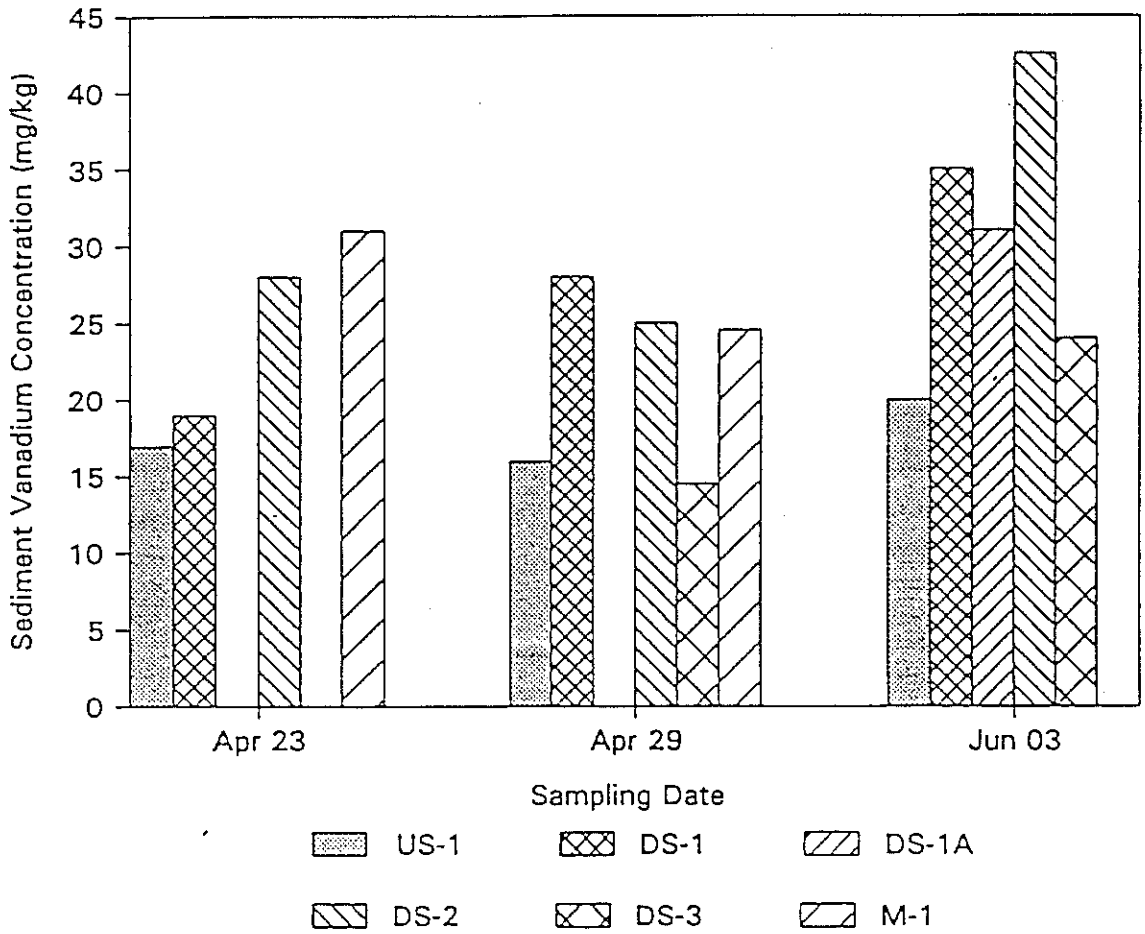


Figure 3-6. Mean concentration of vanadium in sediment samples collected at six sites on three dates following the spill.

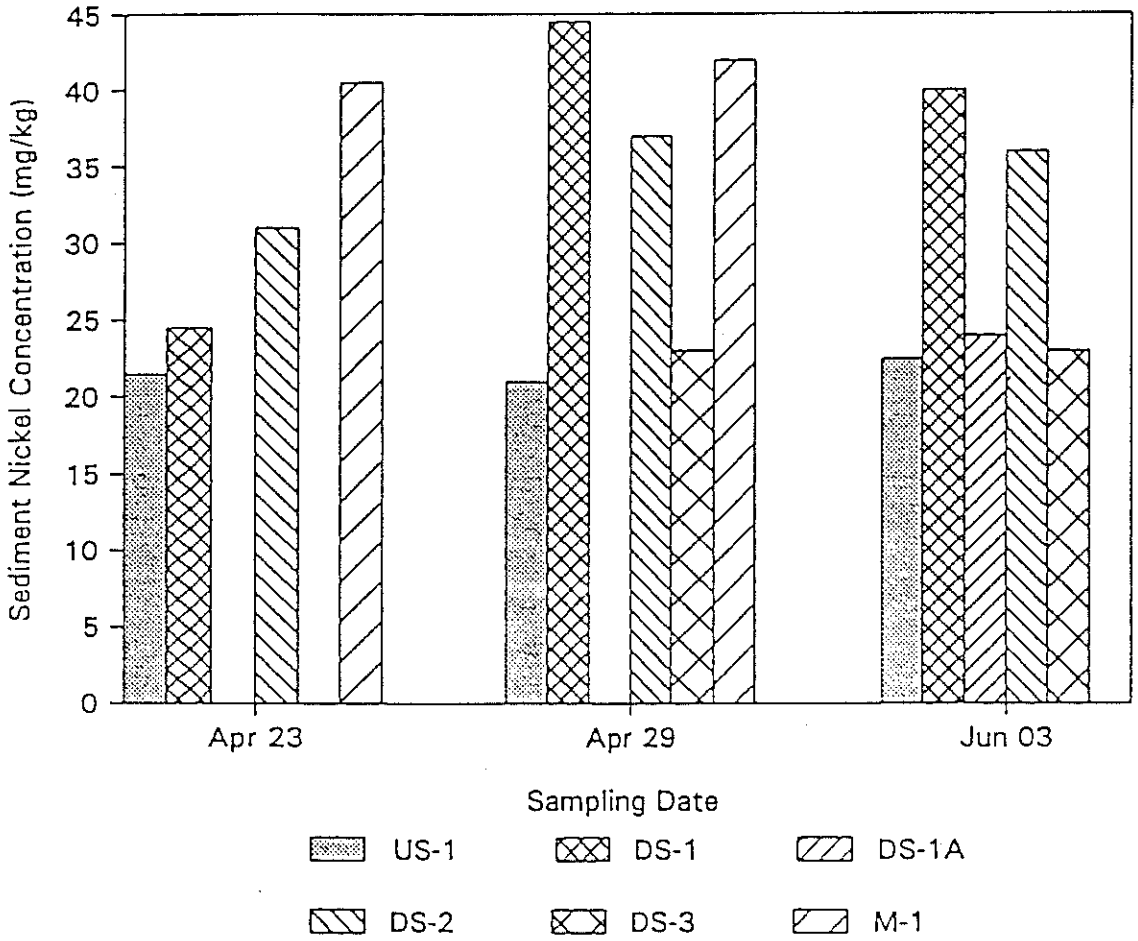


Figure 3-7. Mean concentration of nickel in sediment samples collected at six sites on three dates following the spill.

(Meyer's Ditch) (Figure 3-8). Concentrations of selenium in the sediment were notably higher at all sites during the first sampling period, and decreased dramatically in samples collected during the followup sampling (Figure 3-9). While concentrations at US-1 remained fairly constant throughout all three sampling periods, sediment concentrations at the downstream sites and Meyer's Ditch changed over the course of the study (see Figures 3-5 and 3-6). These changes could be due to resuspension, mixing, and resettling of sediments that can be caused by rainfall and an increase in flows and turbulence in streams. The higher concentration of zinc in the sediments corresponds to the higher levels of zinc in the water column (Figure 3-1). However, high levels of other metals in the sediment (such as selenium) suggest that these metals may also have been at toxic levels in the water, but were not detected due to relatively high method detection levels.

3.2 Biological

3.2.1 Fish Kill

Fish kill counts in Meyer's Ditch and Raccoon Creek indicated that few dead were observed after the acidic material leak. A ground reconnaissance conducted along the entire length of Meyer's Ditch revealed only one dead minnow. A shoreline boat survey in Raccoon Creek from its confluence with Little Raccoon Creek and Lake Erie resulted in 10 dead carp. Since dead carp also were observed by Brent Kuenzli from the Ohio Environmental Protection Agency (Ohio EPA) during a drive along Pickerel Creek, which was not affected by the leak, the dead carp in Raccoon Creek may have resulted from natural causes. If the acidic material had affected fish in Raccoon Creek, it is expected that considerably more fish would have been observed during the survey.

The estimated number of dead fish in Little Raccoon Creek is presented in Table 3-2. By extrapolating the counts in the seven 100-yard segments to the entire 3-mile section of Little Raccoon Creek, an estimated 555 dead fish were present in the study area. The most abundant species in the fish kill estimates included creek chub (*Semotilus atromaculatus*) (195), minnows (Family Cyprinidae) (188), and white sucker (*Catostomus commersoni*) (142). In addition, 30 dead green sunfish (*Lepomis cyanellus*) were present in Little Raccoon Creek. When examining the fish kill counts by individual segments (Figure 2-1; Appendix A, Table A-1), the majority of the dead fish were observed in segments 3, 4, and 5. None of the species observed in the fish kill counts are considered to be gamefish species by Ohio DNR.

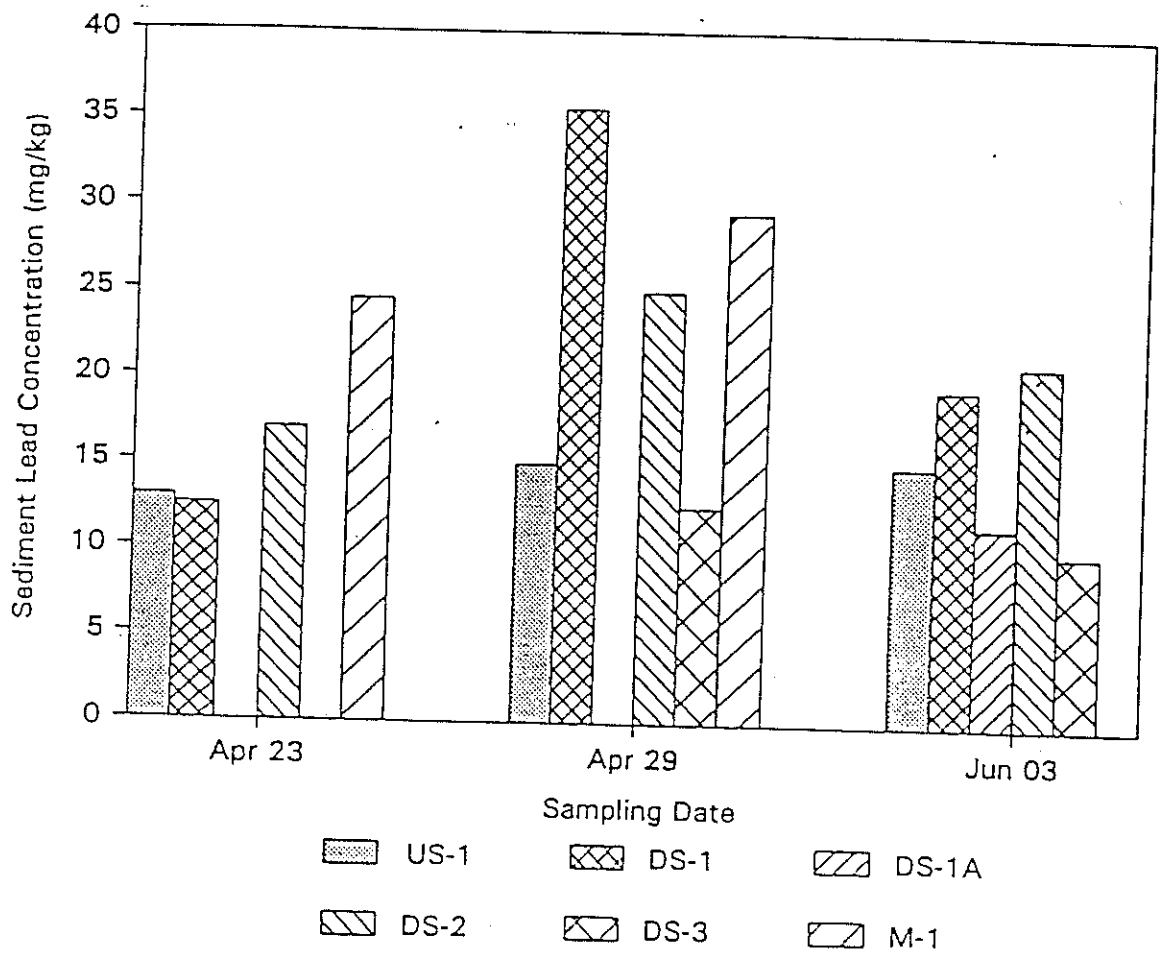


Figure 3-8. Mean concentration of lead in sediment samples collected at six sites on three dates following the spill.

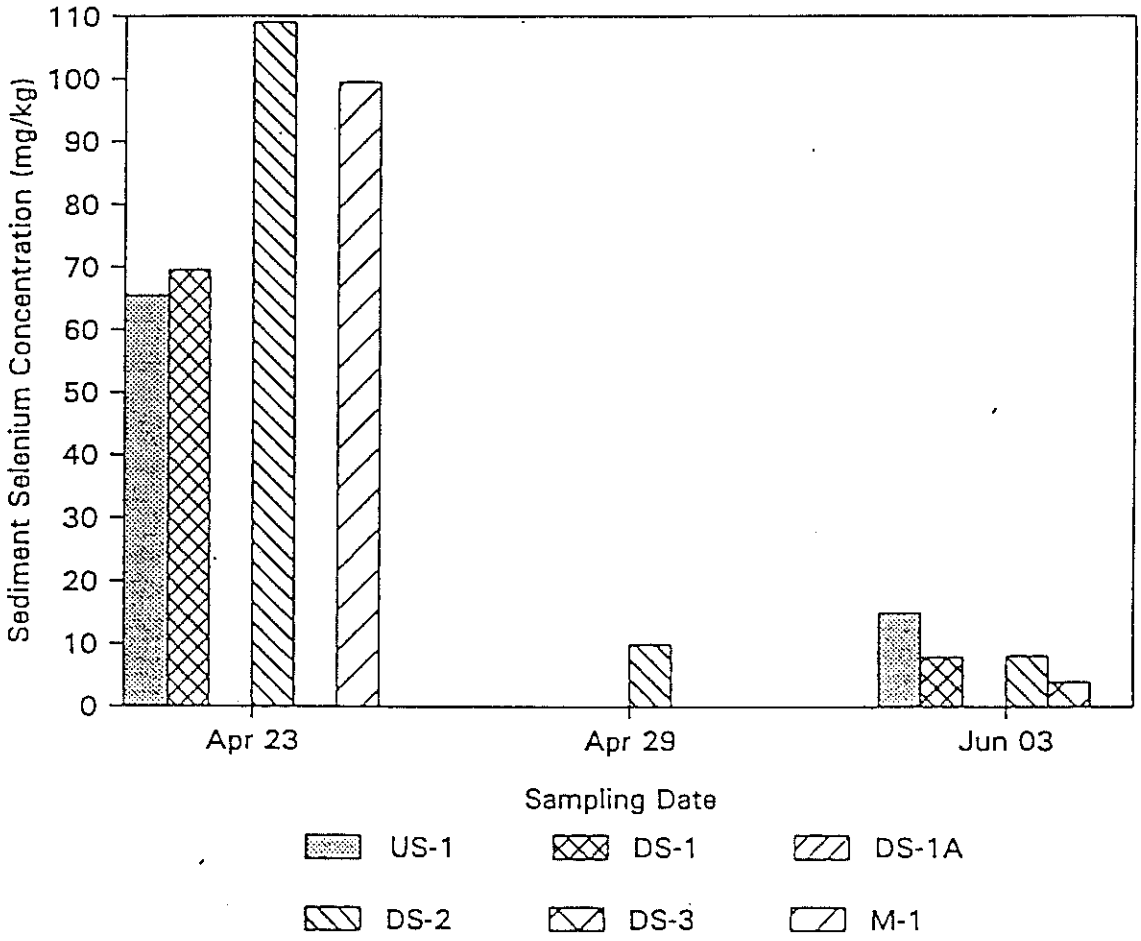


Figure 3-9. Mean concentration of selenium in sediment samples collected at six sites on three dates following the spill.

Table 3-2

Estimated Total Number of Fish
Killed in Little Raccoon Creek

Species	Size (Length) Category	Total Count[1]	Kill Estimate[2]
White Sucker	1 to 3 inches	2	2 x 7.5 = 15
	4 to 6 inches	5	5 x 7.5 = 37.5 = 37
	>12 inches	12	12 x 7.5 = 90
			142
Green Sunfish	2 inches	3	3 x 7.5 = 22.5 = 23
	3 inches	1	1 x 7.5 = 7.5 = 7
			30
Minnows	Not measured	25	25 x 7.5 = 188
Creek Chub	Not measured	26	26 x 7.5 = 195
Total Estimate		74	555

[1]Total number of dead fish observed in the seven 100-yard segments.

[2]Fish kill estimate was calculated using the following "estimate factor":

$$\textit{Estimate Factor } (E) = 1{,}760 \textit{ yards } x \frac{T}{L}$$

Where: T = Total Length of Stream Affected by Spill.
L = Total Length of Transects Examined.

$$E = 1{,}760 \textit{ yards } x \frac{3 \textit{ miles}}{700 \textit{ yards}}$$

Where: E = 7.5

3.2.2 Benthic Macroinvertebrates

Most of the organisms collected in Little Raccoon Creek were pollution-tolerant organisms, with tolerance quotients of 108 (USDA 1985) (Table 3-3). Two of the most abundant organisms, *Limnodrilus hoffmeisteri*, a tubificid worm, and *Chironomus* sp., a dipteran midge, are commonly found in soft sediments from both lotic (flowing water) and lentic (lakes and ponds) systems. Macroinvertebrate densities ranged from 1,347 organisms/m^2 at DS-2 to 4,730 organisms/m^2 at DS-1 (Figure 3-10). The mean density at the reference location (US-1) was 1,724 organisms/m^2. The total number of taxa ranged from 7 at DS-2 to 13 at DS-1A (Figure 3-11). The number of taxa does not include empty shells of fingernail clams (Sphaeriidae) and gastropods that were collected in the grab samples. Empty Unionid (large freshwater clams) were also observed along Little Raccoon Creek during the initial visit to the site, suggesting a clam population at some point in the past. There were no significant differences in either density or number of taxa among the sites.

Additional information regarding the macroinvertebrate community structure at the four locations was provided by Shannon Diversity and Evenness. Both Shannon Diversity and Evenness were highest at US-1 (Figures 3-12 and 3-13). These differences in the indices are primarily a result of changes in the composition of the benthic community at sites DS-1 and DS-1A, and the densities of specific taxa. At DS-1, for example, *Limnodrilus hoffmeisteri* and *Chironomus* sp. comprised over 85 percent of the total density. At US-1, on the other hand, *L. hoffmeisteri* comprised only 36 percent of the total density and *Chironomus* sp. was absent. Some species identified at US-1 were not identified at either DS-1 or DS-1A. Those include *Cricotopus bicinctus*, *C. tremulus*, and Ephydridae. Neither amphipods nor isopods were collected at DS-1. Statistical analysis ($\alpha = 0.05$) showed that Shannon Evenness was significantly lower at DS-1, when compared to US-1.

Based on computations of Invertebrate Community Indices according to Ohio EPA (1987), macroinvertebrate communities in Little Raccoon Creek are considered to be low quality. Total scores for the four locations ranged from 0 at DS-2 to 4 at US-1 (Table 3-4). The slightly higher score at the reference location was due to the presence of Tribe Tanytarsini midges. However, the slightly higher score at the reference site does not indicate a substantially higher quality community at this location compared to the downstream locations.

Table 3-3

Mean Benthic Macroinvertebrate Densities
Collected in Little Raccoon Creek Using a Petite Ponar Grab

Taxon	Station			
	US-1	DS-1	DS-1A	DS-2
Oligochaeta				
Naididae				
Nais sp.		96.98	32.33	64.65
Tubificidae				
Limnodrilus hoffmeisteri	614.18	3588.08	355.58	312.48
Terrestrial Earthworms			53.88	
Hirudinea				
Glossiphonidae			21.55	
Amphipoda				
Gammaridae				
Gammarus sp.	10.78		96.98	
Isopoda				
Asellidae				
Asellus sp.	21.55		21.55	150.85
Ephemeroptera				
Ephemeridae				
Hexagenia sp.			75.43	
Odonata				
Libellulidae				
Plathemis sp.			10.78	
Coleoptera				
Dytiscidae				
Deronectes sp.		10.78		
Diptera				
Ceratopogonidae	10.78	21.55	10.78	
Chironomidae				
Chironomus sp.		441.78	1282.23	635.73

Table 3-3 (Continued)

Taxon	Station			
	US-1	DS-1	DS-1A	DS-2
Cricotopus bicinctus group	237.05			43.10
Cricotopus tremulus group	129.30			43.10
Cryptochironomus sp.	247.83	118.53	43.10	96.98
Procladius sp.		323.25	64.65	
Rheotanytarsus sp.	258.60	75.43		
Ephydridae	43.10			
Gastropoda[2]				
Pelecypoda				
Sphaeriidae[2]				
Sphaerium sp.	150.85	53.88	43.10	
Total Mean Density:	1724.00	4730.23	2111.90	1346.88
Total Number of Taxa:	10	9	13	7
Shannon Diversity Index[3]:	1.82	0.95	1.45	1.49
Shannon Evenness Index[3]:	0.79	0.43	0.57	0.77

[1]Mean density calculated for four replicates/location.

[2] Some empty shells were found.

[3] Calculated using Natural Log.

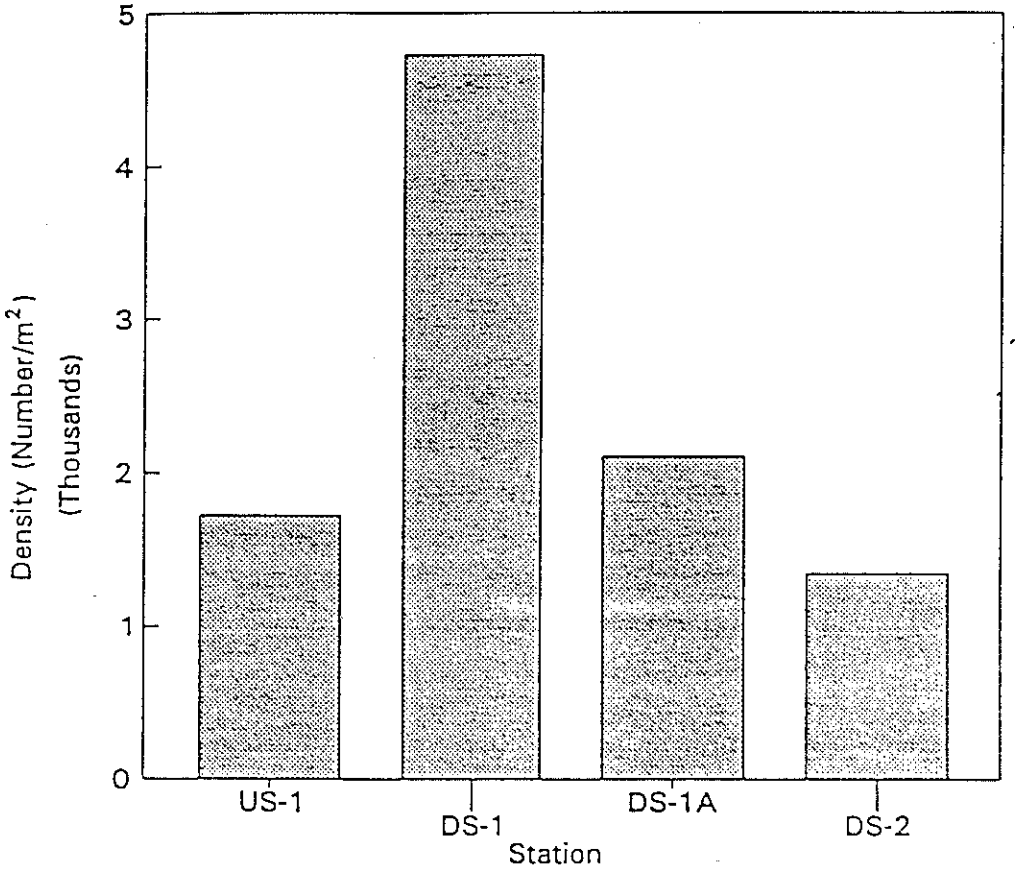


Figure 3-10. Mean density (Number/m^2) of benthic macroinvertebrates collected at each station in Little Raccoon Creek.

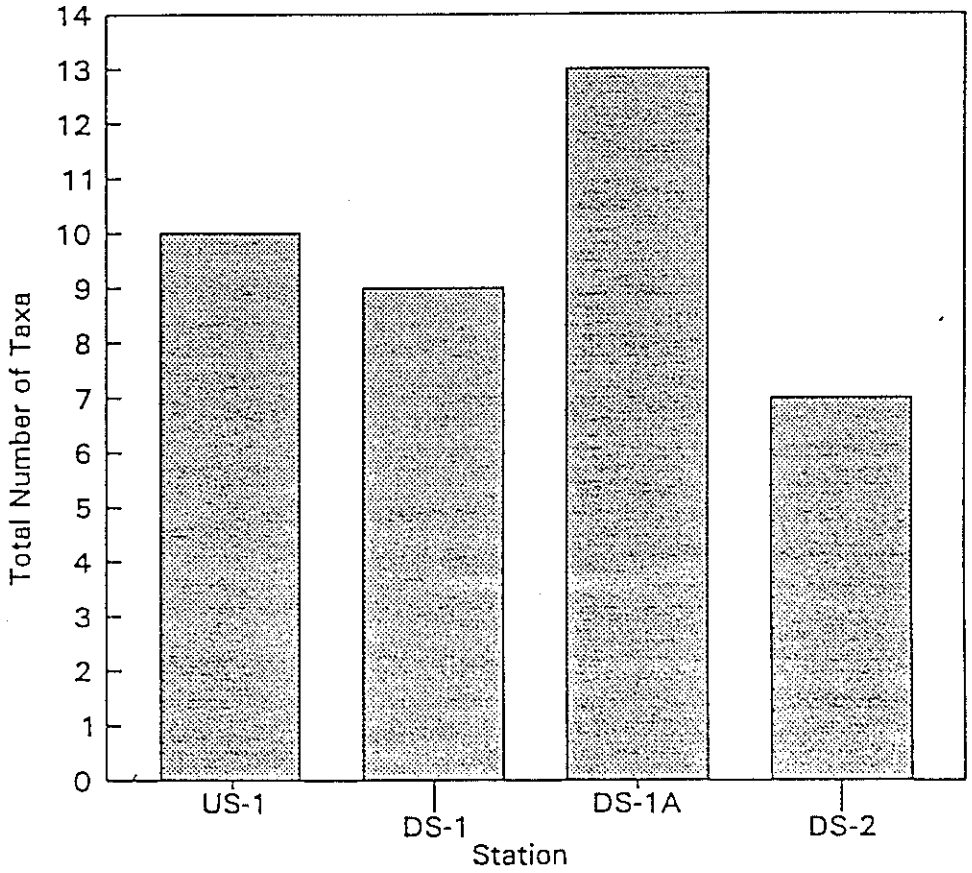


Figure 3-11. Total number of benthic macroinvertebrate taxa collected at each station in Little Raccoon Creek.

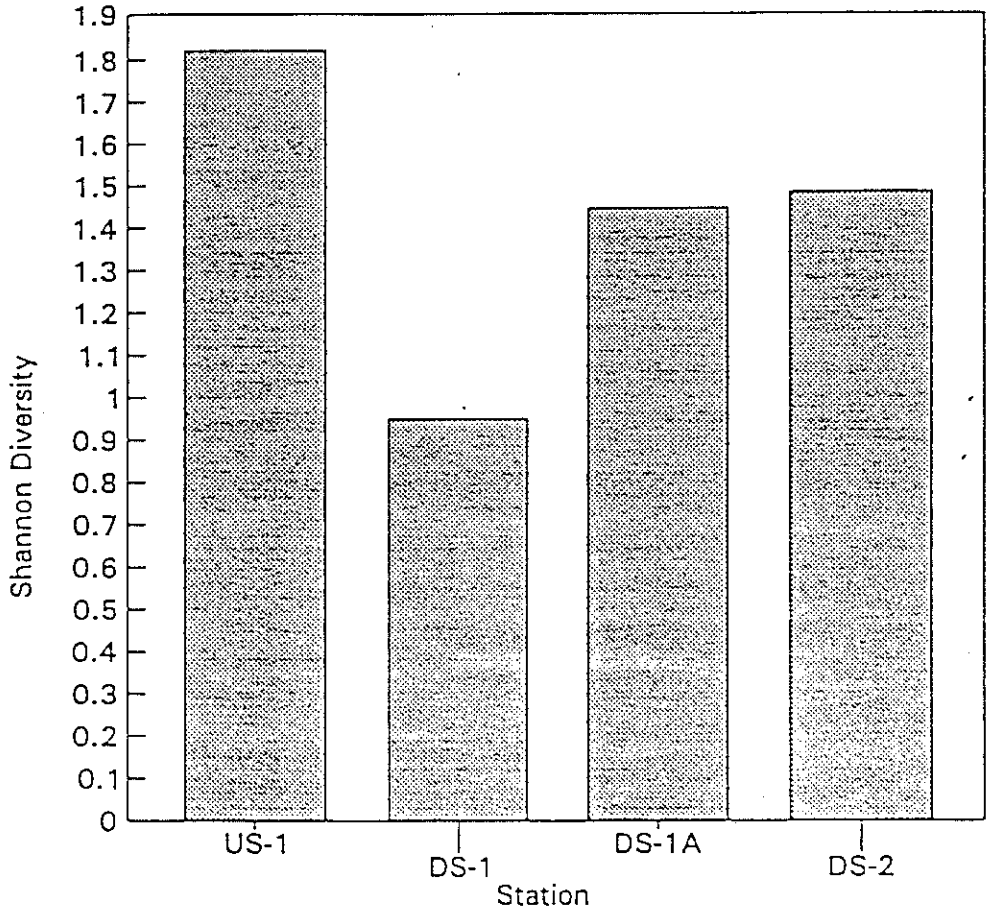


Figure 3-12. Shannon diversity of benthic macroinvertebrate populations collected at each station in Little Raccoon Creek.

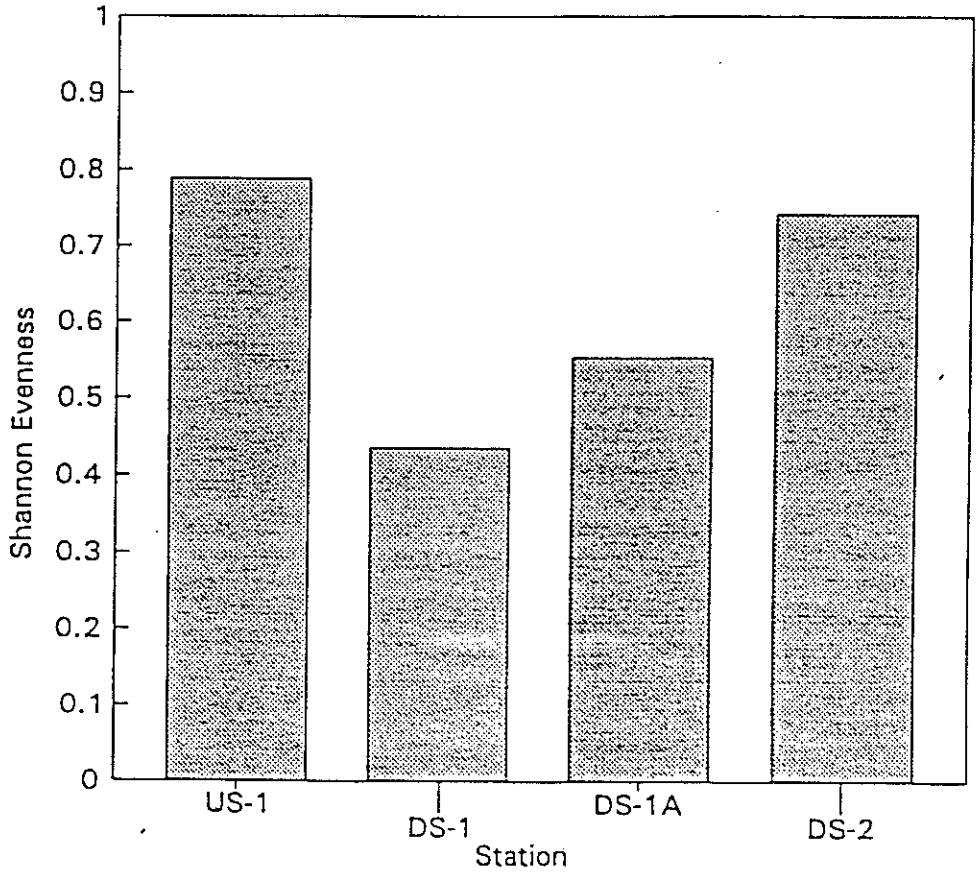


Figure 3-13. Shannon evenness of benthic macroinvertebrate populations collected at each station in Little Raccoon Creek.

Table 3-4

Invertebrate Community Indices for Sampling Locations in Little Raccoon Creek

Parameters	US-1		DS-1		DS-1A		DS-2	
	No.	Score	No.	Score	No.	Score	No.	Score
1. Total Number of Taxa	10	0	9	0	13	0	7	0
2. Total Number of Mayfly Taxa	0	0	0	0	1	0	0	0
3. Total Number of Caddisfly Taxa	0	0	0	0	0	0	0	0
4. Total Number of Dipteran Taxa	6	0	5	0	4	0	4	0
5. Percent Mayflies	0%	0	0%	0	0%	0	0%	0
6. Percent Caddisflies	0%	0	0%	0	0%	0	0%	0
7. Percent Tribe Tanytarsini Midges	15%	4	2%	2	0%	0	0%	0
8. Percent Other Dipterans and Non-Insects	85%	0	98%	0	100%	0	100%	0
9. Percent Tolerant Organisms	49%	0	87%	0	79%	0	75%	0
10. Total Number of Qualitative Ephemeroptera, Plecoptera, and Trichoptera (EPT) Taxa	0	0	0	0	1	0	0	0
Total Scores		4		2		2		0

3.2.3 Fish Populations

The relatively low water level in Little Raccoon Creek upstream of its confluence with Meyer's Ditch limited its use as a reference site for comparison with location DS-1. For this reason, the emphasis in this assessment was placed on the composition and abundance of fish populations at DS-1 and DS-1A, where dead fish had been observed during the fish kill counts.

Electrofishing surveys conducted in Little Raccoon Creek on June 2, 1993, resulted in a total of nine taxa from the four sampling locations (Table 3-5). The taxa belonged to four families, which included Cyprinidae (minnows and carp), Catostomidae (suckers), Cyprinidontidae (killifishes), and Centrarchidae (sunfishes). The majority of the taxa (five) belonged to Family Cyprinidae. In general, few taxa were collected at the sampling locations. Location DS-1A contained the highest number of taxa with seven, while four taxa were collected at locations DS-1 and DS-2. The reference site, US-1, contained only two fish taxa. Fish distribution in Little Raccoon Creek was different depending on the species. Green sunfish, fathead minnow, and white sucker were found throughout most of the stream, since they were collected at three or four of the locations. The following species were collected only at one location: goldfish and orangespotted sunfish at DS-2, and blackstripe topminnow at DS-1A.

Population estimates in Little Raccoon Creek showed that moderate to high numbers of fish were present. As shown in Table 3-6, the estimated number of fish per acre was 4,646 at DS-1 and 34,902 at DS-1A. The most abundant taxa at these two locations included minnows and green sunfish. Fish numbers at US-1 and DS-2 were considerably lower with estimates of 871 and 1,694 fish per acre, respectively.

Habitat characterization studies conducted at the fish sampling locations provided information concerning the quality of habitat for aquatic communities. In general, the upper 2.5 miles of Little Raccoon Creek contain a relatively small amount of instream cover for fish (i.e., < 5 percent cover for US-1 and 5 to 25 percent for DS-1, DS-1A, and DS-2). The cover is provided by instream debris and woody material, root wads, and overhanging vegetation. The lower 0.5 mile of Little Raccoon Creek contains instream cover that comprises about 25 to 50 percent of the stream bottom. Bottom substrate in Little Raccoon Creek consists of silt, sand, detritus, and clay. Since gravel and cobble substrate are lacking in this stream, substrate does not provide additional fish cover. The four sampling sites also contained relatively shallow pools and glides; riffles were generally absent. The only notable difference in habitat characteristics at DS-1A, where the highest fish numbers were collected, was that the pools and glides were deeper. Habitat characterization forms for studies conducted in Little Raccoon Creek are included in Appendix B.

Table 3-5

Fish Species Collected in Little Raccoon Creek
on June 2, 1993

Common Name	Scientific Name	Sampling Location			
		US-1	DS-1	DS-1A	DS-2
Minnows and Carp	Cyprinidae				
Goldfish	*Carassius auratus*				X
Brassy minnow	*Hybognathus hankinsoni*			X	
Common shiner	*Notropis cornutus*			X	
Fathead minnow	*Pimephales promelas*	X	X	X	
Creek chub	*Semotilus atromaculatus*		X	X	
Suckers	Catostomidae				
White sucker	*Catostomus commersoni*		X	X	X
Killifishes	Cyprinodontidae				
Blackstripe topminnow	*Fundulus notatus*			X	
Sunfishes	Centrarchidae				
Green sunfish	*Lepomis cyanellus*	X	X	X	X
Orange spotted sunfish	*Lepomis humilus*				X
Total Number of Taxa		2	4	7	4

Table 3-6

Fish Population Estimates for Sampling Locations in Little Raccoon Creek

Taxa	Number/Acre			
	US-1	DS-1	DS-1A	DS-2
Goldfish	0	0	0	605
Creek chub	0	0	2,505	0
Minnows	218	2,831	18,731	24
White sucker	0	290	2,178	48
Green sunfish	653	1,307	12,033	895
Orange spotted sunfish	0	0	0	48
Total[1]	871	4,646	34,902	1,694

[1]Total fish population was calculated from total fish collected in two passes using the Seber and LeCren (1967) method rather than the summation of population estimates for all taxa at a sampling location.

3.3 Toxicity Testing

3.3.1 Water Toxicity

All of the water samples collected from the downstream sites (DS-1, DS-2, and DS-3) on April 23 were acute and chronically toxic to *Ceriodaphnia dubia* (Table 3-7). After 48 hours, 100 percent mortality was observed in water collected from these sites. Water collected from US-1 demonstrated a slight chronic effect, with an NOEC of 25 percent stream water.

Less toxicity was observed in the fathead minnow tests. No toxicity was observed in water from US-1; no 48-hour acute toxicity was observed in the downstream samples. However, there was chronic toxicity in all downstream waters, with DS-1 showing the most toxicity to fathead minnows, and DS-3 showing the least.

Toxicity was greatly reduced in samples collected on May 13 (May 17 from DS-1) (Table 3-7). Water from DS-1 still demonstrated some chronic toxicity to *Ceriodaphnia dubia*, and DS-2 water had an NOEC of 12.5 percent for fathead minnows. However, all acute toxicity had disappeared. The control survival (in laboratory water) in the fathead minnow test conducted with DS-3 water collected on May 13 was actually below the 80 percent EPA guideline. However, because survival was similar in all concentrations, this test was accepted as accurate reflection of water toxicity.

3.3.2 Sediment Toxicity

Toxicity of sediment to the amphipod, *Hyalella azteca*, is presented as percent survival (Table 3-8). Survival in the reference sediment was 95 percent, and survival at the three tested sites (US-1, DS-1 and DS-2) was significantly lower than that of the reference sediment. However, when compared against sediment from US-1, survival of *Hyalella azteca* was not significantly lower at DS-1 and DS-2. Therefore, although sediments in Little Raccoon Creek may be toxic to the test organism, the test did not indicate that sediments downstream of Meyer's Ditch were any more toxic than sediments upstream of Meyer's Ditch.

Table 3-7

Toxicity of Stream Water Collected on Two Dates from Little Raccoon and Raccoon Creeks

Endpoint	Date[1]	Station			
		US-1	DS-1	DS-2	DS-3
		Ceriodaphnia dubia			
48-H LC_{50}[2]	April 23	>100[5]	<6.25	<6.25	<6.25
NOEC[3]	April 23	25	<6.25	<6.25	<6.25
IC_{25}[4]	April 23	>100	1.6	1.6	1.6
48-H LC_{50}	May 13	>100	>100	>100	>100
NOEC	May 13	100	6.25	100	100
IC_{25}	May 13	>100	10.2	>100	>100
		Pimephales promelas			
48-H LC_{50}	April 23	>100	>100	>100	>100
NOEC	April 23	100	25	50	100
IC_{25}	April 23	>100	31.7	39.4	94.0
48-H LC_{50}	May 13	>100	>100	>100	>100
NOEC	May 13	100	100	12.5	100
IC_{25}	May 13	>100	>100	100	>100

[1]The second sample from DS-1 was actually collected on May 17; samples from other sites were collected on May 13.

[2]The concentration at which 50 percent of the test organisms die.

[3]No Observed Effects Concentration.

[4]Impact Concentration at which there is a 25 percent reduction in organism performance.

[5]Values are presented as percent stream water; the lower the value, the more toxic the water.

Table 3-8

Toxicity of Stream Sediment to *Hyalella azteca* Collected from Little Raccoon Creek

Sediment/Station	Percent Survival	Significantly Different from Reference Sediment?	Significantly Different from Upstream Control (US-1)?
Reference Sediment	95	NA	NA
US-1 (Control)	63	Yes	NA
DS-1	48	Yes	No
DS-2	65	Yes	No

4.0 DISCUSSION

Analytical chemistry results indicate that several metals were present in the sediments downstream of Meyer's Ditch at concentrations greater than what was seen at US-1, upstream of the confluence. For many of these metals, there were corresponding elevated levels in the water column, primarily in the dissolved, and therefore, bioavailable form. Since concentrations of some elements (e.g., selenium) were also apparently high at US-1, it is possible that some metals were present in stream sediments prior to the leak. However, the higher levels at the downstream sites in samples collected during the first sampling period indicate that some metals, at least, entered Little Raccoon Creek through Meyer's Ditch, probably during the leak. As the pH in Little Raccoon Creek increased following the initial release, metals in the water column precipitated onto sediments (as evidenced by the orange/red precipitate found throughout Little Raccoon Creek). The concentrations measured in the sediments from later sampling periods, while still often high, were different from initial concentrations due, most likely, to one or more storm events which sent large volumes of turbulent water down the creek, thus remixing the existing sediments.

Invertebrates, such as *Ceriodaphnia dubia*, are more sensitive to metals than are most vertebrates, such as the fathead minnow. Although this is also true of other toxicants, the presence of some dissolved metals (such as zinc) at toxic levels strongly suggests that it is, in fact, metal toxicity that affected the test organisms. High concentrations of metals in the sediment suggest that toxic concentrations of other metals, even though they were not detected with the analytical methods used, may have been present in the water column at the time the initial toxicity sample was collected.

Following the rainstorm, and subsequent increases in flow, soon after the leak, concentrations of most metals in the water decreased, as did toxicity. Some metals, such as lead, were higher in the second set of analytical samples; some metals may have become resuspended after the rainstorm. However, it is also possible that lead, perhaps along with other materials, entered Little Raccoon Creek as nonpoint source runoff during the rainstorm. The presence of other materials, possibly nonmetals, may account for the few occurrences of chronic toxicity in the second set of toxicity samples, although those were collected 2 weeks later.

There is no definitive evidence that benthic macroinvertebrate populations were adversely impacted by the leak. Density actually increased downstream of Meyer's Ditch and the number of taxa did not decrease significantly. However, the decrease in Shannon Diversity and

Evenness (which was significant) implies that population structure may have been affected. The extreme toxicity of the water soon after the leak could have had some effects on the benthic community, and probably did affect, in some way, any zooplankton community that may have been supported by Little Raccoon and Raccoon Creeks. However, without having quantitative information on benthic populations prior to the leak, it is not possible to conclude that any differences in macroinvertebrate community structure are due to the acidic material leak. The absence of significant upstream/downstream differences in sediment toxicity indicate that conditions approximately 1 month following the spill were not hazardous to sediment-dwelling organisms.

Regardless of the possible impacts of the spill, the benthic macroinvertebrate communities of Little Raccoon Creek, both upstream and downstream of Meyer's Ditch, are typical of impacted streams. The taxa were pollution-tolerant, and many of the species are very common in polluted systems. The presence of weathered Unionid clam shells implies that the stream may have once supported a much healthier benthic community. However, any degradation occurred long before the April 1993 leak of acidic material.

Observations made after the acidic material leak into the Raccoon Creek drainage indicated that fish were killed in the 3-mile section of Little Raccoon Creek between its confluences with Meyer's Ditch and Raccoon Creek. The fish kill counts in Little Raccoon Creek estimated that approximately 555 fish were killed by the leak. The majority of the fish observed in the fish kill counts were creek chub, minnows, and white sucker. Although some fish were killed due to the material leak, population studies conducted in Little Raccoon Creek indicated that moderate to high numbers of fish were still present in the stream. The only notable change in the post-leak fish population study was that large-sized white suckers were not present. Large white sucker will likely return to Little Raccoon Creek during high water periods prior to spawning in the next several years. Typically, this species moves into small tributary streams to spawn and then returns to larger streams later in the year.

5.0 CONCLUSIONS

5.1 Chemistry

The following conclusions were made regarding the effects of the acidic material leak on water and sediment chemistry:

- Certain metals, in toxic amounts, were released into Little Raccoon Creek as a result of the acidic material leak. Zinc, and possibly selenium, manganese, and other metals were present in a bioavailable form in the water column;

- Sediments contained high levels of several metals; concentrations were generally higher downstream of the confluence with Meyer's Ditch; and

- Dissolved concentrations of previously toxic materials decreased in the second and third sampling periods. Concentrations of some materials increased, particularly during the third sampling period. This may be due to the concentration of ions during low-water conditions.

5.2 Toxicity

The following conclusions were made regarding the toxicity of the stream water and sediment on test organisms:

- Water collected at downstream stations on April 23 was very toxic to *Ceriodaphnia dubia*, and somewhat toxic to fathead minnows. Water collected in Little Raccoon Creek upstream of the confluence with Meyer's Ditch was generally not toxic to these organisms;

- Water collected on May 13 and May 17 (for DS-1 only) was generally not toxic; and

- There was no significant difference in survival of *Hyalella azteca* in sediments from US-1, DS-1, and DS-2.

5.3 Benthic Macroinvertebrates

Based on macroinvertebrate sampling in Little Raccoon Creek, there was no evidence of significant damage on macroinvertebrate communities that could be attributed to the acidic material leak. The following information summarizes the results used in making this conclusion:

- Macroinvertebrate density was highest immediately downstream of Meyer's Ditch;
- The number of taxa and taxonomic composition were similar at the four sampling locations. The number of taxa collected at the reference location was 10, while 7 to 13 taxa were present at the downstream locations;
- Shannon and Evenness Diversity was higher at the reference location. Evenness was significantly lower at DS-1. However, it cannot be determined if this decrease is related to the leak; and
- Invertebrate Community Indices calculated for the four locations indicated that the macroinvertebrate community was considered to be low quality at all locations. Most organisms found at all sites were pollution-tolerant and typical of impacted streams.

5.4 Fish

The conclusion of the fish studies was that no significant damage occurred in the fish populations in the Little Raccoon drainage. The basis for making this conclusion is provided below:

- Based on the fish population studies in Little Raccoon Creek, the fish kill estimate comprised a relatively small portion of the overall population numbers.
- As a result of the relatively high reproductive rates for fish populations in Little Raccoon Creek, fish numbers should return to pre-leak conditions within 1 or 2 years; and
- Large white sucker were removed from Little Raccoon Creek due to this leak. However, spawning movements and development of young suckers in the stream are expected to replenish the large fish.

6.0 REFERENCES

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APPENDIX A

FISH KILL COUNTS IN LITTLE RACCOON CREEK

Table A-1

Fish Kill Counts in Little Raccoon Creek

Species	Segments[1]							Total
	1	2	3	4	5	6	7	
White sucker	0	1	3	5	8	2	0	19
Green sunfish	0	0	3	0	1	0	0	4
Minnows	0	0	4	7	13	1	0	25
Creek chub	0	0	4	4	15	1	2	26
	0	1	14	16	37	4	2	74

[1]Each segment was approximately 100 yards in length; see Figure 2-1 for segment locations.

APPENDIX B

HABITAT CHARACTERIZATION FORMS

0900 – 0930 hr.

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: [ ]

Stream: Little Raccoon Creek RM: ____ Date: 6/7/93 River Code: ____

Location: US-1 (100 ft above Myers Pitch) Crew: Leggett, Patti

1) SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present):

SUBSTRATE SCORE: [ ]

TYPE	POOL	RIFFLE	
	POOL RIFFLE ✓	silt	
☐ ☐-BLDER /SLABS[10]			☐ ☐-GRAVEL [7]
☐ ☐-BOULDER [9]			☑ ☐-SAND [6] 40 60
☐ ☐-COBBLE [8]			☐ ☐-BEDROCK[5]
☐ ☐-HARDPAN [4]			☐ ☐-DETRITUS[3] 40
☐ ☐-MUCK [2]			☐ ☐-ARTIFIC.[0]

SUBSTRATE QUALITY — Substrate Origin (Check all): ☐-LIMESTONE [1] ☐-RIP/RAP [0] ☐-TILLS [1] ☐-HARDPAN [0] ☐-SANDSTONE [0] ☐-SHALE [-1] ☐-COAL FINES [-2]

Silt Cover (Check One): ☐-SILT HEAVY [-2] ☑-SILT MODERATE [-1] ☐-SILT NORMAL [0] ☐-SILT FREE [1]

? Extent Of Embeddedness (Check One): ☐—EXTENSIVE [-2] ☐—MODERATE[-1] ☑—LOW[0] ☐—NONE[1]

TOTAL NUMBER OF SUBSTRATE TYPES: ☐> 4 [2] ☑ <= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

COMMENTS: silt covers sand. (about 2-3" silt)

COVER SCORE: [ ]

2) INSTREAM COVER

TYPE (Check All That Apply)

- ☐-UNDERCUT BANKS [1]
- no → ☒-OVERHANGING VEGETATION [1]
- ☐-SHALLOWS (IN SLOW WATER) [1]
- ☐-DEEP POOLS [2]
- ☐-ROOTWADS [1]
- ☐-BOULDERS [1]
- ☐-OXBOWS [1]
- ☐-AQUATIC MACROPHYTES [1]
- ☑-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)

- ☐ - EXTENSIVE > 75% [11]
- ☐ - MODERATE 25-75% [7]
- ☑ - SPARSE 5-25% [3] ← no
- ☒ - NEARLY ABSENT < 5% [1]

COMMENTS: Vegetation cover provided during higher flows; water level was low during survey.

CHANNEL: [ ]

3) CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY	DEVELOPMENT	CHANNELIZATION	STABILITY	MODIFICATIONS/OTHER	
☐ - HIGH [4]	☐ - EXCELLENT [7]	☒ - NONE [6]	☐ - HIGH [3]	☐ - SNAGGING	☐ - IMPOUND.
☒ - MODERATE [3]	☐ - GOOD [5]	☐ - RECOVERED [4]	☒ - MODERATE [2]	☐ - RELOCATION	☐ - ISLANDS
☐ - LOW [2]	☐ - FAIR [3]	☐ - RECOVERING [3]	☐ - LOW [1]	☐ - CANOPY REMOVAL	☐ - LEVEED
☐ - NONE [1]	☒ - POOR [1]	☐ - RECENT OR NO RECOVERY [1]		☐ - DREDGING	☐ - BANK SHAPING
				☐ - ONE SIDE CHANNEL MODIFICATIONS	

COMMENTS: shallow pools & short in length

RIPARIAN: [ ]

4) RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

"River Right Looking Downstream"

RIPARIAN WIDTH (L R Per Bank)	EROSION/RUNOFF - FLOOD PLAIN QUALITY (L R Most Predominant Per Bank)	(L R Per Bank)	BANK EROSION
☒ ☒-WIDE>50m [4]	☒ ☒-FOREST, SWAMP [3]	☐ ☐-URBAN OR INDUSTRIAL[0]	☒ ☒-NONE OR LITTLE [3]
☐ ☐-MODERATE 10-50 [3]	☐ ☐-OPEN PASTURE/ ROWCROP[0]	☐ ☐-SHRUB OR OLD FIELD[2]	☐ ☐-MODERATE [2]
☐ ☐-NARROW 5-10m [2]	☐ ☐- RESID.,PARK,NEW FIELD [1]	☐ ☐-CONSERV. TILLAGE [1]	☐ ☐-HEAVY OR SEVERE[1]
☐ ☐-VERY NARROW 1-5m [1]	☐ ☐-FENCED PASTURE [1]	☐ ☐-MINING/CONSTRUCTION [0]	
☐ ☐-NONE[0]		None	

COMMENTS: minimal erosion along banks.

POOL: [ ]

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX DEPTH (Check 1)	MORPHOLOGY (Check 1)	POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)	
☐- >1m [6]	☐-POOL WIDTH > RIFFLE WIDTH [2]	☐-TORRENTIAL[-1]	☐-EDDIES[1]
☐- 0.7-1m [4]	☒-POOL WIDTH = RIFFLE WIDTH [1]	☐-FAST[1]	☐-INTERSTITIAL[-1]
☐- 0.4-0.7m [2]	☐-POOL WIDTH < RIFFLE W. [0]	☐-MODERATE [1]	☐-INTERMITTENT[-2]
☐- < 0.4m [1]		☒-SLOW [1]	
☒—<0.2m [Pool = 0]			

☐-NO POOL[0]

COMMENTS: Few riffles

RIFFLE: [ ]

RIFFLE/RUN DEPTH	RIFFLE/RUN SUBSTRATE	RIFFLE/RUN EMBEDDEDNESS
☐ - GENERALLY >10 cm,MAX>50 [4]	☐-STABLE (e.g.,Cobble, Boulder) [2]	☐-EXTENSIVE [-1] ☐-MODERATE[0]
☐ - GENERALLY >10 cm,MAX<50 [3]	☐-MOD. STABLE (e.g.,Pea Gravel) [1]	☒-LOW. [1] ☐-NONE[2]
☐ - GENERALLY 5-10 cm [1]	☒-UNSTABLE (Gravel,Sand) [0]	
☒ - GENERALLY < 5 cm (Riffle = 0)		

☐-NO RIFFLE[0]

COMMENTS

GRADIENT: [ ]

6) Gradient (feet/mile): ____ %POOL: 80 %RIFFLE: 10 %RUN: 10

0930 – 1000 hr

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: [ ]

RM _____ Date 6/3/93 River Code _____

Stream Little Raccoon Creek

Location DS-1 (about 100 ft downstream of Myers Ditch) Crew: Pettit, Paggett

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present):

SUBSTRATE SCORE: [ ]

TYPE	POOL	RIFFLE	Substrate Origin (Check all)
	POOL RIFFLE ✓ silt	POOL RIFFLE	
O-BLDER /SLABS[10]		O-GRAVEL [7]	
O-BOULDER [9]		X-SAND [6]	70 60 O-LIMESTONE [1] O-RIP/RAP [0]
O-COBBLE [8]		O-BEDROCK[5]	O-TILLS [1] O-HARDPAN [0]
O-HARDPAN [4]		O-DETRITUS[3]	O-SANDSTONE [0]
O-MUCK [2]		O-ARTIFIC.[0]	O-SHALE [-1]
			O-COAL FINES [-2]

TOTAL NUMBER OF SUBSTRATE TYPES: O> 4 [2] O— <= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

Silt Cover (Check One)
X-SILT HEAVY [-2] O-SILT MODERATE [-1]
O - SILT NORMAL [0] O - SILT FREE [1]

Extent Of Embeddedness (Check One)
O—EXTENSIVE [-2] O—MODERATE[-1]
X—LOW[0] O—NONE[1]

COMMENTS Few riffles present

COVER SCORE: [ ]

2] INSTREAM COVER

TYPE (Check All That Apply)
O -UNDERCUT BANKS [1]
O -OVERHANGING VEGETATION [1]
O -SHALLOWS (IN SLOW WATER) [1]
O -DEEP POOLS [2]
X -ROOTWADS [1]
O -BOULDERS [1]
O -OXBOWS [1]
O -AQUATIC MACROPHYTES [1]
X -LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)
O - EXTENSIVE > 75% [11]
O - MODERATE 25-75% [7]
X - SPARSE 5-25% [3]
O - NEARLY ABSENT < 5% [1]

COMMENTS: Low water level limits cover provided by rootwads.

CHANNEL: [ ]

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY	DEVELOPMENT	CHANNELIZATION	STABILITY	MODIFICATIONS/OTHER	
O - HIGH [4]	O - EXCELLENT [7]	X - NONE [6]	O - HIGH [3]	O - SNAGGING	O - IMPOUND.
O - MODERATE [3]	O - GOOD [5]	O - RECOVERED [4]	X - MODERATE [2]	O - RELOCATION	O - ISLANDS
X - LOW [2]	O - FAIR [3]	O - RECOVERING [3]	O - LOW [1]	O - CANOPY REMOVAL	O - LEVEED
O - NONE [1]	X - POOR [1]	O - RECENT OR NO RECOVERY [1]		O - DREDGING	O - BANK SHAPING
				O - ONE SIDE CHANNEL MODIFICATIONS	

COMMENTS: Few riffles

RIPARIAN: [ ]

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

"River Right Looking Downstream"

RIPARIAN WIDTH
L R (Per Bank)
O X'-WIDE>50m [4]
O O'-MODERATE 10-50 [3]
X O'-NARROW 5-10m [2]
O O'-VERY NARROW 1-5m [1]
O O'-NONE[0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY
L R (Most Predominant Per Bank)
O X-FOREST, SWAMP [3]
X O-OPEN PASTURE/ ROWCROP[0]
O O- RESID.,PARK,NEW FIELD [1]
O O-FENCED PASTURE [1]
L R (Per Bank)
O O-URBAN OR INDUSTRIAL[0]
O O-SHRUB OR OLD FIELD[2]
O O-CONSERV. TILLAGE [1]
O O-MINING/CONSTRUCTION [0]
None

BANK EROSION
X X-NONE OR LITTLE [3]
O O-MODERATE [2]
O O-HEAVY OR SEVERE[1]

COMMENTS: Bank erosion low.

POOL: [ ]

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX DEPTH (Check 1)
O- >1m [6]
O- 0.7-1m [4]
O- 0.4-0.7m [2]
X < 0.4m [1]
O—<0.2m [Pool = 0]

MORPHOLOGY (Check 1)
O'-POOL WIDTH > RIFFLE WIDTH [2]
X-POOL WIDTH = RIFFLE WIDTH [1]
O'-POOL WIDTH < RIFFLE W. [0]

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)
O'-TORRENTIAL[-1]
O'-FAST[1]
O'-MODERATE [1]
X'-SLOW [1]
O'-EDDIES[1]
O'-INTERSTITIAL[-1]
O'-INTERMITTENT[-2]

O- NO POOL[0]

COMMENTS:

RIFFLE: [ ]

RIFFLE/RUN DEPTH
O - GENERALLY > 10 cm,MAX>50 [4]
O - GENERALLY > 10 cm,MAX<50 [3]
O - GENERALLY 5-10 cm [1]
X - GENERALLY < 5 cm [Riffle = 0]

RIFFLE/RUN SUBSTRATE
O-STABLE (e.g.,Cobble, Boulder) [2]
O-MOD. STABLE (e.g.,Pea Gravel) [1]
X-UNSTABLE (Gravel,Sand) [0]

RIFFLE/RUN EMBEDDEDNESS
O-EXTENSIVE [-1]
X-LOW. [1]
O-MODERATE[0]
O-NONE[2]

O-NO RIFFLE[0]

COMMENTS

GRADIENT: [ ]

6] Gradient (feet/mile): _____ %POOL: 95 %RIFFLE: 5 %RUN: _____

Differences between DS-1 & US-1.

DS-1 is slightly deeper with more instream cover. Stream is slightly wider at DS-1. Silt cover is greater @ DS-1. Gradient is lower @ DS-1.

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: [ ]

Stream: Little Raccoon Cr. RM: ____ Date: 6/3/97 River Code: ____

Crew: Baggett, Patti

Location: 05-1A

1) SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present):

SUBSTRATE SCORE: [ ]

TYPE	POOL	RIFFLE		POOL	RIFFLE
☐☐-BLDER /SLABS [10]			☐☐-GRAVEL [7]		
☐☐-BOULDER [9]			☐☐-SAND [6]		
☐☐-COBBLE [8]			☐☐-BEDROCK [5]		
☐☐-HARDPAN [4]			☐☒-DETRITUS [3]		25
☐☒-MUCK [2]		75	☐☐-ARTIFIC. [0]		

Substrate Origin (Check all): ☐-LIMESTONE [1] ☐-RIP/RAP [0] ☐-TILLS [1] ☐-HARDPAN [0] ☐-SANDSTONE [0] ☐-SHALE [-1] ☐-COAL FINES [-2]

Silt Cover (Check One): ☐-SILT HEAVY [-2] ☒-SILT MODERATE [-1] ☐-SILT NORMAL [0] ☐-SILT FREE [1]

Extent Of Embeddedness (Check One): ☐—EXTENSIVE [-2] ☐—MODERATE [-1] ☒—LOW [0] ☐—NONE [1]

TOTAL NUMBER OF SUBSTRATE TYPES: ☐> 4 [2] ☐— <= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

COMMENTS: Clay, detritus, & silt substrate. No riffles. Some silt on top of muck (clay)

COVER SCORE: [ ]

2) INSTREAM COVER

TYPE (Check All That Apply)

☐-UNDERCUT BANKS [1]
☒-OVERHANGING VEGETATION [1]
☐-SHALLOWS (IN SLOW WATER) [1]
☐-DEEP POOLS [2]
☐-ROOTWADS [1]
☐-BOULDERS [1]
☐-OXBOWS [1]
☐-AQUATIC MACROPHYTES [1]
☒-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)

☐-EXTENSIVE >75% [11]
☐-MODERATE 25-75% [7]
☒-SPARSE 5-25% [3]
☐-NEARLY ABSENT < 5% [1]

COMMENTS: site has more cover than 05-1 but still rated as sparse

CHANNEL: [ ]

3) CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY	DEVELOPMENT	CHANNELIZATION	STABILITY	MODIFICATIONS/OTHER	
☐-HIGH [4]	☐-EXCELLENT [7]	☐-NONE [6]	☐-HIGH [3]	☐-SNAGGING	☐-IMPOUND.
☐-MODERATE [3]	☐-GOOD [5]	? ☒-RECOVERED [4]	☒-MODERATE [2]	☐-RELOCATION	☐-ISLANDS
☒-LOW [2]	☐-FAIR [3]	☐-RECOVERING [3]	☐-LOW [1]	☐-CANOPY REMOVAL	☐-LEVEED
☐-NONE [1]	☒-POOR [1]	☐-RECENT OR NO RECOVERY [1]		☐-DREDGING	☐-BANK SHAPING
				☐-ONE SIDE CHANNEL MODIFICATIONS	

COMMENTS: may have been channelized

RIPARIAN: [ ]

4) RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

"River Right Looking Downstream"

RIPARIAN WIDTH (L R (Per Bank))

☐☐-WIDE > 50m [4]
☐☐-MODERATE 10-50 [3]
☐☐-NARROW 5-10m [2]
☒☐-VERY NARROW 1-5m [1]
☐☒-NONE [0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY (L R (Most Predominant Per Bank))

☐☐-FOREST, SWAMP [3]
☐☒-OPEN PASTURE/ ROWCROP [0]
☒☐- RESID_PARK_NEW FIELD [1]
☐☐-FENCED PASTURE [1]

(L R (Per Bank))

☐☐-URBAN OR INDUSTRIAL [0]
☐☐-SHRUB OR OLD FIELD [2]
? ☐☐-CONSERV. TILLAGE [1]
☐☐-MINING/CONSTRUCTION [0]
— None

BANK EROSION

☐ ☒-NONE OR LITTLE [3]
☐ ☐-MODERATE [2]
☐ ☐-HEAVY OR SEVERE [1]

COMMENTS:

POOL: [ ]

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX DEPTH (Check 1)

☐- >1m [6]
☐- 0.7-1m [4]
☒- 0.4-0.7m [2]
☐- < 0.4m [1]
☐—<0.2m (Pool = 0]

MORPHOLOGY (Check 1)

☐-POOL WIDTH > RIFFLE WIDTH [2]
☐-POOL WIDTH = RIFFLE WIDTH [1]
☒-POOL WIDTH < RIFFLE W. [0]
no riffles

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)

☐-TORRENTIAL [-1]
☐-FAST [1]
☐-MODERATE [1]
☒-SLOW [1]
☐-EDDIES [1]
☐-INTERSTITIAL [-1]
☐-INTERMITTENT [-2]

☐-NO POOL [0]

COMMENTS:

RIFFLE: [ ]

RIFFLE/RUN DEPTH

☐-GENERALLY > 10 cm, MAX > 50 [4]
☐-GENERALLY > 10 cm, MAX < 50 [3]
☐-GENERALLY 5-10 cm [1]
☒-GENERALLY < 5 cm (Riffle = 0]

RIFFLE/RUN SUBSTRATE

☐-STABLE (e.g., Cobble, Boulder) [2]
☐-MOD. STABLE (e.g., Pea Gravel) [1]
☐-UNSTABLE (Gravel, Sand) [0]
Not applicable

RIFFLE/RUN EMBEDDEDNESS

☐-EXTENSIVE [-1]
☒-LOW. [1]
☐-MODERATE [0]
☐-NONE [2]

☐-NO RIFFLE [0]

COMMENTS: no riffles

GRADIENT: [ ]

6) Gradient (feet/mile): ____ %POOL: 100 %RIFFLE: ____ %RUN: ____

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: [ ]

Stream Little Raccoon Creek RM _____ Date 6/7/93 River Code _____

Location RS-2 (about 100 ft upstream of Raccoon Cr. confluence) Crew Daggett, Patti

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present):

SUBSTRATE SCORE: [ ]

TYPE	POOL	RIFFLE
O-BLDER /SLABS[10]		
O-BOULDER [9]		
O-COBBLE [8]		
O-HARDPAN [4]		
X-MUCK [2]	100	
O-GRAVEL [7]		
O-SAND [6]		
O-BEDROCK[5]		
O-DETRITUS[3]		
O-ARTIFIC.[0]		

Substrate Origin (Check all): O-LIMESTONE [1] O-RIP/RAP [0] O-TILLS [1] O-HARDPAN [0] O-SANDSTONE [0] O-SHALE [-1] O-COAL FINES [-2]

Silt Cover (Check One): O-SILT HEAVY [-2] X-SILT MODERATE [-1] O-SILT NORMAL [0] O-SILT FREE [1]

Extent Of Embeddedness (Check One): O—EXTENSIVE [-2] O—MODERATE[-1] X—LOW[0] O—NONE[1]

TOTAL NUMBER OF SUBSTRATE TYPES: O> 4 [2] O— <= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

COMMENTS No riffles present. Clay & black organic matter dominated substrate. Small amount of silt over muck.

COVER SCORE: [ ]

2] INSTREAM COVER

TYPE (Check All That Apply)

O-UNDERCUT BANKS [1]
X-OVERHANGING VEGETATION [1]
O-SHALLOWS (IN SLOW WATER) [1]
O-DEEP POOLS [2]
X-ROOTWADS [1]
O-BOULDERS [1]
O-OXBOWS [1]
O-AQUATIC MACROPHYTES [1]
X-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)

O - EXTENSIVE > 75% [11]
X - MODERATE 25-75% [7]
O - SPARSE 5-25% [3]
O - NEARLY ABSENT < 5%[1]

COMMENTS: Depths ranged from about <0.5 to 3.5 ft; cover provided by overhanging veg., grasses, & instream deb

CHANNEL: [ ]

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY	DEVELOPMENT	CHANNELIZATION	STABILITY	MODIFICATIONS/OTHER	
O - HIGH [4]	O - EXCELLENT [7]	X - NONE [6]	O - HIGH [3]	O - SNAGGING	O - IMPOUND.
X - MODERATE [3]	O - GOOD [5]	O - RECOVERED [4]	X - MODERATE [2]	O - RELOCATION	O - ISLANDS
O - LOW [2]	O - FAIR [3]	O - RECOVERING [3]	O - LOW [1]	O - CANOPY REMOVAL	O - LEVEED
O - NONE [1]	X - POOR [1]	O - RECENT OR NO RECOVERY [1]		O - DREDGING	O - BANK SHAPING
				O - ONE SIDE CHANNEL MODIFICATIONS	

COMMENTS: 2 beds in about 500 ft section

RIPARIAN: [ ]

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

"River Right Looking Downstream"

RIPARIAN WIDTH (L R (Per Bank))

X O'-WIDE> 50m [4]
O O'-MODERATE 10-50 [3]
O O'-NARROW 5-10m [2]
O X'-VERY NARROW 1-5m [1]
O O'-NONE[0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY (L R (Most Predominant Per Bank))

X O-FOREST, SWAMP [3]
X O-OPEN PASTURE/ ROWCROP[0]
O- RESID.,PARK,NEW FIELD [1]
O O-FENCED PASTURE [1]

L R (Per Bank)

O O-URBAN OR INDUSTRIAL[0]
O O-SHRUB OR OLD FIELD[2]
O O-CONSERV. TILLAGE [1]
O O-MINING/CONSTRUCTION [0]

None

BANK EROSION

X O-NONE OR LITTLE [3]
O O-MODERATE [2]
O O-HEAVY OR SEVERE[1]

COMMENTS: _____

POOL: [ ]

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX DEPTH (Check 1)

O- >1m [6]
X 0.7-1m [4]
O- 0.4-0.7m [2]
O- < 0.4m [1]
O—<0.2m (Pool = 0)

MORPHOLOGY (Check 1)

O'-POOL WIDTH > RIFFLE WIDTH [2]
O -POOL WIDTH = RIFFLE WIDTH [1]
X -POOL WIDTH < RIFFLE W. [0]

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)

O'-TORRENTIAL[-1]
O'-FAST[1]
O'-MODERATE [1]
X-SLOW [1]
O'-EDDIES[1]
O'-INTERSTITIAL[-1]
O'-INTERMITTENT[-2]

O- NO POOL[0]

COMMENTS: No riffles

RIFFLE: [ ]

RIFFLE/RUN DEPTH

O - GENERALLY >10 cm,MAX>50 [4]
O - GENERALLY >10 cm,MAX<50 [3]
O - GENERALLY 5-10 cm [1]
X - GENERALLY < 5 cm (Riffle = 0)

RIFFLE/RUN SUBSTRATE

O-STABLE (e.g.,Cobble, Boulder) [2]
O-MOD. STABLE (e.g.,Pea Gravel) [1]
O-UNSTABLE (Gravel,Sand) [0]

RIFFLE/RUN EMBEDDEDNESS

O-EXTENSIVE [-1]
X-LOW. [1]
O-MODERATE[0]
O-NONE[2]

O-NO RIFFLE[0]

COMMENTS Not applicable

GRADIENT: [ ]

6] Gradient (feet/mile): _____ %POOL: 100 %RIFFLE: _____ %RUN: _____

pool/glide no riffles.

ENSR

ENSR Consulting and Engineering

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