Tim Ehli

# Quality Assurance Project Plan

### COMPOSITE SAMPLING FOR SOIL VOC ANALYSIS

Project No. LV470850 (4-70.85) Contract No. 68-C5-0091 Document Control No. QAO 60-00-01

by Lockheed Martin Environmental Services 980 Kelly Johnson Drive Las Vegas, Nevada 89119

for Brian Schumacher, Work Assignment Manager and Acting Branch Chief Environmental Sciences Division

NATIONAL EXPOSURE RESEARCH LABORATORY U.S. ENVIRONMENTAL PROTECTION AGENCY LAS VEGAS, NEVADA 89193-3478

approved by

LM Project Manager

Marti Minnich LM Technical Task Lead	Date		
Vicki Ecker LM Quality Assurance Repre	Date esentative		
<u> </u>			

Date

Brian Schumacher Date EPA Work Assignment Manager and Acting Branch Chief

George Brilis Date EPA Quality Assurance Manager

# TABLE OF CONTENTS

Α.	Project Management	1
	1. Project Organization	1
	2. Problem Definition	2
	2.1 Purpose for Compositing	2
	2.2 How to Composite for a Representative Mean Concentration	5
	3. Project Description	
	4. Data Quality Objectives	
	4.1 Project Quality Objectives	
	4.2 Instrument Measurement Performance Criteria	8
	5. Documentation and Records	
В.	Data Acquisition	9
	6. Experimental Design	9
	6.1 Site Selection	
	6.2 Field Sampling Procedures	
	6.3 Laboratory Procedures	
	6.4 Sample Tracking	
	6.5 Design Rationale and Assumptions	14
	7. Analytical Methods	
	8. Quality Control	15
	8.1 Bias	
	8.2 Precision	17
	8.3 Instrument Detection Limits and Contamination	18
	9. Instrument Calibration and Frequency	19
	10. Data Management	

C. Assessment/Oversight	20
11. Assessment and Response Actions	20
12. Reports to Management	
D. Data Validation and Usability	
13. Data Review, Validation, and Verification Requirements	
14. Reconciliation of Data Quality Objectives	21
References	22
Figure 1. Project Organizational Chart	2
Figure 2. Terminology for Study	7
11gulo 2. Tollimiology for study	,
Figure 3. Location of Cores within a Plot	12
Figure 4. Sampling Scheme within a Core	12
11gure 4. Samping Scheme within a Core	12
Table 1. Volatile Organic Compounds of Interest	10
Table 2. Compositing Scheme	13
Table 3. QA/QC Samples, Frequency, and Acceptance Criteria	16
Tuble 5. Viv QC bumples, i requency, and receptance criteria	10

# **Distribution List**

- G. Brilis, ESD-LV QA Manager
- B. Schumacher, ESD-LV Work Assignment Manager

October 1, 2004
Page iv of 23

V. Ecker, LM QA Representative M. Minnich, LM Technical Task Lead J. Zimmerman, LM Field Chemist

### A. Project Management

#### 1. Project Organization

The project organization and names of responsible individuals are given in Figure 1. The Work Assignment Manager (WAM), Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), is responsible for direction and oversight of this project. Dr. Schumacher will be responsible for supervising the analytical work, including all applicable quality control procedures, and all recording of laboratory activities and observations in the project notebooks. George Brilis, ESD-LV Quality Assurance Manager, will ensure that the project conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) Quality Assurance (QA) Representative, Vicki Ecker, will verify that the Quality Assurance Project Plan (QAPP) is comprehensively developed and implemented.

The LM Task Lead, Marti Minnich, will be responsible for ensuring that the QAPP is implemented, that procedural documentation is regularly reviewed, that the project schedule is followed, and that deliverables meet the goals of the project. Dr. Minnich will review all procedures with the Field Chemist and make decisions for any necessary adjustments or clarifications to procedures during implementation. She is responsible for all communications with the WAM, including reports of any major problems, required modifications to the QAPP, and draft and final reports.

The LM Field Chemist, John Zimmerman, will be responsible for organizing and implementing the field collection efforts and laboratory preparation of samples. He will also be responsible for providing technical support for the laboratory procedures as specified in this QAPP. He will assist in data management and report preparation, as needed. Mr. Zimmerman will communi-

October 1, 2004
Page 2 of 23

cate progress to the Task Lead on a weekly basis.

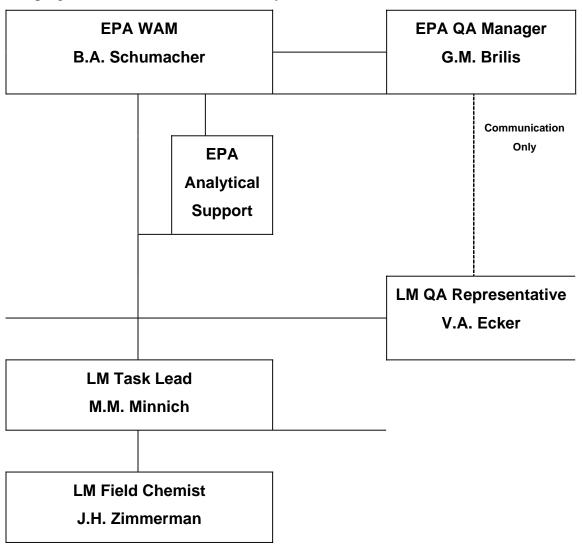


Figure 1. Project Organizational Chart

# 2. Problem Definition

Page 3 of 23

# 2.1 Purpose for Compositing

Any effort to collect, homogenize, and subsample soil contaminated with VOCs effectuates volatile analyte losses (Lewis et al., 1994). Therefore, it is recommended that all VOC samples are collected with minimal disruption of the soil (SW-846 Method 5035, USEPA, 1997). Soil which is destined for VOC analysis is generally not homogenized or mixed and subsampled in any manner. For sampling of all other environmental contaminates, the use of composite samples to accomplish spatial averaging and to contain costs is recommended (e.g., Soil Screening Guidance, USEPA, 1996). For soil VOC samples, the standard protocol for achieving better representativeness is to increase the sampling density (i.e., increase the number of samples from within a given area). This option can be pressed to the maximum that the budget will allow, but research data have shown extreme variability within short distances (West et al, 1995; Schumacher and Minnich, in review). Much of the existing soil VOC data are highly variable and of questionable site representativeness.

West et al. (1995) reported on spatial variability of soil VOC concentrations at a former land treatment unit used for the disposal of waste oils and solvents. Intensive sampling was conducted on the site which measured approximately 37 m by 81 m. During the first sampling event, 176 samples were collected from 21 sampling locations, bored to 6.6 m deep. During the second sampling event, 204 samples were collected from 42 sampling locations, bored to 4.2 m deep. The variability of the VOC concentration within a short distance was demonstrated in this study by collecting field sample duplicates within the same 30-cm depth interval of a 2.5-cm core. VOC concentrations in these duplicates commonly varied more than an order of magnitude. In addition, the study compared three different spatial models as to their ability to interpolate existing VOC concentrations. A partial data set was used to derive the interpolating function of each model, and predicted values for the remaining data points were compared to measured values. In general, the predicted values differed from the measured values by an order of magnitude. West et al. (1995) deduced that numerous field analyses would be more cost

October 1, 2004

Page 4 of 23

effective than using sparse data sets of off-site laboratory analyses and complex spatial models to infer soil VOC concentrations.

October 1, 2004
Page 5 of 23

Schumacher and Minnich (in review) reported on the variability of soil VOC concentrations at two Superfund sites for samples collected within 15-cm depth intervals. Comparison of data from adjacent samples often exhibited differences of an order of magnitude (relative percent differences as high as 191%). Two other parameters measured over the same depth interval, organic carbon content and clay content, demonstrated relative percent differences of up to 161% and 116%, respectively. At these sites, soil variability within 15 cm was nearly as variable as the differences in VOC concentrations.

The standard method for the analysis of soil VOCs, the low-level purge-and-trap procedure (SW-846 Method 5035, USEPA, 1997), analyzes 5 grams of soil or less. The small amount of soil, collected without homogenization and subsampling from the immediate vicinity can only be considered representative of that particular 5-g sample. This is confirmed by the high variability of field duplicate samples. Furthermore, an individual soil VOC sample cannot be reanalyzed (or checked) by the low-level method because the entire sample is used in the analysis. As stated above, when using the low-level sampling/analysis method the only way to increase the sample representativeness in a given area of a site is to increase the number of samples collected and analyzed.

Two reasons relevant for the collection of composite soil VOC samples are cited in the overviews by Garner et al. (1988) and Gagner and Crockett (1996). First, composite sampling can be an economic decision when the costs for analyzing a sample are high relative to the sampling costs; fewer samples will be analyzed, thus reducing the overall cost of analysis. Secondly, composite sampling reduces the intersample variance, thereby providing a more precise estimate of a mean concentration. It is this second reason that is expected to make composite sampling for soil VOCs a more attractive alternative than the current procedures.

October 1, 2004
Page 6 of 23

Compositing procedures can be used for VOCs in soils if the sample is analyzed by the high-level method (SW-846 Method 5035, USEPA, 1997), the procedure whereby a methanol extract of the soil is analyzed. The high-level method has a higher detection limit (approximately an order of magnitude higher at a 1:1 soil-to-methanol ratio) than samples analyzed by the low-level method. Although a higher detection limit elicits an initially negative response, the potential increase in representativeness, accuracy, and precision over the current methods makes soil sample compositing worthy of consideration. Reanalysis of a sample when one of the quality control specifications are not met is a potential feature with this method. Depending on the action levels or other applicable criteria for a site, it follows that a potentially more accurate and cost-effective sampling strategy would be to composite samples and analyze them by the high-level method rather than persevere with numerous discrete 5-g samples by the low-level method.

## 2.2 How to Composite for a Representative Mean Concentration

Jenkins et al. (1996) studied the short-range heterogeneity in explosives-contaminated soils at nine locations within three military installations. They compared sampling error with analytical error from samples taken within a 122-cm radius circle, and found that sampling error was always larger than analytical error. Analytical and subsampling errors combined produced a mean relative standard deviation (RSD) of about 10% with extremes from 5 to 20%. Sampling errors (using seven discrete samples within the 122-cm circle), produced RSD values that ranged from 50 to 150%. At five of the nine locations, the short-range differences were so large that the use of classical normal distribution statistics to fractionate the error was not possible (logarithmic units had to be used to evaluate the data). By collecting replicates of both discrete and composite samples, they compared the accuracy and precision of composite sampling with discrete sampling. All samples were taken from homogenized lots of soil and, thus, the precision data included the variability introduced from analytical noise and the thoroughness of the soil homogenization procedures. For the sites and analytes in their study, they found that there was no justification for performing replicate analyses of homogenized composites unless the RSD of

October 1, 2004

Page 7 of 23

sampling is lower than 50%.

When composite sampling is selected to achieve better representation of the area of interest, the decision-making unit or "support" must be defined (e.g., a backhoe scoopful or surface-0.5 acre). Schumacher et al. (1998) suggest, "the smallest practical volume... operationally defined by the sampling and remediation equipment to be used during site restoration" as a way to select the sampling support. The Soil Screening Guidance (USEPA, 1996) offers a default exposure area of 0.5 acre for surface soil contamination, based on the size of an average suburban residential lot.

After determining the support size and dividing the area into sampling blocks, the number of specimens (individual soil samples) to include in the composite sample must be decided. When specimens are collected from within a support, the number of specimens included in the composite does not affect the detection limit. The VOC concentration in the composited sample will not be "diluted" with cleaner soil, because the concentration of interest is the concentration of the support. To obtain the most accurate estimate of the mean concentration, a very large number of specimens in the composite would be desirable, the limit being the case in which all of the soil within the support is included in the composite. Practical issues of cost and sample size must be balanced by some minimum number of specimens to reach a desirable level of precision. Jenkins et al (1996) suggest that, "a flexible sampling plan would evolve with the understanding that it was subject to modifications (if necessary) as results accumulate." The study described herein explores the number and placement of specimens to be included in a composite sampling scheme for VOCs in soil.

October 1, 2004
Page 8 of 23

### 3. Project Description

The objective of the study is to demonstrate a procedure for collecting composite samples for soil VOCs to be analyzed by the high-level purge-and-trap methanol extraction. The study will explore the effects of the number and orientation of specimens in the composite on the accuracy and precision, and hence, representativeness, of the data.

A support or plot size of 1 m<sup>3</sup> will be studied. Five cores will be removed from the plots, each to a vertical depth of 1 m. From each core, 5-g soil specimens will be collected at depths of 20, 30, 40, 50, 60, 70, and 80 cm for a total of seven individual specimens per core. Soil specimens will be placed into 5 mL of methanol in a 40-mL septum-sealed vial. Thus, 35 field specimens per plot will be collected. There will be a minimum of six plots in this study, optimally three plots at each of two sites. The terminology for plots, cores, specimens, etc. is depicted in Figure 2.

Figure 2. Terminology for Study

Compositing will be executed by EPA personnel in the EPA laboratory by combining aliquots of the methanol extracts into analytical samples. The compositing scheme, shown in Table 2 (Section 6.2), will consist of four treatments, or ways of compositing the extracts, and a set of control samples. Three composite analytical samples will be generated for each treatment and two analytical replicates of composite samples will be collected for each plot (Section 8.2). In addition to the composite samples, each of the 35 individual samples will be analyzed separately, creating a total of 52 analytical samples per plot. All samples will be analyzed by purge-and-trap introduction into a gas chromatograph with mass spectrometer detector (GC/MS).

### 4. Data Quality Objectives

## 4.1 Project Quality Objectives

To meet the project objectives, the data and the interpretation of those data must be reliable. Critical to this experiment are the soil VOC concentration measurements. Analytical or measurement quality objectives (MQOs) are set for precision, bias, and detection limits. The laboratory MQOs for each type of analyses are given below. Quality control samples and their associated DQOs are discussed in Section 8.

#### 4.2 Instrument Measurement Performance Criteria

Precision for each VOC will be expressed as the percent difference (%D) between ongoing calibration standard responses and the initial calibration response. The MQO for precision will be to achieve an %D  $\leq$  15% between initial and ongoing calibration standards. Analytical duplicate samples (composited and pure) are expected to achieve a relative percent difference (RPD)  $\leq$  25%.

Bias for each VOC will be determined by comparing the analyte concentrations from a QC check standard (a certified, second-source standard) relative to the initial calibration curve values. The second-source standard will be analyzed in duplicate for each initial calibration curve. The MQO for bias will be a %R of  $100 \pm 20\%$ .

The instrument detection limit (IDL) is the lowest concentration of an analyte that the measurement system can consistently detect and/or measure in replicate standards. The IDL for the purge-and-trap GC/MS system is 10 ng on-column for each VOC of interest.

#### 5. Documentation and Records

All soil VOC concentration data will be generated in electronic and hard copy formats via the instrument-associated software. All data will be transferred to electronic spreadsheets for analysis and presentation. The records of the study will be maintained by LM for two years after the final report is accepted and then transferred to the client for storage.

### **B.** Data Acquisition

#### 6. Experimental Design

#### 6.1 Site Selection

Two sites will be selected to provide data representing different VOC compounds and different environments. The WAM will identify appropriate field sites and secure access to these sites. The main criteria for site selection will be: (1) the presence of one or more of the VOCs listed in Table 1 at a concentration equal to or greater than 500 ng/g in the surface meter of soil, (2) a clay content of at least 20% or silt plus clay content greater than 50% for at least half of the top meter of soil (by depth), (3) sampling locations must not contain boulders, cobbles, or abundant coarse

gravel, and (4) the site will have no known PCB contamination. Plots within each site will consist of three areas where the VOC concentrations are presumed to be high.

The initial list of VOCs for this study is based on the most commonly detected contaminants in groundwater near RCRA disposal sites (Plumb, 1991). [Note: Originally listed as trans-1,2-dichloroethene in Plumb (1991), the compound commonly found is now considered to be cis-1,2-dichloroethene, attributed to the fact that the *cis* and *trans* isomers were not resolved in the early analyses (Howard, 1990).] The candidate compounds for this project are listed in Table 1 in order of decreasing detection frequency.

Table 1. Volatile Organic Compounds of Interest

Compound	Frequency of Detection at RCRA Sites (%)	
Trichloroethylene (TCE)	27.6	
Toluene	27.3	
Benzene	25.1	
cis or trans-1,2-Dichloroethene	24.2	
Tetrachloroethylene (PCE)	23.2	
Ethyl benzene	22.8	
1,1-Dichloroethane	22.5	
1,1,1-Trichloroethane	21.1	
Chloroform	18.9	
Chlorobenzene	18.0	
1,2-Dichloroethane	17.1	
1,1-Dichloroethene	15.7	

#### 6.2 Field Sampling Procedures

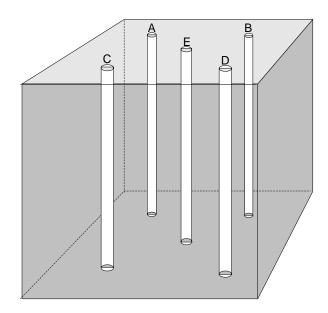
A Geoprobe or similar hydraulic probe will be used to collect continuous sample cores to a depth of approximately 1 m. The probe will be fitted with a single-use polymer liner (thin-walled polyethylene terephalate glycol, or PETG) with an internal diameter of 3.8 cm and a length of approximately 1.1 m. A fresh PETG liner will be used for each core.

At each site, three 1 m<sup>3</sup> plots will be delineated. As depicted in Figure 3, five cores will be collected from each plot, one near each corner of the square (designated cores A through D) and a core in the center of the square (designated core E). Immediately after removal, cores will be taken to a sampling table and cut into sections (through both the liner and soil) at 20, 30, 40, 50, 60, 70 and 80 cm below the ground surface. After each cut, a member of the sampling crew will remove approximately 5 g of soil from the exposed surface (top end of the cut) using a truncated syringe (Figure 4). The soil will be placed in a 40-mL septum-sealed vial containing 5 mL of methanol and sealed. The vials will be placed on ice and shipped to the EPA laboratory in Las Vegas for analysis.

#### 6.3 Laboratory Procedures

The methanol extracts of the specimens will be subsampled and combined into composite samples in fresh 40-mL septum-sealed vials according to the scheme given in Table 2. Four treatments will consist of composite samples made up of 4 or 10 specimens per composite, with the collection orientation spanning across the 5 cores versus within single cores (Table 2). There will be 3 composite samples per treatment. The fifth treatment will be a 100-µL aliquot from a single specimen taken from the midpoint (50 cm depth) of a core. This treatment will then be duplicated in the sample analysis described below. Duplicates of two composite samples will be collected and analyzed for each plot. The schedule for composite duplicates is given in Section

8.2.



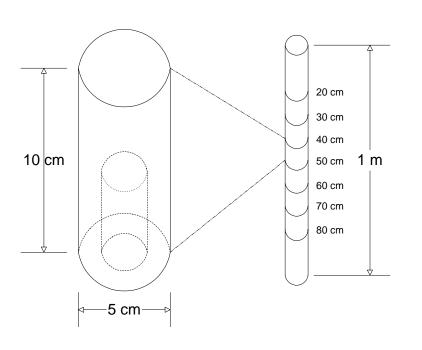


Figure 3.
Location of
Cores Within a
Plot

Figure 4. Sampling Scheme within a Core

Table 2. Analytical Compositing Scheme

Treatment	Aliquot size in composite	Specimens in Analytical Samples 1-3		
		AS 1	AS 2	AS 3
<b>T1</b> – 10 specimens	10 μL/specimen	cores A-E depths 20 & 80	cores A-E depths 30 & 70	cores A-E depths 40 & 60
T2–10 specimens	10 μL/specimen	cores A & D depths 20, 30, 50, 70, 80	cores C & E depths 20, 30, 50, 70, 80	cores B & E depths 20, 30, 50, 70, 80
T3 – 4 specimens	25 μL/specimen	cores A-D depth 50	cores B-E depth 40	cores A,B,D,E depth 60
T4 – 4 specimens	25 μL/specimen	core E – depths 20, 40, 60, 80	core A – depths 20, 40, 60, 80	core B – depths 20, 40, 60, 80
T5 –control, 1 specimen	100 μL/specimen	core B depth 50	core C depth 50	core E depth 50

After preparing the composite samples, aliquots ( $100 \,\mu\text{L}$ ) from all 35 discrete specimens will be subsampled for analysis. The mean VOC concentrations of these 35 samples will comprise a grand mean to which the composite sample analyses will be compared for representativeness.

October 1, 2004
Page 15 of 23

Analytical samples are to be stored chilled (4 <sup>0</sup>C) and analyzed within 8 days of field sample collection and within 3 days of the methanol aliquot removal procedure.

#### 6.4 Sample Tracking

Each of the 35 individual field specimens per plot will be labeled by plot id, core id, and depth. Plots will be assigned letters beginning at the end of the alphabet. Thus, "Z-B-30" would be the sample from plot Z, core B, depth 30 cm. Individual analytical samples will retain the original field sample labels. Composited analytical samples will be labeled with treatments assigned as shown in the compositing scheme given in Table 2. These samples will have the plot, treatment, analytical sample (AS) number. Thus, "Z-T3-2" would indicate a sample from plot Z, treatment 3, AS 2. Duplicates (when analyzed) will have a trailing lower case letter. Therefore, "Z-T3-2a" would be a duplicate of the previous sample.

#### 6.5 Design Rationale and Assumptions

The project measures the VOC concentrations of 35 soil specimens (approximately 175 g) and uses this data to serve as an estimate for the VOC concentration of 1 m³ of soil (approximately 1.4 x 10³ Kg); the mean of these 35 analyses is referred to as a "grand mean". Obviously, the mean soil concentration determined in this manner will not necessarily coincide with the true mean soil concentration. Instead, the experiment measures whether composite samples of 4 or 10 specimens, can better estimate the values measured in the 35 specimens that represent the plot. These specimens are taken from up to five cores, or as few as one core. Data from the composite treatments and control samples will be compared to the data from the 35 individual specimens with respect to precision (standard deviation of the three analytical samples versus standard deviation of the 35 samples) and accuracy (deviation of the treatment mean from the grand mean). In any case, the combined data of 35 individual VOC analyses is taken to be a better estimate of the soil concentration in that m³ of soil than any sampling scheme which

would be typically used at a hazardous waste site.

### 7. Analytical Methods

All field specimen vials will be chilled prior to opening and removing an aliquot of the methanol extract. All 100- $\mu$ L analytical samples of methanol extracts will be analyzed using the low-level soil procedure from SW-846 Method 5035 (USEPA, 1997). Water (10-mL) containing the internal standards (ISs) and system monitoring compounds (SMCs) will be added to the vial by the automated purge-and-trap instrument. Analysis will follow the GC/MS procedures in SW-846 Method 8260 (USEPA, 1997) under the quality control parameters described below.

### 8. Quality Control

Table 3 summarizes the QA/QC samples, acceptance criteria, and corrective actions for the soil VOC data. A general discussion of the project QC and specific QC components for VOCs is presented in sections 8.1 through 8.3.

#### 8.1 Bias

Bias in the samples and analytical system will be monitored by: (1) checking the tune of the mass spectrometer every 24 hours with bromofluorobenzene (BFB) as ion abundance ratios, (2) comparing the data generated in the initial calibration curve with concentrations of the analytes measured in a second-source QC check standard, (3) area counts of the internal standards added to every 40-mL vial, and (4) surrogate compound recoveries. Acceptance criteria for these samples are given in Table 3.

Percent recovery (%R) of the QC check standard will be calculated as follows:

October 1, 2004

Page 17 of 23

$$%R = 100 (S/C_{sa})$$

where S is the measured concentration and  $C_{sa}$  is the nominal concentration of a given analyte in the standard. All standards will be certified standards from a reputable manufacturer. The %D for IS area counts is calculated as shown in Section 8.2.

Table 3. QA/QC Samples, Frequency, and Acceptance Criteria

QC Sample	Purpose	Frequency	Acceptance Criteria	Corrective Action
Bromofluoro- benzene (BFB)	Analytical bias	Beginning of each 24-hour analytical period	Ion abundance ratio, Method 8260	Reanalyze, perform instrument maintenance
QC Check Standard (QCCS)	Analytical bias	Duplicates per system each time a new IC is analyzed	$%R = 100 \pm 20\%$	Reanalyze; obtain new lot or vendor QCCS
Internal Standard (IS) Area Counts	Analytical bias	Each sample, blank, and standard	%D = -50% to +100%	Reanalyze if blank or standard, flag data
Surrogate Recovery	Analytical bias	Each sample, blank, and standard	$%R = 100 \pm 25\%$	Reanalyze once, flag data
Initial Calibration (IC)	Precision	Prior to sample analysis and if OCC fails	%RSD of each RF≤ 15%	Perform instrument maintenance, reanalyze
On-going Calibration Check (OCC)	Precision, calibration drift	Beginning and end of each 12-hour analytical period	%D from IC ≤ 15%	Reanalyze, perform instrument maintenance
Analytical Duplicates	Precision	3 out of 35 discrete analyses; 2 out of 12 composite analyses/plot	IS, OCC, and blanks within criteria; RPD≤ 25%	Flag data
Instrument Detection Limit	Detection limit	7 samples prior to sample analysis	10 ng on detector	Perform instrument maintenance, reanalyze
Instrument Blank	Detection limit, contamination	Beginning of each 12 hour analytical period	Below analyte IDL or sample values ≥5x Instrument Blank	Reanalyze, perform instrument maintenance, flag data
Travel Blank	Contamination, detection limit	2 per plot	Below analyte IDL	Flag data

Page 19 of 23

#### 8.2 Precision

Precision represents the reproducibility of measurements under a given set of conditions and provides an estimate of random error (Taylor, 1987). Method precision will be monitored by (1) examining the consistency of analyte response factors over the range of the calibration curve and (2) analyzing on-going calibration check (OCC) standards for VOCs.

In conjunction with the initial calibration curve, precision will be established for each analyte as the %RSD of the response factor (RF) from each point of a five-point calibration curve. The RF of the standard is defined as:

$$RF = (A_S \times C_{IS}) \div (A_{IS} \times C_S)$$

Where  $A_S$  and  $A_{IS}$  are the area of the standard and its associated internal standard, respectively.  $C_S$  and  $C_{IS}$  are the nominal concentration of the standard and its associated internal standard,

$$%RSD \sim = {SD_{n-1}}$$
 over  ${mean} \sim x \sim 100$ 

respectively. The %RSD is given as:

where  $SD_{n-1}$  is the standard deviation of the replicate measurements.

The %D of an OCC from the initial calibration response will be calculated as follows:

$$%D = (R1 - R2)/R1 \times 100,$$

where "R1" is the initial calibration peak area count and "R2" is the subsequent or daily peak area count.

October 1, 2004

RPD = 
$$\{(C1 - C2) \sim x \sim 100\%\}$$
 over  $\{(C1 + C2)/2\}$ 

The precision of sample duplicates will be calculated as the relative percent difference (RPD): where, C1 = larger of the two observed values

C2 = smaller of the two observed values.

Duplicates for the composite samples will be collected as follows (treatment/analytical sample):

Plot Z: T1/AS1 and T3/AS1;

Plot Y: T2/AS2 and T4/AS2;

Plot X: T1/AS3 and T3/AS3;

Plot W: T2/AS1 and T4/AS1;

Plot V: T1/AS2 and T3/AS2;

Plot U: T2/AS3 and T4/AS3

#### 8.3 Instrument Detection Limits and Contamination

The laboratory-derived instrument detection limit (IDL) will be established following the procedure of USEPA (1992). The IDL is defined as follows:

$$IDL = 3.14(sd)$$

where *sd* is the standard deviation (n-1 degrees of freedom) for the analytical results from seven replicate low-level standards and 3.14 is the Student's t-value for a one sided 99% confidence level. IDLs will be reported in ng on-column.

Travel blanks are used to monitor the exposure of samples to contamination during shipping and storage. Two blanks will be included in each cooler. It is assumed that the samples from each

Page 22 of 23

plot will fit in a single cooler for shipment. If contamination is detected in a travel blank (values > IDL), all data associated with that blank will be flagged.

Instrument blanks (the laboratory water added to purge samples and used to make standards) monitor any potential contamination during analysis. Instrument blanks will be included at the beginning of each 12-hour analytical period, or at the beginning and end of any run less than 12 hours. If contamination (any target analyte at a concentration above the IDL) is detected in an instrument blank at the beginning of a run, no samples will be analyzed until the problem has been identified and corrected. Data from the second half of the run will be flagged if contamination is discovered in a blank at the end of a run. If sample concentrations associated with the contaminated blank are  $\geq 5X$  the blank contamination, the data will be considered acceptable for use in data analysis steps.

### 9. Instrument Calibration and Frequency

The instruments will be calibrated basically as specified in SW-846 Method 8260 (USEPA, 1997). Modifications include a reduced list of target analytes, no system performance check compounds, no laboratory matrix spike/matrix spike duplicate samples, and acceptance criteria as listed in Table 3. A five-point calibration curve consisting of standards at the nominal concentrations of 10, 50, 100, 500, and 1000 ng total on-column will be prepared for each analyte of interest at the sites. A new calibration curve is warranted if fresh OCC standards do not meet the acceptance criteria (Table 3).

### 10. Data Management

The task of data management for this study includes: (1) tracking VOC data, (2) creating macros to transfer the data from the various electronic files to electronic spreadsheets, (3) calculating soil concentrations (dry weight basis) from the raw data. Copies of the raw data will be

maintained by the EPA laboratory performing the analyses. Records of the raw data will be compiled on Quattro Pro spreadsheets by LM and data manipulations will be performed by LM using SAS Insights. LM will maintain electronic copies of the data and data analysis steps for at least 2 years after the draft report is submitted to the EPA WAM.

### C. Assessment/Oversight

### 11. Assessment and Response Actions

Problems that arise beyond those anticipated in this QAPP may be caused by uncontrolled laboratory or field factors such as spurious contamination, instrument failure, or unanticipated data analysis problems. Corrective actions for nonroutine problems generally require an assessment of the problem with respect to the project objectives and cost considerations. LM management will be notified if problems require additional resources. The WAM will be consulted if any modifications to, or significant deviations from this QAPP are needed.

### 12. Reports to Management

The LM Task Lead is responsible for monthly progress reports to the ESD-LV WAM. Separate written communications will be forwarded regarding any modifications to this QAPP. A project draft report will be prepared, to include a project summary, a description of the methods, results, and a discussion of the results. Appendices to the report will include: (1) all raw data, (2) a QA/QC report which outlines the results of QC procedures and discusses these results in relation to the initial QA objectives.

### **D.** Data Validation and Usability

# 13. Data Review, Validation, and Verification Requirements

All data generated by the EPA analysts will be checked for adherence to the QAPP and method QC criteria. The analysts will clearly mark data to indicate which calibration curve, instrument blanks, and OCC samples correspond with each sample, as applicable. Any QC violations will noted and flagged with data qualifiers. Samples that can be reanalyzed will be repeated in a timely fashion.

Data will be considered valid for an analyte if all associated QC criteria are met for the analyte. Any datum generated with corresponding QC values outside of the expected range will be rechecked by LM, then flagged and discussed in the QA/QC report. Justification for the inclusion or exclusion of qualified data in the data analysis steps will be based in context with the entire data set.

### 14. Reconciliation of Data Quality Objectives

The reconciliation of DQOs will be performed as follows:

- (1) A review of all data will be conducted to assess the quality with respect to the QC parameters as discussed above. Data with one or more QC violations will be assessed with respect to the overall dataset for consistency. Decisions will be made whether or not to include qualified data in the subsequent data analysis steps.
- Data that have been verified to be of acceptable quality will be evaluated with respect to the statistically significant differences in the treatments at the  $p \le 0.5$  level.
- (3) Conclusions will be stated in terms of trends and statistically significant correlations.

#### References

Gagner, S.D. and A.B. Crockett. 1996. Compositing and Subsampling of Media Related to Waste Management Activities. Proceedings of the Twelfth Annual Waste Testing and Quality Assurance Symposium. July 23-26, 1996, Washington, DC. pp. 22-29.

Garner, F.C., M.A. Stapanian, and L.R. Williams. 1988. Composite Sampling for Environmental Monitoring. *In* L.H. Keith, ed., <u>Principles of Environmental Sampling</u>. American Chemical Society, Washington, DC.

Howard, P.H., et al. (Eds). 1990. <u>Handbook of Environmental Fate and Exposure Data for Organic Chemicals</u>. Vol. I and II. Lewis Publishers, Chelsea, MI.

Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, T.A. Ranney, and P.W. Schumacher. 1996. Assessment of sampling error associated with collection and analysis of soil samples at explosives-contaminated sites. US Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Special Report 96-15.

Lewis, T.E., A.B. Crockett, R.L. Siegrist. 1994. Soil sampling and analysis for volatile organic compounds. Environ. Monitoring and Assessment 30:213-246.

Plumb, Jr., R.H. 1991. The occurrence of Appendix IX organic constituents in disposal site ground water. Ground Water Monitoring Review. Spring. 157-164.

Schumacher, B.A. and M.M. Minnich. (In Review.) Extreme short-range variability in VOC-contaminated soils. Submitted to Environ. Sci. Technol.

October 1, 2004
Page 27 of 23

Schumacher, B.A., J.J. van Ee, and E.J. Englund. 1998. Soil Sampling at Hazardous Waste Sites. *In* R.A. Meyers, ed., <u>Encyclopedia of Environmental Analysis and Remediation</u>. John Wiley & Sons, Inc. New York, NY.

Taylor, J.K. 1987. <u>Quality Assurance of Chemical Measurements</u>. Lewis Publishers, Inc., Chelsea, MI. 328 pp.

USEPA. 1996. Soil Screening Guidance: User's Guide 2<sup>nd</sup> Edition. Office of Emergency and Remedial Response. U.S. Environmental Protection Agency. Washington, DC 20460. EPA/540/R-96/018.

USEPA. 1997. Test Methods for Evaluating Solid Waste, Update III. (SW-846). Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.

West, O.R., R.L. Siegrist, T.J. Mitchell, and R.A. Jenkins. 1995. Measurement error and spatial variability effects on characterization of volatile organics in the subsurface. Environ. Sci Technol. 29:647-656.