Revision 2
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Quality Assurance Project Plan for

THE ORDER OF THE ADDITION OF A PRESERVATIVE / EXTRACTANT TO A SOIL SAMPLE: INFLUENCE ON RECOVERY OF VOCS

Task Order 9T2Z054TMA
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by
Lockheed Martin Environmental Services
Las Vegas, Nevada 89119

for
Dr. Brian Schumacher, Client Representative
Environmental Sciences Division

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A. Project Management

1. Project Organization

The project organization and names of responsible individuals are given in Figure 1. The Client Representative, Dr. Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), will be responsible for direction and oversight of all field sampling and analytical laboratory work for this project. This includes review of all applicable quality control procedures and results, and of all documentation of laboratory activities and observations in project notebooks. George Brilis, ESD-LV Quality Assurance (QA) Manager, will ensure that the project planning and the Quality Assurance Project Plan (QAPP) conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) QA Representative will verify that the QAPP is comprehensively developed and implemented.

The LM Task Lead will be responsible for ensuring that:

- the QAPP is implemented,
- the project schedule is followed,
- decisions are made concerning any necessary adjustments or clarifications to procedures during implementation,
- procedural documentation is regularly reviewed,
- deliverables meet the goals of the project,
- communications with the Client Representative are maintained, including reports of any major problems, required modifications to the QAPP, and draft and final written reports.

Both LM and EPA personnel will participate in field efforts. The sampling personnel will be responsible for conducting the field procedures in accordance with this QAPP, implementing the

sampling of soil vapor and soil, and recording technical observations and environmental conditions during field operations as specified in this QAPP.

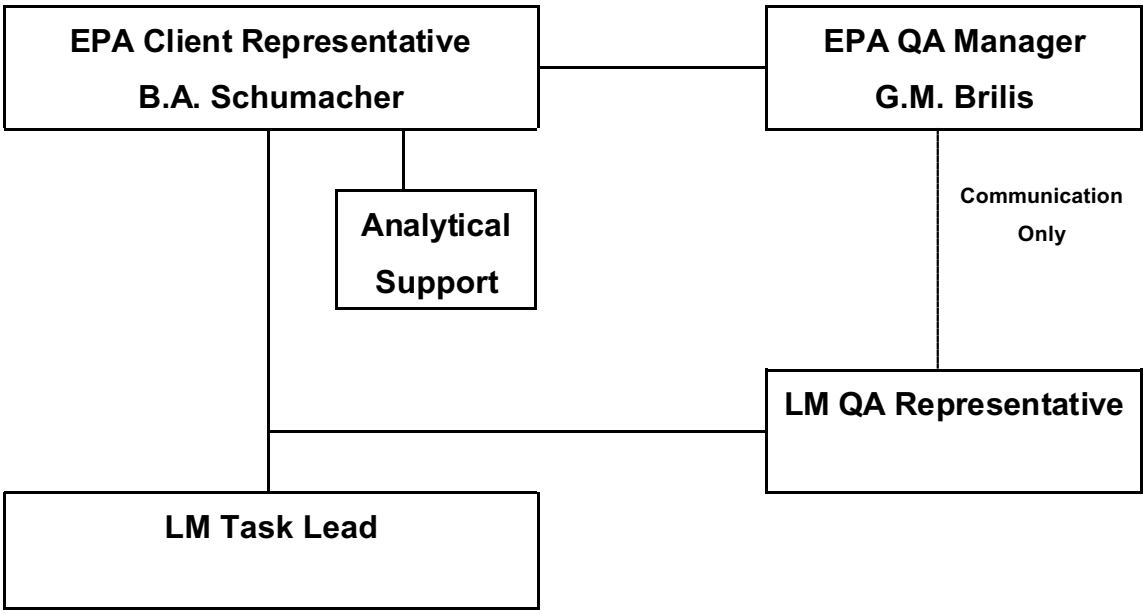

Figure 1. Project Organization Chart

2. Problem Definition

Improved methods for the sampling and analysis of soils containing VOCs have emphasized techniques to minimize the loss of these contaminants. Guidance in Update III of SW-846 Method 5035 recommends that soil samples taken for VOC analysis are immediately sealed in 1) sample vials containing a preservative/extractant, or 2) hermetically sealed sampling devices (e.g., EnCore™, SoilCore™) from which they will be transferred to sample vials as soon as possible, or analyzed within 48 hr (USEPA, 1997). Samples thought to contain low levels (<200 µg/Kg) of VOC contamination are preserved/extracted with a 5-mL aliquot of an acidified water

solution. Samples thought to contain high levels (>200 µg/Kg) of VOC contamination are preserved/extracted with a 10-mL aliquot of methanol. Method 5035 (USEPA, 1997) specifies that the preservative/extractant is aliquoted into the sample vial prior to the addition of the soil sample. Although it is anticipated that most samples will be processed using the procedure as written (i.e., addition of soil to a vial already containing the preservative/extractant), there are likely to be occasions when preservative addition will follow the placement of the soil into the vial. The effect of the order of preservative/extractant addition on VOC recovery has not been definitively demonstrated.

Jenkins and Schumacher (1987) addressed this issue in a paper using tetraglyme as an extraction solvent for VOCs in soil. Two sets of five aliquots of a dry soil were spiked with chloroform, benzene, trichloroethylene (TCE), and toluene. Each set was processed by one of two treatments:

1) The preservative/extractant was aliquoted into a sample vial followed by the addition of the soil sample.
2) The soil sample was placed into a sample vial and allowed to stand for one minute, after which the preservative/extractant was added.

At the 95% confidence level there was a significant difference between the results from the two procedures for the more volatile compounds (i.e., chloroform and benzene). Treatment 1 samples exhibited higher mean recoveries for chloroform (16.0%) and benzene (10.4%) than the recoveries measured on samples processed with Treatment 2.

Hewitt and Lukash (1996) conducted an experiment to quantify the effect of the addition of water to a soil sample after it had been transferred to an empty sample vial (experimental), compared to samples transferred to sample vials already containing water (control). Sixteen subsamples of TCE-contaminated soil were collected at each of four depths (38, 40, 43, and 45 cm below ground surface). At each depth, four sets of four random subsamples were composited into sample vials (a total of 16 composite samples). Presumably to minimize the effects of spatial

variability, two of the four samples from each depth were processed as controls and two were processed by the experimental parameters as described below in Table 1:

Table 1. Experimental Parameters from Hewitt & Lukash (1996)

Sample Depth (cm)	Time lapse prior to addition of water (min)	Temporary Cap
38	2	Parafilm® "M"
40	20	PTFE-faced, gray butyl rubber septa and aluminum crimp top
43	200	PTFE-faced, gray butyl rubber septa and aluminum crimp top
45	0.1	None

From the results (Table 2), the authors concluded that even with the immediate addition of water to samples from the 45 cm depth, measurable TCE was lost as compared to the control. However, the time required to composite the four small plugs into a vial might have contributed to the analyte losses reported for the experimental samples.

Table 2. Analytical Results for Duplicate Samples
(Hewitt & Lukash, 1996)

Sample Depth (cm)	TCE Conc. (ug/g)	
	Control	Experimental
38	1.7, 1.6	0.50, 0.50
40	1.7, 1.5	0.53, 0.69
43	1.9, 2.1	0.60, 0.59
45	1.7, 1.6	1.3, 1.1

Further investigation is needed on the timing of preservative/extractant addition and its correlation to the measured soil VOC concentration. These investigations should determine not only the most appropriate order of addition of preservative/extractant but also the effect of other parameters (e.g., different soil types, compound concentrations, different compounds) upon a selected addition technique.

3. Project Description

The purpose of this study is twofold: to determine the correlation between the timing order of addition of a preservative/extractant to soils containing a known amount of VOCs and the losses of those VOCs from the soils; and to observe the effect of soil and compound characteristics on this correlation. Three soils with varying properties will be fortified with VOCs for use in this study. One third of the subsamples for each fortified soil will placed into vials that contain a preservative/extractant (Treatments 1 and 4). One third of the subsamples for each fortified soil will be placed into empty vials and the preservative/extractant added to the vials (Treatments 2 and 5). The remaining third of the subsamples for each fortified soil will be placed into empty vials, sealed, and stored chilled for 24 hr, after which the preservative/extractant will be added to the vials (Treatments 3 and 6). The effect of these treatments will be quantified as the recovery

of the individual VOCs from the fortified soils. Soil properties that will be examined for correlations are percent sand, silt, clay, and organic carbon.

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. Data quality objectives (DQOs) for measuring VOC concentrations in soil are discussed below. Quality control samples and their associated DQOs are discussed in Section 8.

4.2 Instrument Measurement Performance Criteria

Precision will be established for each analyte as the percent difference (%D) of ongoing calibration standard responses. The DQO for precision will be to achieve an %D of $\leq$ 15% between the mid-point standard of the initial calibration curve and ongoing calibration check standards.

Bias in the analytical system will be determined by comparing the concentrations determined from the initial calibration curve with the concentration of a second-source-certified multicomponent standard. The second-source standard will be analyzed once for each initial calibration curve. The DQO for bias will be a %D $\leq$ 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. A gas chromatograph/mass spectrometer (GC/MS) IDL DQO of 10 ng on-column for each analyte of interest is expected.

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. If the client directs LM to prepare a QA report, final report, or draft article, the client will provide all required data in electronic and hard copy formats. 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. If the client prepares a QA report, final report, and/or draft article, copies of all records of the study in the custody of LM will be supplied to the client.

B. Data Acquisition

6. Experimental Design

This study consists of six treatments, half of which use water as the preservative/extractant and half which use methanol as the preservative/extractant. Subsamples of three soils will be identically fortified with eight VOCs. Soil VOC concentrations will be measured in seven soil replicates for each of the six treatments, for each of four soils (126 samples total). All prepared vials for all treatments will be stored at 4°C until analyzed. All samples will be analyzed within 72 hr of preparation.

The preservatives/extractants to be used in this study are those specified in USEPA Method 5035 for low- and high-concentration soil samples. Samples for this study will be analyzed by purge-and-trap/gas chromatography/mass spectrometry (PT/GC/MS) in accordance with SW-846 methods 5035 and 8260 (discussed in Section 7). Soils to be used in this study are described in Table 3. Analytes to be used in the study are benzene, toluene, ethyl benzene, o-xylene, chlorobenzene, 1,1-dichloroethene, TCE, and tetrachloroethene (PCE).

Table 3. Characteristics of Soils

Soil Designation	Soil Horizon	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)
Hayesville	B	46	22	32	0.2
Charleston	A	61	31	8	3.8
New England A	A	47	48	5	4.2

6.1 Fortification of Soils

Soils will be spiked and subsampled one soil at a time, to permit the analysis of one set of samples to be completed before spiking samples of the next soil. A methanolic stock solution of the eight analytes at 400 µg each analyte/mL will be prepared from certified standards. The petroleum aromatics will be obtained as a 2000 µg/mL standard mixture and the chlorinated analytes obtained as individual 2000 µg/mL standards. Two milliliters of each of the five standards will be mixed to obtain 10 mL of a stock standard at 400 µg/mL.

Water Extraction Treatments - For each of the soils in Table 3, 100 g of air-dried soil will be placed in a paint can and mixed with water to achieve 10% to 20% gravimetric water content, based on observation, in order to obtain a soil consistency that is easily homogenized. An aliquot of the VOC stock spiking solution (100µL) will be injected into the soil just prior to sealing the can to achieve a moist, spiked soil with target analytes at 400 ng/g dry soil. The fortified soil will be mixed on an end-over-end mixer for 24 hr and then refrigerated at 4 °C to lower the vapor pressure of the headspace prior to subsampling. During the subsampling procedure the moist, fortified soil will be kept chilled (approximately 0 °C) with the use of an overpack of ice water or blue ice and water.

Methanol Extraction Treatments - For each of the soils in Table 3, 200 g of air-dried soil will be placed in a paint can. As above, the soils will be moistened to achieve 10% to 20% gravimetric water content based on observation, in order to obtain moist, but not wet, soil. An aliquot of the VOC stock spiking solution (600 µL) will be injected into the soil just prior to sealing the can to achieve a spiked soil with target analytes at 1200 ng/g dry soil. The moist, fortified soil will be mixed on an end-over-end mixer for 24 hr and then refrigerated at 4 °C to lower the vapor pressure of the headspace prior to subsampling. During the subsampling procedure the moist, fortified soil will be kept chilled with an overpack of ice water or blue ice and water.

6.2 Treatments

The water or methanol preservative/extractant will be aliquoted into the vials using a repipetter. The average weight of the water and methanol aliquots will be determined by measuring the weight of five subsamples of water and five subsamples of methanol dispensed from the repipetter. Soil will be subsampled using a truncated, 10-mL, disposable syringe. All weights will be recorded to the nearest 0.01 g. The sample tracking form for recording weights is shown in Figure 2.

Sample ID	Weight before soil	Weight after soil	Soil Weight

Figure 2. Sample Weight Tracking Form

Water Extraction - The procedures for preparing the replicates of the three treatments are as follows:

Treatment 1 - An aliquot (5 mL) of water and a stir bar are added to a vial and the weight of the vial, cap, and contents is recorded. A subsample (~2 g) of the moist, fortified soil is added to the vial and the vial is sealed. The vial is then reweighed and the weight recorded.

Treatment 2 - A vial and cap plus stir bar is weighed and the weight recorded. A subsample (~2 g) of the fortified, moist soil is placed in the vial. A 5-mL aliquot of water is added to the vial, the vial is sealed, reweighed, and the weight recorded.

Treatment 3 - A vial and cap plus stir bar is weighed and the weight recorded. A subsample (~2 g) of the fortified, moist soil is placed in the vial. The vial is then sealed, reweighed, and the weight recorded. After storage of the vial at 4 °C for 45 - 60 hr (to simulate shipping time from field site), the sample will be analyzed. An aliquot of water (10 mL) will be added to the vial by the autosampler at the time of the analysis.

Methanol Extraction - The procedures for preparing the replicates of the three treatments are as follows:

Treatment 4 - An aliquot (5 mL) of methanol is added to a vial and the weight of the vial and cap plus methanol is recorded. A subsample (~5 g) of the moist fortified soil is added to the vial and the vial is sealed. The vial is then reweighed and the weight recorded.

Treatment 5 - A vial plus stir bar is weighed and the weight recorded. A subsample (~5 g) of moist, fortified soil is placed in the vial. Methanol (5 mL) is added to the vial and the vial is sealed. The vial is then reweighed and the weight recorded.

Treatment 6 - A vial and cap plus stir bar is weighed and the weight recorded. A subsample (~5 g) of moist, fortified soil is placed in the vial. The vial is then sealed, reweighed, and the weight recorded. After storage of the vial at 4 °C for 22 - 28 hr (to simulate shipping time from field site), an aliquot (5 mL) of methanol will be added to the vial, and the vial will be resealed and stored at 4 °C for a minimum of 20 hr before an aliquot of methanol is removed for analysis. Samples will be analyzed no longer than 72 hr after soil was placed in the vials.

Sequence of Sample Preparation - All water treatments for a particular soil will be prepared, followed by all methanol treatments, to avoid opening two cans of spiked soil concurrently. During the subsampling, replicate subsamples of each moist, fortified soil will be prepared in rounds to minimize potential bias caused by volatilization. Round 1 will start with the addition of a soil subsample to a Treatment 1 vial, then the addition of soil subsamples to the other two types of water treatment vials, in sequential order. Round 2 starts with a Treatment 2 vial, and so on until all seven replicates for each of the three treatments have been prepared for a total of seven rounds (Table 4). Treatments 4 through 6 will repeat the sequence, beginning with Treatment 4, replicate 1 and ending with Treatment 6, replicate 7.

Sample Storage - The samples will be stored in a refrigerator at 4 °C until analyzed. Sample analysis will begin 40 - 60 hr after sample preparation to simulate shipping and handling time of samples sent from a field site. Sample analysis for these treatments should be completed within 72 hr of sample preparation.

Table 4. Sequence for Preparation and Analysis of Samples[a]

Round	Treatment - Replicate	Treatment - Replicate	Treatment - Replicate
1	1-1	2-1	3-1
2	2-2	3-2	1-2
3	3-3	1-3	2-3
4	1-4	2-4	3-4
5	2-5	3-5	1-5
6	3-6	1-6	2-6
7	1-7	2-7	3-7

[a]Treatments 1 through 3 in the table represent treatments 4 through 6 when methanol is the preservative/extractant.

6.3 Sample Tracking

Samples will be labeled according to soil, treatment, and replicate number. The soil type will be indicated with a two-letter code. Treatments will be numbered 1 through 6 and replicates will be numbered 01-07. For example, a sample ID "HA-2-03" would represent the Hayesville soil, Treatment 2, replicate 3. Sample ID numbers and weights will be entered on the Soil Sample Tracking Form during sample preparation; other pertinent information concerning sample handling will be recorded in the laboratory notebook. Analytical data will be tracked by entering the sample ID at the time of analysis and delivering both hard copy and electronic copies of the data for transfer onto the spreadsheets and statistical packages for analysis. A printout of the analytical sequence file, including the sample ID and volume of water added by the autosampler will be part of the raw data package.

6.4 Design Rationale and Assumptions

These experiments have been designed with the assumption that, in general, soil-to-soil variability will be greater than within-soil variability and that water treatments will not necessarily be comparable to methanol treatments. Therefore, Treatments 1 through 3 will be compared within each soil type and Treatments 4 through 6 will be compared within each soil type. Each analyte will be treated as an independent variable because of previous evidence that the physicochemical properties of each compound leads to independent data for different compounds.

The superior order of addition of the preservative/extractant to the soil sample will be defined as the protocol which provides a statistically significant higher mean recovery of one or more analytes from a soil. A multiple regression technique may be applied to determine the degree to which the soil characterization parameters are useful for predicting the appropriate order of addition of preservative/extractant to different soil types for each type of preservative/extractant.

7. Analytical Methods

VOCs will be quantified in the soil samples by PT/GC/MS at the EPA ESD-LV laboratory. Extraction/sample introduction by SW-846 Method 5035 (modifications as described below) will be used in conjunction with analysis via SW-846 Method 8260B (USEPA, 1992). The handling, preparation, and analysis of soil samples will be performed as generally described in CMB SOP #310, *Analysis of Volatile Organics in Soil using Purge-and-Trap/ Gas Chromatography/ Mass Spectrometry*. Sample containers to be used for soil storage and analysis are precleaned, 40-mL glass vials with Teflon®-lined, septum-sealed screw caps, commonly known as VOA vials. Samples are to be analyzed in the same order they were prepared to minimize potential analytical bias between treatments.

Water Extraction - SW-846 Method 5035 - Treatments 1 and 2 samples will have 5 mL of water added to the vials and Treatment 3 samples will have 10 mL of water added to the vials by the automated purge-and-trap instrument. Internal standards (ISs) and surrogates will be introduced with the water. The instrument will be calibrated for the analytes of interest only. Required QC samples are described in Section 8.

Methanol Extraction - SW-846 Method 5035 Modifications - A 100-µL subsample of each high-level soil sample methanol extract will be analyzed as a Method 5035 low-level soil. The subsample will be transferred to a 40-mL VOA vial. Water (10 mL) containing the ISs and surrogates will be added to the vial by the automated purge-and-trap instrument. Smaller aliquots of the methanol will be analyzed if necessary to bring the instrument response within the calibration curve.

8. Analytical Quality Control

The laboratory must adhere to the quality control (QC) procedures specified in methods 5035 and 8260 and the project-specific acceptance criteria described in this section. The method QC components are summarized in Table 5.

8.1 GC/MS Mass Calibration

A mass calibration or tune of the analytical system is performed when the system is initially set up, after the mass spectrometer has been shut down, or whenever there is a mass misassignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perflurotributylamine (FC43) is the compound which is used to perform the mass calibration of the instrument. The FC43 spectrum must meet the criteria presented in Appendix A. If the criteria are not met the system must be retuned or instrument maintenance must be performed until the system can meet the criteria.

Table 5. QC Procedures, Acceptance Criteria, and Corrective Actions

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Mass Calibration (Tune/FC43)	Initial system startup, after system shutdown, if mass misassignment occurs	See Appendix A	Perform autotune, instrument maintenance
Tune Check Standard (BFB)	Beginning of 12-hr analytical period	Ion abundance ratio, see Appendix B	Perform instrument maintenance, reanalyze, retune
Initial Calibration (IC)	Prior to initial sample analysis, and if OCCS fails	%RSD ≤ 20%	Determine problem, correct, reanalyze
Quality Control Check Standard (QCCS)	Each time a new IC is analyzed	%D ≤ 20% of IC responses	Reanalyze, check all calculations, obtain new lot or manufacturer's QCCS
Instrument Detection Limit (IDL)	Prior to sample analysis	Meet IS %R and surrogate %R	Perform instrument maintenance, and/or reanalyze
Ongoing Calibration Check Standard (OCCS)	Beginning and end of each 12- hr analytical period	%D ≤ 15% of mid-point IC standard response	Reanalyze std., perform instrument maintenance, new IC, reanalyze, flag data "D"
Instrument Blank (IB)	Beginning of each 12- hr analytical period	Below analyte IDL or sample values ≥ 5x IB concentration	Reanalyze, perform instrument maintenance, flag data "B"
Internal Standard (IS) Recovery	Each sample, blank, and standard	%R = 50% to 200%	Reanalyze if blank, standard or methanol trt; flag data "I"
Surrogate Recovery	Each sample, blank, and standard	%R= 100% ± 25%	Reanalyze if blank, standard or methanol trt; flag data "S"

8.2 Tune Check Standard

Prior to the start of sample analysis and at the beginning of each 12-hr analytical period a GC/MS tune check standard is to be analyzed. The tune check standard is a solution containing the compound 4-Bromofluorobenzene (BFB) at a concentration of 25 ng. Proper tuning of the mass spectrum is necessary to produce standardized fragmentation patterns of target and non-target compounds. The mass spectrum produced for the BFB must meet all of the criteria in Appendix B. If the criteria are not met then the instrument must be retuned.

8.3 Initial Calibration

An initial calibration (IC) curve is generated before any samples are analyzed (Section 9). The acceptance limit of the IC curve is an RSD of the response factors $\leq$ 20%. If the IC curve or ongoing calibration check data are outside of the method QC requirements, the analyst must determine the source of the problem, make any necessary adjustments (to instrument, software, or standards), and recalibrate the instrument.

8.4 Quality Control Check Standard

The Quality Control Check Standard (QCCS) is analyzed immediately following every initial calibration of the instrument. The QCCS is a second-source-certified standard that is analyzed to ensure the accuracy of the standard used to calibrate the instrument. The QC acceptance criteria are %D $\leq$ 20% for each of the nominal analyte concentrations. The corrective action if the QC acceptance criteria are not achieved is to reanalyze the QCCS; if the results do not meet criteria, the reason must be determined prior to analysis of samples.

8.5 Instrument Detection Limit

The instrument detection limit (IDL) will be determined using the standard deviation of seven replicate standards, spiked at a low concentration (≤20 ng). Each of the replicate samples are expected to meet the criteria for IS and surrogate recoveries. The anticipated IDL is 10 ng on-column for each of the target analytes.

8.6 Ongoing Calibration Check Standard

The Ongoing Calibration Check Standard (OCCS) is analyzed several times each day: 1) following the BFB and instrument blank; 2) at the end of each 12-hr analytical time period; or 3) at the end of the analysis sequence within a 12-hr analytical time period. The results of the OCCS are used to verify the stability of the instrument response. The QC acceptance criteria are %D ≤ 15 % of the nominal values of the midpoint calibration standard. The corrective actions for a OCCS outside the QC acceptance criteria are: 1) reanalyze the OCCS once; 2) if the QC criteria are still not met, the reason must be determined and corrected prior to sample analysis; or 3) if the ending OCCS is out of QC acceptance criteria, samples are to be flagged and/or reanalyzed. The data from samples with water as the preservative/extractant (Treatments 1, 2, and 3) must be flagged with a "D" if the instrument was out of calibration. Samples prepared with methanol as the preservative/extractant (Treatments 4, 5, and 6) should be reanalyzed if possible, or flagged with a "D" otherwise.

8.7 Instrument Blanks

Instrument blanks (IBs) are used to monitor instrument contamination. An IB will be included at the beginning and end of each 12-hr analytical period or more often if the analyst deems necessary. If the blank is contaminated with target analyte(s) above the analyte IDL, samples should not be analyzed until corrective action has been taken. If the blank at the end of a sampling period is contaminated, sample data will be considered acceptable if the target analyte concentration(s) are at least five times greater than the blank concentration(s) for the offending

analyte(s). If contamination can not be eliminated or the sample concentrations do not meet the aforementioned criteria, results for all samples associated with the contaminated blank must be flagged "B."

8.8 Internal Standards

The Internal Standards (IS) are added by the autosampler into every standard, blank, and sample analyzed. The IS are used in the quantification of detected compounds, to take into account any changes within the mass spectrometer during the analysis. The IS QC acceptance criteria are %Rs = 50% to 200% of the mean IC values. The corrective actions for IS recovery outside the QC acceptance criteria are: 1) reanalyze the sample once; 2) if the QC criteria are still not met the reason must be determined and corrected prior to further sample analysis. All data with IS recoveries outside the QC criteria are to be flagged with an "I."

8.9 Surrogates

The surrogate compounds are added by the autosampler into every standard, blank and sample analyzed. The surrogate compound recoveries are used to monitor the purge and GC components of the analysis system. The QC acceptance criteria are %Rs ± 25% of the spiked values. The corrective action for surrogate recoveries outside of the criterion is to reanalyze any blank, standard, or the sample treated with methanol as the preservative/extractant. If the QC criteria are still not met the reason must be determined and corrected prior to further sample analysis. Any sample data with surrogate recoveries outside the QC criteria are to be flagged with an "S."

8.10 QC Calculations

Precision - Precision represents the reproducibility of measurements under a given set of conditions and provides an estimate of random error (Taylor, 1987). Instrument precision will be

monitored by analyzing ongoing calibration check standards. The percent difference (%D) 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.

The precision of the laboratory preparation of moist, VOC- fortified soils is confounded with the analytical precision. It will be calculated as the relative standard deviation (RSD) of the seven replicate measurements of each soil.

$$RSD = \frac{SD_{n-1}}{mean} \times 100$$

where SD_{n-1} = standard deviation of the replicate measurements. RSDs will be calculated for each VOC in each soil by treatment. These replicates will be used to determine the sum of the analytical and soil sample preparation precision.

Bias - Laboratory bias will be estimated by (1) the %D of the target analytes measured in the QCCS versus the midpoint standard of the IC curve, and (2) %R of the surrogates. Percent recovery of the surrogates will be calculated as follows:

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

where S is the measured concentration and C_{sa} is the nominal concentration of the standard or surrogate.

IDL - The IDL will be 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 (USEPA, 1992).

9. Instrument Calibration and Frequency

The instrument will be calibrated as specified in SW-846 Method 8260 in conjunction with modified SW-846 Method 5035 (USEPA, 1997). Modifications include a reduced list of target analytes, no system performance check compounds, and no laboratory matrix spike/matrix spike duplicate samples. All samples will be analyzed as low-level soil samples on a single calibration curve. The five-point calibration curve (IC), consisting of standards at the nominal concentrations of 10, 100, 500, 750, and 1000-ng total on-column, will be prepared for each analyte of interest. A new calibration curve is warranted if fresh OCCS samples do not meet the acceptance criteria (Table 5).

10. Data Management

The EPA Client Representative will be responsible for the management of all laboratory-generated data. If the Client Representative tasks LM to prepare a final report, the EPA will provide a copy of all VOC data, soil characterization data, and associated QC data. Lockheed Martin will assume data management responsibility for steps associated with analyzing the data and writing the report. If the Client Representative prepares the final report, LM will provide all data to the EPA. The task of data management for this study includes: (1) maintaining unique data labels, (2) tracking QC data with sample data, (3) tracking sample dilutions and instrument replicates (4) tracking soil moisture data to correct results to a dry weight basis, (5) creating

spreadsheet macros to transfer the electronic data from one software environment to another, minimizing errors that can accumulate from transferring large amounts of data, and (6) maintaining electronic backup of data.

C. Assessment/Oversight

11. Assessment and Response Actions

Problems that arise beyond any anticipated in this QAPP may be caused by uncontrolled laboratory factors such as spurious contamination, instrument malfunctions, or data analysis software problems. Corrective actions for non-routine problems generally require an assessment of the options with respect to project objectives, schedule, and cost considerations. LM management and the Client Representative will be notified of any problems encountered during project implementation and will be directly involved if corrective actions require additional resources. The Client Representative will be consulted if there are any modifications to, or significant deviations from this QAPP.

12. Reports to Management

The Task Lead will be responsible for monthly progress reports to the Client Representative. Separate written communications will be forwarded to the Client Representative regarding any modifications to this QAPP. If the Client Representative requests a draft report it will include a project summary, a description of the methods, analytical results, and a discussion of the results. Appendices will include: (1) a copy of all raw data, and (2) a QA report which outlines the results of QC procedures and discusses these results with respect to the initial project and QA objectives.

D. Data Validation and Usability

13. Data Review, Validation, and Verification Requirements

Results will be considered valid for a characterization parameter if all applicable QC data are within method or QAPP-specified acceptance windows. Any data generated with the corresponding BFB, OCCS, IB, IS, or surrogates outside of the expected range will be flagged and discussed in the QA 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

A Data Quality Assessment (DQA) process will be used for reconciliation of DQOs. This process is designed to determine how well the data satisfy their intended use. The assessment process will be performed as follows:

(1) A review of all data will be conducted to assess the quality with respect to the QC parameters.

(2) Once the data have been verified to be of acceptable quality, means and standard deviations will be calculated and graphs of the data generated. Plots of soil VOC concentrations and standard deviations will be generated for each soil, by treatment. This information will be used to identify patterns, relationships, or potential anomalies.

(3) An analysis of variance procedure and means difference testing will be conducted to determine statistically significant differences ($p \leq 5\%$) among the treatments. Other statistical tests may be selected based on the distribution of the data both within and between treatments. All assumptions for any statistical procedures deemed appropriate will be identified and verified as acceptable.

(4) Conclusions will be drawn, based on the results of the statistical tests. All steps will be described in the written report.

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Appendix A
Mass Calibration Criteria

Mass Ratio

Mass (m/z)	Target Percent of Mass 69
69	100
131	25.0 - 60.0
219	25.0 - 60.0
414	1.4 - 4.0
502	0.8 - 4.0

Isotope Ratio

Mass Ratio	Target Percent
70/69	0.8 - 1.3
132/131	2.0 - 3.4
220/219	3.5 - 5.2
415/414	7.2 - 10.8
503/502	8.1 - 12.1

Appendix B

BFB Ion Abundance Ratio Criteria

Mass (m/z)	Relative Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	Base Peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2 percent of mass 174
174 *	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

* All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.