Quality Assurance Project Plan for

EFFECTS OF SOIL DISTURBANCE ON
VOC EMISSIONS FROM AGED, CONTAMINATED SOIL

Task Order No. 9T2Z054TMA
Contract No. GS-35F-4863
Document Control No. QAO 4-2

by
Lockheed Martin Environmental Services
Las Vegas, Nevada 89119

for
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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, Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), is responsible for direction and oversight of this project. He will also supervise all laboratory analytical work on this project. George Brilis, ESD-LV Quality Assurance (QA) Manager, will ensure that the project conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) QA Representative will verify that the Quality Assurance Project Plan (QAPP) is comprehensively developed and implemented. and will provide data review and technical editing on project reports as needed.

The LM Task Lead will be responsible for ensuring that:
- the QAPP is implemented,
- procedural documentation is regularly reviewed,
- necessary procedural adjustments/clarifications are made during project implementation,
- LM operations conform to the project schedule,
- deliverables meet the specifications of the project,
- communications with the Client Representative are effective, including reports of any major problems, required modifications to the QAPP, and draft and final reports.

Both LM and EPA personnel will participate in the field efforts. The sampling personnel will be responsible for conducting all field sampling and handling operations in accordance with this QAPP. Lockheed Martin personnel will also provide technical support for the laboratory procedures as needed.
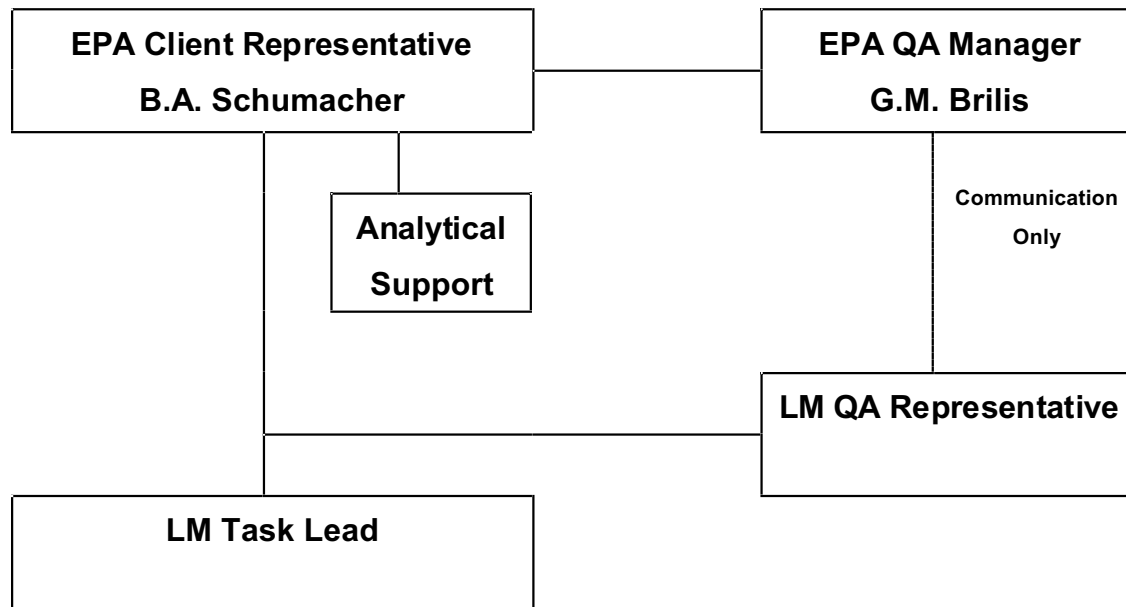
Figure 1. Project Organization Chart

2. Problem Definition

A soil exposed to volatile organic compounds (VOCs) may remain contaminated for years. Rates of volatilization, mass flow, leaching, and degradation all tend to decline within a short time after the contamination event due to the decreasing concentration of the contaminant(s). The residual concentration of VOCs in soil is generally understood to exist as small, *in situ* globules of the contaminants, plus any product that has diffused into soil micropores or soil organic matter (Steinberg et al., 1987; Ball and Roberts, 1991; Pignatello and Xing,1996).

The EPA is interested in determining the vapor release rate of residual VOCs months or years after a contamination event. In particular, the EPA would like to gather data to evaluate the

potential for human exposure should someone dig, churn, or otherwise displace VOC-contaminated soil. To obtain such data, an approach must be selected that can measure VOC vapors in the field as the soil is disturbed. The technique would ideally measure low contaminant concentrations, i.e., parts per billion/volume (ppbv) in air, and track the release rate of VOCs to determine changes in the concentration occurring over a few minutes. The air sampling should relate the quantity of VOCs to a specific area or volume of soil.

These data could be utilized by atmospheric scientists or air monitoring specialists for exposure assessments or for model estimates of soil contributions to atmospheric contamination. Data could also be used in conjunction with other soil characteristics which influence the vapor loss rates to estimate contaminant losses occurring during field sampling for soil VOCs.

3. Project Description

The investigations are based on measuring the release of VOCs: (1) from an "intact" soil core immediately after removal from its native position in the field, and (2) after the same soil core is disaggregated. These measurements of contaminant vapors will be repeated on cores at four diverse sites to compile data on the release of VOCs from different soil types under varying conditions. Soil immediately above and below the test core will be collected and analyzed for soil VOC concentration, gravimetric moisture content, particle size distribution, and organic carbon content. This gross characterization of the soils in the study will offer some guidelines for determining which soil factors influence the rate of VOC vapor release from contaminated soil.

Briefly, the procedures in this study rely on collecting the air flowing through a small chamber containing the contaminated soil. An intact soil core, approximately 3" diameter by 3" length, will be placed in the chamber. Inlet air will be circulated through a charcoal filter and outlet air through sorbent tubes destined for analysis by thermal desorption (TD). The outlet air will be split with a Y- tube to generate duplicate adsorption sample tubes. The VOC vapors in the

chamber air will be collected in four 5-minute intervals: (1) immediately after placing an intact core in the chamber, (2) after disaggregating the soil core, and (3) once again on the disaggregated soil to monitor the vapors during a second and third 5-minute interval. All adsorption tubes will be shipped to the Las Vegas EPA laboratory in chilled containers and analyzed for VOCs by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). The sample preparation, analytical methods, and storage parameters for the TD/GC/MS procedures are taken from Pankow et al. (1998) and Compendium Method TO-17 (USEPA, 1997). Soil VOC concentrations of the test cores will be estimated based on analyses of subsamples from the soil immediately above and below the each core using both high- and low-level purge-and-trap/GC/MS methods (SW-846 Methods 5035 and 8260, USEPA, 1997a and USEPA, 1998). These subsamples, along with the soil characterization subsamples, will also be shipped to the Las Vegas EPA laboratory in chilled containers.

Laboratory start-up time (instrument calibration, tube precleaning, internal standard addition to tubes, preparation of travel spike samples, etc.) is expected to require approximately 4 weeks before the first field sampling expedition and approximately 1 week before any subsequent trips. The field sampling is expected to be conducted in two 1-week sampling trips. The laboratory analysis of the samples may require up to 2 weeks for each week of field work, to be completed no later than 3 weeks after the last field samples are shipped (adhering to a 27-day holding time for the TD samples).

4. Data Quality Objectives

4.1 Project Quality Objectives

The project objectives are to determine the VOC vapor release rates from numerous field-contaminated soils and to compare the rates of release among the soils. Data will be collected from moderately to highly contaminated samples at four sites with varying physical and chemical characteristics. VOC vapor concentrations and rates of release are expected to be influenced by

the soil contaminant concentrations, the nature of the contaminants, the soil type, and the environmental conditions (e.g., ambient temperature during sampling). To facilitate comparability of the data among sites, analytical bias will need to be tightly controlled. These data are expected to be of value to researchers interested in VOC emissions resulting from physical disruption of a soil matrix, as might be caused by children digging in contaminated soil. Analytical or measurement quality objectives (MQOs) are set for precision, bias, and detection limits. The ambient field temperature and barometric pressure will be recorded as each set of vapor samples are collected from a soil core (to correct for the molar volume of air, see Appendix 1). The laboratory MQOs for each type of analyses are given below. Details about the QA/QC samples, frequency of analysis, and corrective actions are discussed in Section 8.

4.2 Measurement Performance Criteria–VOCs

Precision for each VOC on each analytical system (thermal desorption and purge-and-trap) 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.

Bias for each VOC on each analytical system 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. For both TD and purge-and-trap analyses, the MQO for bias will be a %R of $100 \pm 20\%$. Bias arising from transport and storage of the TD tubes and the methanol extracts of soil VOCs (high-level samples) will be determined from the recoveries of the travel spikes. The MQO for bias in the travel spikes will be a %R of $100 \pm 25\%$ of the nominal value.

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. An IDL of 20 pmole on-column for each analyte of interest is the objective for the TD/GC/MS system. The

IDL for the purge-and-trap GC/MS system is 10 ng on-column for each analyte of interest.

4.3 Measurement Performance Criteria–Other Parameters

For the organic carbon analysis, precision will be assessed with sample duplicates. The MQO is an absolute difference $\leq$ 5% (organic carbon results will be reported as percent of the soil sample weight). The bias will be assessed using a purchased standard, preferably a soil standard; the standard will receive the same pretreatment as the soil samples. The MQO for bias is a %D $\leq$ 10 between the measured and the nominal standard concentration.

For particle size analysis (PSA), precision will be expressed as the percent relative standard deviation (%RSD) of laboratory soil standard replicates. The MQO is an RSD $\leq$ 20% for sand and silt fractions. Bias will be assessed as the ongoing agreement of a laboratory standard (a test soil run with every batch at the EPA laboratory). The MQO is $\leq$ 15 %D between the mean percent sand and silt (laboratory average) and specific batch data for each size fraction. PSA detection limit is not an issue of concern for this project.

5. Documentation and Records

All VOC data will be generated in electronic and hard copy formats via the instrument-associated software. For the vapor samples, identification and collection data will be recorded on field forms for TD tubes, in the field logbook, and in the instrument sequence files prior to analysis. The TD tubes will be etched with consecutive numbers for temporary identification of the sample outside of the plastic storage bags. Soil VOC sample vials will be labeled in the field using indelible ink, and recorded in the field logbook and instrument sequence files. Instrument output will be transferred to electronic spreadsheets for analysis and presentation.

Soil moisture data, organic carbon analyses, and PSA will be tracked by a sample identification number recorded on the sample container, entered into the field logbook, and entered into an

electronic spreadsheet after generation of the results. Laboratory replicates of a soil sample will be labeled with a trailing "a," "b," etc. All records of the study generated during data analysis by LM will be maintained by for two years after the final report is accepted and then transferred to the EPA Client Representative for storage.

B. Data Acquisition

6. Experimental Design

The study is designed to investigate the release of VOC vapors from a known volume of contaminated soil before and after disrupting the sample. The term, "before disruption," is loosely used because the soil core will be removed from its *in situ* location and placed in a chamber, using care not to disaggregate the sample during this transfer. The release of VOC vapors from the intact core will be monitored, followed by disturbance of the core and three sets of VOC vapor measurements from the disturbed core.

Six cores will be monitored from each of four sites. By using the Y-tube splitter, each of the cores will generate eight VOC vapor samples: one set of duplicates before disturbing the soil and three sets of duplicates after disturbing the soil. Soil VOC samples will include one sample for the low-level method and one sample for the high-level method (in methanol), with duplicates for each of these methods collected twice per site. Additional soil associated with each test core will be collected in a quantity sufficient for analyzing duplicate samples for organic carbon analysis, single samples for PSA, and a subsample for soil moisture content.

6.1 Site Selection

The EPA Client Representative will identify appropriate field sites and secure access to such 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, (2) the contamination

event(s) must have occurred at least 5 years prior to sampling, and (3) the site will contain no known contamination with PCBs. Sites will be selected to collect data from different soil types; various VOC compounds may be present at the sites. The contamination may extend below the surface into the groundwater, but contaminated soil to be used in this study should be accessible within 2 m of the surface.

Table 1. Project VOCs and Selected Properties

Compound	MW (g mole^{-1})	Vapor pressure[a] (mm Hg, 25 $^{\circ}$C)	Henry's Constant[a] (atm m^3 mole^{-1})
chloroform	120	246	4.35 x 10^{-3}
1,1-dichloroethane	99	227	5.87 x 10^{-3}
cis 1,2-dichloroethene	97	200 (35 $^{\circ}$C)	3.37 x 10^{-3}
1,1,1-trichloroethane	133	124	8.00 x 10^{-3}
benzene	78	95	5.43 x 10^{-3}
1,2-dichloroethane	99	79	9.77 x 10^{-4}
trichloroethene (TCE)	131	69	10.30 x 10^{-3}
toluene	92	28	5.94 x 10^{-3}
tetrachloroethene (PCE)	166	18	14.90 x 10^{-3}
chlorobenzene	113	12	3.45 x 10^{-3}

[a] from Howard et al. 1990.

Sampling locations within each site will consist of three areas where the contaminant concentrations are presumed to be very high and three areas where the concentrations are expected to be only moderate. "High" and "moderate" are relative terms, to be defined at each site based on available site characterization data.

6.2 Vapor Collection Apparatus

The sample chamber will consist of a 1-qt (0.946-L) paint can with modifications for air inlet and outlet ports (Figure 2). In the center of the can bottom, a hole will be drilled and a Swagelok bulkhead fitting inserted to form an air inlet. The inlet will have a valve so that it can be closed when the pump is not circulating air and a small charcoal filter to minimize contamination from ambient air. In the center of the lid, a hole will be drilled and a bulkhead fitting inserted to form the outlet port. Again, a valve will be placed next to the bulkhead fitting, to isolate the chamber when the soil core is being disturbed, or the TD tubes are being changed. A programmable, personal air-sampling pump will be used to circulate air through the system. The air leaving the sample chamber will be split with a Y-tube to pass through parallel TD tubes. The intact core sample will be lowered into the sample chamber on a wire mesh tray suspended from three wire chains in a tripod style (Figure 3). It will have three, 2-cm high pegs to act as feet that hold the sample over the inlet port at the bottom of the can. The tray will facilitate the insertion of an undisturbed soil core; it will also facilitate disturbing the soil by physically disrupting the core when the sample chamber is tumbled.

The vapor TD tubes will be stainless steel, 8.9-cm long by 0.64-cm diameter, sealed at each end with brass Swagelok endcaps fitted with Teflon ferrules (recommended by the manufacturer for long-term storage). Each tube will contain 180 mg Carbotrap B on the inlet side, followed by 70 mg Carboxen 1000 (Supelco Inc., Bellefonte, PA). The more easily sorbed compounds will be retained near the front of the tube on the weaker sorbent (Carbotrap B) while the low molecular weight, less easily sorbed compounds will be retained on the stronger sorbent (Carboxen 1000). All of the tubes will be spiked with internal standard in the laboratory (Section 7.1),
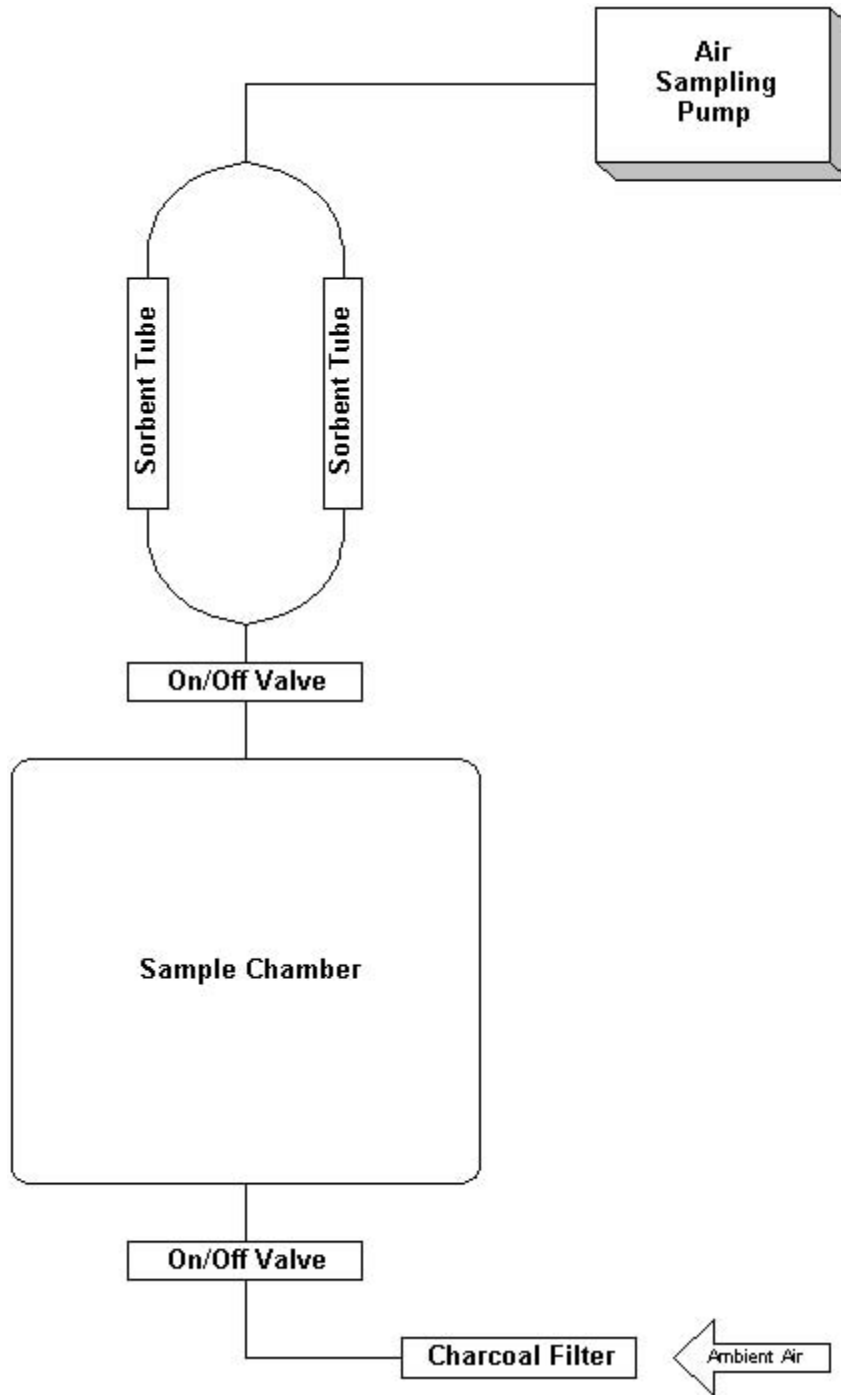
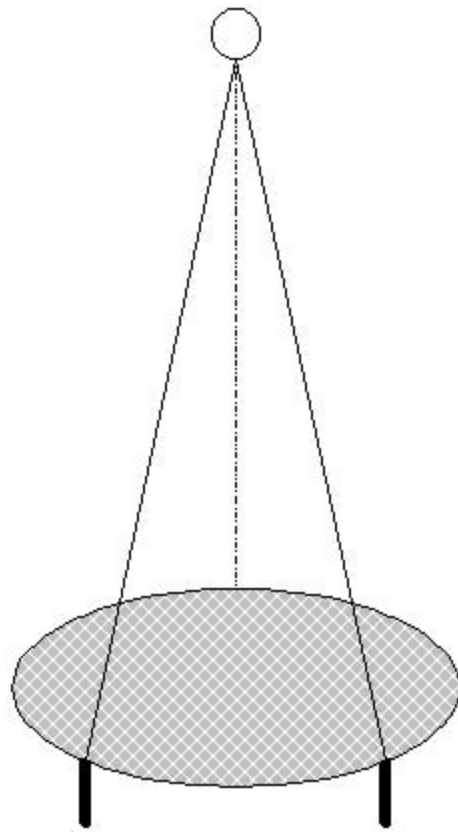Figure 2. Schematic of the vapor sampling apparatus.

Figure 3. Wire mesh tray for lowering soil into chamber.

and placed in zip-closure plastic bags for transport to and from the field.

6.3 Analytes

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 more 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 are listed, with their key properties, in order of decreasing vapor pressure in Table 1. Non-customized, multianalyte gas calibration standards that include all but two of these compounds are commercially available. TCE and chloroform will need to be purchased as custom gas standards and added separately during injection into the TD tubes.

6.4 Sample Collection Procedures

The soil will be removed from its native field position in an 18" split-spoon sampler with brass or stainless steel liners that are precut into 3" lengths over the lower 12" section (Figure 4). The section of the core to be used for vapor analysis will be the second 3" length from the top. If the soil disrupts easily, the core will be left in the liner and transferred to the wire mesh tray. If the soil is cohesive, the core will be removed from the liner (slid or cut from liner, depending on the soil) and carefully placed on the mesh tray. The tray will be set in the sample chamber and the chamber sealed immediately.

The TD tubes should be equilibrated at ambient temperature (outside of the ice chest) for approximately 30 minutes just prior to use. One liter of the chamber air (approximately equivalent to the chamber volume plus dead space in the inlet port, outlet port, and Y-tube) will be sampled immediately after adding the soil core. A personal air-sampling pump will be set at an airflow of 200 mL/min for 5 minutes. Each TD tube will collect VOCs from 0.5 L of air at a flow of 100 mL/min. After the initial 5 minutes of vapor collection from the undisturbed sample, the valves will be shut to isolate the chamber. The TD tubes will be removed, end capped,
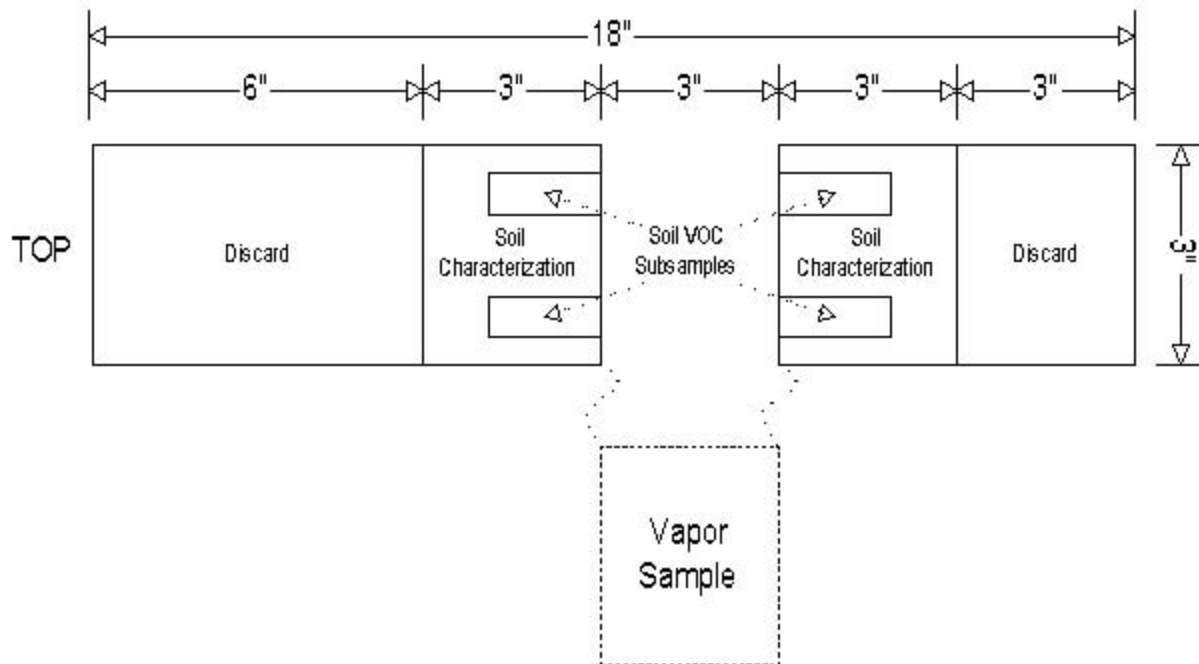
Figure 4. Sampling the Field Soil Core

returned to the appropriate storage bags, and set on ice. A second set of TD tubes will be placed on the sampling apparatus.

While the TD tubes are exchanged, another technician will disturb the soil. Without opening the chamber, the soil core will be disturbed by tumbling or agitating the chamber for approximately 1 minute or until the movement of the soil inside seems fluid. The chamber will be reconnected to the pump and a second set of TD samples will be collected under the same flow rates and conditions described above. To determine the potential for continued release of vapors from the soil, a third and fourth set of TD samples will be collected after additional 1-minute agitation of the soil prior to vapor collection.

While one technician is placing the vapor test core in the sample chamber, two other technicians

will sample the soil just above and below the test core for soil VOCs and other characterization parameters (Figure 4). Using a disposable syringe with the tip removed, approximately 2.5 g of soil from each side of the vapor test core will be composited in a vial and sealed immediately for use in the analysis of VOCs by the low- level purge-and-trap/GC/MS method. Simultaneously, a second set of approximately 2.5 g of soil from each side of the test core will be put in a vial containing 5 mL of methanol for analysis of VOCs by the high-level purge-and-trap method. Approximately 5 g of soil will be removed from each side and composited in a moisture tin. Approximately 15 g of soil from each side will be removed for the organic carbon and PSA; this sample will be placed in a plastic zipper bag to be opened and air dried before shipping, if possible. Duplicate soil VOC samples will be collected for one out of every three sample cores for both the high-and low-level methods.

All samples destined for VOC analysis will be placed on ice in the field, shipped chilled, and stored in the refrigerator (4 $^{\circ}$C) until analysis. A separate ice chest will be used for storing and shipping the methanol-preserved samples. The organic carbon/PSA samples will be chilled if not air dried.

A fresh sample chamber will be used for each soil core. The air temperature and barometric pressure will be taken and recorded in the field notebook during the second 5-minute adsorption period for each vapor test core. Observations on the disaggregation of the soil core will be made after the vapor samples have been collected. Preservation of the low-level purge-and-trap samples will require freezing (-12 $^{\circ}$C) within 48 hours of collection.

6.5 Design Rationale and Assumptions

Each soil and site is expected to have somewhat different factors controlling the release of VOC vapors. The concentration of the VOCs in the soil is predicted to affect the concentration of the vapors released, but no direct proportionality across sites or compounds is expected. This study is designed to examine and compare the different quantities of vapor released and the different

responses to soil disturbance among soils and sites. The proportion of soil VOCs released as vapor from each soil will be inferred, both before and after disturbance. The release rates may be related to soil moisture content and, if so, would vary at a specific site over time.

For example, on a fine-textured soil, a high moisture content could inhibit the rate of VOC vapor release and the rate of release may therefore depend on the degree of agitation or disaggregation of the soil core. Alternatively, a very coarse soil at a low soil moisture content may release VOCs even during the time required to move a core from the split spoon sampler to the chamber. If a dry soil core shows no increase in the release of VOCs resulting from the disturbance, it would imply that the VOCs were lost very easily, probably even before agitating the sample. Any sample that shows a steady or increased release rate during the experiment has the potential to affect exposure levels over a longer period of time than a soil that releases the VOCs rapidly when disturbed.

The basic assumption underlying this project is that data from a large number of sites and soil types will provide enough information to demonstrate correlations between the soil VOC concentration, the vapor release rate, and soil parameters. The specific compounds and concentrations of the VOCs at each site are expected to vary independent of the soil factors. Specific correlations may be difficult to formulate without an extended data set. To guard against premature conclusions using a limited data set, correlation coefficients of 0.95 or greater will be required in formal hypothesis testing.

7. Analytical Methods

7.1 Thermal Desorption

7.1.1 Preparation of TD Tubes. New, preconditioned tubes will be precleaned by heating for 30 min at 370 $^\circ$C while purging with ultrapure He gas at 100 mL/min. (If new and unconditioned, precleaning will require 2 hour per tube.) Endcaps will be precleaned by baking at 150 $^\circ$C for 90

minutes. The TD tubes will be assembled (finger tight) after cleaning and stored in the refrigerator (4 $^{\circ}$C) in plastic zip-closure bags. Subsequent use of the TD tubes will require no precleaning unless the previous use indicated unusually high levels of contaminants.

Internal standards (IS) will be spiked on every tube using a commercially available Method TO-14 internal standard/tuning mix: bromochloromethane, 4-bromofluorobenzene, chlorobenzene-d5, and 1,4-difluorobenzene (Restek, Bellefonte, PA). Each TD tube will be connected to a tank of ultrapure N_2 gas through a Swagelok tee containing a septum port sidearm. The N_2 gas will flow through the inlet end of the TD tube at 50 mL/min, and 1.22 mL of a 1 ppmv mix of the IS compounds will be injected into the stream of N_2, supplying 50 pmole of each compound (see Appendix 2). Fifteen minutes of N_2 flowing through each tube after injection of the IS compounds will be allotted to insure complete transfer of the IS compounds onto the sorbent. Once spiked, the tubes will be sealed with the long-term brass Swagelok endcaps, placed in the plastic bags and stored cold (4 $^{\circ}$C).

Travel spike tubes will be prepared using the procedures described above for adding IS compounds. To prepare these samples, 100 pmoles of the standard gas mixture (245 µL of each of the 10 ppmv standards) will also be added to the sidearm during the IS addition (see Appendix 2). Tubes will be spiked with IS and travel compounds no more than 4 days before field use. This means that the freshly spiked tubes will be shipped from the laboratory via overnight express to the field site as needed during sampling events.

7.1.2 Analysis of TD Tubes. Analysis will closely follow the methods reported by Pankow et al. (1998). In that study, 79 analytes were sorbed onto TD tubes packed with Carbotrap B and Carboxen 1000. The recovery of the analytes of interest in this project (as listed in Table 1) were within 10% of the initial value after 27 days of storage on the TD tubes. We assume that the holding time of 27 days can be achieved if we adhere to the procedures of Pankow et al.

Before each sample tube is desorbed and analyzed, the instrument (Perkin-Elmer ATD 400) will

test for leaks within the sample desorption system. TD tubes that fail the test will be resealed by the autosampler and replaced in the sample carousel. These tubes can then be inspected by the analyst, any obvious problems can be corrected, and the sample will be returned to the carousel for analysis.

Immediately before analysis, tubes will be purged with N_2 gas at 50 mL/min for 8 min at ambient temperature to remove water. Each tube will then be desorbed at 360 °C for 15 minutes using 60 mL/min flow of ultrapure He on a Perkin-Elmer ATD 400. The "air-toxics trap" at -10 °C will be used as an intermediate focus prior to transfer to a GC/MS. A one-third split-to-vent may be necessary to reduce the amount of water on the column. The focusing trap will be desorbed at a 40 °C/s ramp to 370 °C and held for 3 min with a flow of He at 4 mL/min. The flow will be directed at 32 psi onto the GC column at 45 °C through heated (200 °C), deactivated silica tubing.

A 60-m capillary GC column (DB-VRX, 0.25 mm id, 1.4 µm film thickness, or equivalent) will be used. The initial GC oven temperature program will be: hold for 10 min at 45 °C; 12 °C/min to 190 °C; hold for 2 min; 6 °C/min to 240 °C; hold for 2 min. The GC/MS transfer line (210 °C) should end within 1 mm of the MS source.

7.2 Purge-and-Trap

7.2.1 Preparation of the Vials. Vials for the purge-and-trap analysis will be precleaned, 40-mL glass vials with Teflon-lined, septum-sealed screw tops. For the high-level analysis, vials will be prepared by adding 5 mL of purge-and-trap grade methanol; the sealed vials will be weighed and the weights recorded in the field notebook. Travel spike vials will be prepared in the field for both low-level and high-level analysis. For the low-level analysis, 0.25 µL of a 2000 µg/mL VOC matrix spike mix (500 ng) will be added to the low-level vials. For the high-level method, 5 µL of the same 2000 µg/mL spike mix (10 µg) will be added to each vial (5 mL of methanol); this will supply 200 ng in the 100 µL aliquot used for analysis.

7.2.2 Analysis of Purge-and-Trap Samples. Soil VOCs will be analyzed by purge-and-trap/GC/MS as per SW-846 Methods 5035 and 8260 (USEPA, 1997a). Low-level purge-and-trap samples will be frozen within 48 hours of collection and analyzed within 14 days. High-level samples will be stored in methanol at 4 $^{\circ}$C and analyzed within 14 days. A 100-µL aliquot of each high-level sample will be analyzed following the Method 5035 low-level soil procedure. Water (10 mL), internal standards, and surrogate compounds will be added by the autosampler just prior to analysis.

7.3 Organic Carbon

Analytical procedures will follow the method for the high-temperature induction furnace as described in Section 29-2.2.4 of Nelson and Sommers (1982). Total carbon will be measured on soil after removal of carbonates by an acid pretreatment.

7.4 Particle Size Analysis

Sand, gravel, and cobble fractions will be recovered by sieving. Sieved samples will be pretreated to destroy organic matter and carbonates as deemed necessary by the EPA Client Representative. Analysis of the fines will be by hydrometer as specified in Gee and Bauder (1986). Percentages of silt and clay will be determined from the hydrometer readings, temperature, and Stokes Law.

7.5 Soil Moisture

Samples will be sealed in moisture tins in the field using electrical tape. At the laboratory, the sample tape and lid will be removed and each tin will be weighed to ±0.001 g. Tins will be placed in an oven at 105 $^{\circ}$C for at least 24 hours. The tins will then be allowed to cool and reweighed.

8. Quality Control

Table 2 summarizes the QA/QC samples, acceptance criteria, and corrective actions for the GC/MS studies. A general discussion of the project QC and specific QC components for VOCs by TD/GC/MS and purge-and-trap/GC/MS is presented in sections 8.1 through 8.4. The specific QC samples for organic carbon and PSA are discussed in Section 8.5.

Table 2. VOC 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
Initial Calibration (IC)	Precision	Prior to sample analysis, and if OCC fails	%RSD of each RF≤ 15%	Perform instrument maintenance, reanalyze
QC Check Standard (QCCS)	Analytical bias	Duplicates per system each time a new IC is analyzed	%R = 100 ± 20%	Reanalyze; obtain new lot or vendor QCCS
Instrument Detection Limit	Detection limit	Prior to sample analysis	IS area counts within criteria	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
Sample Duplicate	Precision	TD/GC/MS: every sample. PT/GC/MS: 1 out of 3 samples	IS area counts within criteria	Flag data
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 site	Below analyte IDL	Flag data
Travel Spike	Shipping and handling bias	3 per site, per analysis method	Analyte %R = 100 ± 25%	Flag data
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 ± 25%	Reanalyze once, flag data

* PT/GC/MS samples only

8.1 VOC 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, (2) analyzing on-going calibration check (OCC) standards for VOCs, and (3) analyzing sample duplicates.

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 standard and its associated internal standard, respectively. C_S and C_{IS} are the nominal concentration of the standard and its associated internal standard, respectively. The RSD is given as

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

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

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

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

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

The precision of sample duplicates for TD tubes and soil methanol extractions will be calculated as the relative percent difference (RPD):

$$RPD = \frac{(C1 - C2) \times 100\%}{(C1 + C2)/2}$$

where,   C1 = larger of the two observed values

C2 = smaller of the two observed values.

8.2 VOC 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), (2) comparing the data generated in the initial calibration curve with concentrations of the analytes measured in a second-source QC Check Standard, (3) analysis of travel spike samples, (4) area counts of the internal standards added to every TD tube or 40-mL vial, and (5) surrogate compound recoveries (PT/GC/MS only).

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

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

where S is the measured concentration and C_{sa} is the nominal concentration of a given analyte in the standard or travel spike sample. All standards will be certified standards from a reputable manufacturer.

8.3 VOC 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 pmoles on-column for TD/GC/MS and ng on-column for purge-and-trap/GC/MS.

Travel blanks are used to monitor the exposure of samples to contamination during shipping and storage. If contamination is detected in a travel blank, all data associated with that blank will be flagged.

Instrument blanks 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 faulty blank are $\geq 5X$ the blank contamination, the data will be considered acceptable for use in data analysis steps.

8.4 Organic Carbon QC Samples

Method precision will be monitored by analyzing sample duplicates for each soil. The procedure will include at least one soil standard in every set of 10 samples as a check for bias. The soil standard will have been analyzed by an independent source or method. The standard soil will undergo the same pretreatment(s) as the samples. Each soil sample will be visually inspected after combustion for the burn characteristics and will be rerun if combustion was not complete.

8.5 Particle Size Analysis QC Samples

Method precision will be monitored by analyzing three replicates of a laboratory soil standard. One soil standard is to be included in every batch of 12 samples as a check for bias. The silt and sand content of the standard will be compared with the on-going laboratory mean result for these parameters. A sample duplicate will be included in each batch, randomly selected from the soil provided. QC results will be reported with the sample data.

9. Instrument Calibration and Frequency

9.1 Thermal Desorption

A five-point calibration curve at nominal concentrations of 50, 100, 200, 300, and 500 pmoles will be established for each analyte listed in Table 1. Pure component gas-phase standards (from Scott Speciality Gases or equivalent) at a nominal concentration of 10 ppmv will be acquired. This means that the gas has 1 µmole of each target compound for every mole of gas. A mole of gas occupies 24.5 L at 1 atmosphere pressure and 25 °C. Therefore, a mmole occupies 24.5 mL and a µmole occupies 24.5 µL. A 24.5 µL aliquot of the 10 ppmv gas standard contains 10 pmole of the target gases. The tubes will be spiked with 0.12 , 0.245 , 0.490, 0.735, and 1.225 mL of the 10 ppmv gas to achieve 50, 100, 200, 300, and 500 pmoles of target compounds, respectively. (Confer Appendix 2).

TD tubes will be spiked in the same manner used for adding IS compounds to each tube (Section 7.1.1). A Swagelok tee containing a septum port sidearm will be inserted in the flow path between the TD tube and a tank of ultrapure N_2 gas. The N_2 gas will be set to flow through the inlet end of an TD tube at 50 mL/min and the IS and calibration compounds will be injected into the stream of N_2. Fifteen minutes of N_2 flow per tube will be allotted to insure complete transfer of the calibration and IS compounds onto the TD tubes. A mid-point calibration check tube

(OCC) will be analyzed at the beginning of each sample set and every 12 hours thereafter, or at the beginning and end of each run less than 12 hours.

9.2 Purge-and-Trap

The instrument will be calibrated basically as specified in SW-846 Method 8260; 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 2. A five-point calibration curve consisting of standards at the nominal concentrations of 10, 50, 250, 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 2).

9.3 Organic Carbon

The dry combustion furnace procedure will include at least one soil standard in every set of ten samples. The soil standards will have been analyzed by an independent source or method. Each soil sample will be visually inspected after combustion for the burn characteristics and will be rerun if combustion was not complete.

9.4 Particle Size Analysis

A laboratory soil standard will be included in every batch of 12 samples as a QC check. The silt and sand content of the standard will be compared with the on-going laboratory mean result for these parameters.

9.5 Soil Moisture

When in use, the balance will be calibrated daily against a set of "S" class standard weights. The calibration checks will be recorded with sample weights.

10. Data Management

The task of data management for this study includes: (1) tracking three types of VOC data and three types of soil characterization data, (2) creating macros to transfer the data from the various electronic files to electronic spreadsheets, (3) calculating soil concentrations (dry weight basis) and vapor concentrations (soil volume basis) from the raw data, and (4) correcting vapor data with the proper ambient temperature and barometric pressure data. Records of the raw data will be compiled on Excel spreadsheets for data manipulation and evaluation.

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 EPA Client Representative will be consulted if any modifications to, or significant deviations from this QAPP are needed.

12. Reports to Management

The Task Lead is responsible for monthly progress reports to the EPA Client Representative. Separate written communications will be forwarded regarding any modifications to this QAPP. The draft report will include a project summary, a description of the methods, results, and a discussion of the results. Appendices 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 analysts will be checked for adherence to the QAPP and method QC criteria, and any QC violations will noted and reported by the analysts. Samples that can be reanalyzed will be repeated in a timely fashion. The analysts will clearly mark data to indicate which calibration curve, instrument blanks, and OCC samples correspond with each sample, as applicable.

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 personnel, 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.

(2)   Data that have been verified to be of acceptable quality will be studied for patterns or trends over time by plotting vapor concentrations versus time. Step-wise correlation will be used to look for significant effects of soil VOC concentration, moisture, clay, and organic matter content on the quantity of VOCs released during each 5-min interval.

(3)   After the initial exploration of relationships in the data, any assumptions for the statistical

procedures that are selected will be identified and verified as acceptable. Conclusions will be stated in terms of trends and statistically significant correlations.

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Appendix 1

Calculations for Determining Number of Moles in Sample Chamber

Temperature and pressure correction for the number of moles in the sample chamber is estimated using the universal gas law, $pV = nRT$. That is,

$$n = p \ (1 \ L) \ 0.082^{-1} \ (T)^{-1}$$

where   n = number of moles

p = pressure in atmospheres

R = 0.082 L atm deg^{-1} mole^{-1}

T = temperature °K (°C + 273)

The 1-L chamber contains 0.0408 moles at 25 °C and 1 atm pressure. A single TD tube collects 0.5 L of air, or 0.0204 moles. If 500 pmoles are detected on one TD tube, it would represent 24.5 ppbv in the chamber.

Appendix 2

Calculations for Using 1 ppmv and 10 ppmv Gas Standards

One mole of gas occupies 24.5 L at 25 °C and 1 atm pressure. Therefore, 24.5 mL contains 1 mmole of gas.   A gas standard, to supply 1 ppmv, would contain 1 nmole of analyte in 1 mmole of gas. Standards will be prepared as follows:

Volume of	Quantity of VOC supplied	
gas standard	10 ppmv standard	1 ppmv standard
24.5 µL (0.0245 mL)	= 10 pmoles VOC	= 1 pmole VOC
122.5 µL	= 50 pmole	= 5 pmole
245 µL	= 100 pmole	= 10 pmole
490 µL	= 200 pmole	= 20 pmole
735 µL	= 300 pmole	= 30 pmole
1.22 mL	= 500 pmole	= 50 pmole