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Analytical Protocol for Measurement of Extractable Semivolatile Organic Compounds Using Gas Chromatography/Mass Spectrometry

Office of Research and Development
Homeland Security Research Program

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United States Environmental Protection Agency
Office of Research and Development
Homeland Security Research Program
Cincinnati, Ohio 45268

Acknowledgments

This analytical protocol is for the determination and measurement of the semivolatile organic compounds. The procedures were tested by ALS Environmental (formerly Columbia Analytical Services [CAS]) of Kelso, Washington, in a single-laboratory study funded by the U.S. Environmental Protection Agency's Homeland Security Research Program (HSRP). The procedures also were used during a multi-laboratory exercise funded by the Water Security Division within the U.S. Environmental Protection Agency's Office of Water. Technical support, data evaluation, and procedure modifications were provided by CSC Science and Threat Reduction Solutions.

Disclaimer

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Analytical Protocol for Extractable Semivolatile Organic Compounds

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1.0 SCOPE AND APPLICATION

1.1 In 2004, the U.S. Environmental Protection Agency (EPA) Homeland Security Research Program (HSRP), in collaboration with experts from across EPA and other federal agencies, identified analytical methods for the analysis of extractable semivolatile organic compounds (SVOCs) during environmental remediation following a homeland security event. This protocol is to be applied by the national network of laboratories that has been recruited to the EPA-established Environmental Response Laboratory Network (ERLN) so that their analytical results are consistent and comparable. Summaries of these methods are provided in *Selected Analytical Methods for Environmental Remediation and Recovery* (SAM), 2012.[1] NHSRC is currently using the SAM methods to develop standard analytical protocols for laboratory identification and measurement of target agents during site remediation. These methods will be used to assist in determining the presence of contamination, the effectiveness of decontamination, and site clearance decisions following decontamination. SAM applies the following tiers listed below to indicate a level of method usability for each specific analyte and sample type (SAM Tier definitions and their application to SAM methods are also available at: http://www.epa.gov/homeland-security-research/sam-chemical-methods-query):

SAM Tier I: Analyte/sample type is a target of the method(s). Data are available for all aspects of method performance and quality control (QC) measures supporting its use for analysis of environmental samples following a contamination event. Evaluation and/or use of the method(s) in multiple laboratories indicate that the method can be implemented with no additional modifications for the analyte/sample type.

SAM Tier II: (1) The analyte/sample type is a target of the method(s) and the method(s) has been evaluated for the analyte/sample type by one or more laboratories, or (2) the analyte/sample type is not a target of the method(s), but the method has been used by laboratories to address the analyte/sample type. In either case, available data and/or information indicate that modifications will likely be needed for use of the method(s) to address the analyte/sample type.

SAM Tier III: The analyte/sample type is not a target of the method(s), and/or no reliable data supporting the method's fitness for intended use are available. Data from other analytes or sample types, however, suggest that the method(s), with significant modification, may be applicable.

1.2 This analytical protocol is for the determination of the contaminants listed in the table below. The procedures are based on EPA SW-846 Methods 8270D, 8290A, 3511, 3535A, 3540C/3541, 3545A, and 3570 (References 16.1 – 16.8) and were tested in a single-laboratory for measurement of the specific SVOCs in water, soil, air filters, and wipes. The procedures also were tested for dichlorvos, mevinphos and tetramethylene-disulfotetramine (TETS) in water during a multi-laboratory exercise.

Laboratory performance data are provided in Section 17.0 for the analyte/sample type combinations listed in the table below. An "X" in the table below indicates that the protocol meets the SAM Tier II definition of laboratory testing for the analyte/sample type combination. Shaded areas indicate that the protocol meets the SAM Tier III

[1] SAM and its methods are available at: http://www.epa.gov/homeland-security-research/sam.

definition of laboratory testing for the analyte/sample type combination. The entries shaded in grey with no "X" indicate the analyte/sample type combination meets the SAM Tier III definition of insufficient supporting data. SAM considers five of the 21 analytes listed to be "Not of concern" in air.

Target Analytes and Sample Matrices

Semivolatile Compounds	CAS RN*	Matrix **			
		Water	Sand/Soil	Air Filters	Wipes
Chlorfenvinphos	470-90-6	X	X	X	X
Chlorpyrifos	2921-88-2	X	X	X	X
Dichlorvos	62-73-7	X	X	X	X
Dicrotophos	141-66-2	X	X	X	X
Disulfoton	298-04-4	X	X	X	X
Fenamiphos	22224-92-6	X	X	X	X
Methyl parathion	298-00-0	X	X	X	X
Mevinphos	7786-34-7	X	X	X	X
Parathion	56-38-2	X	X	X	X
Phencyclidine	77-10-1	X	X	X	X
Phorate	298-02-2	X	X	X	X
Phosphamidon	13171-21-6	X	X	X	X
Tetramethylenedisulfotetramine (TETS)	80-12-6	X	X	X	X
Crimidine	535-89-7	X	X	Not a concern	X
1,4-Dithiane	505-29-3	X	X	Not a concern	X
1,4-Thioxane	15980-15-1	X	X	Not a concern	X
Chloropicrin	76-06-2	X		X	
Strychnine	57-24-9	X		Not a concern	X
Tetraethyl pyrophosphate (TEPP)	107-49-3	X			
Dimethylphosphite	868-85-9		X	X	X
Nicotine	54-11-5		X	Not a concern	X

* Chemical Abstracts Service (CAS) Registry Number

** An "X" indicates that the protocol meets the SAM Tier II definition of laboratory testing for the analyte/sample type combination. Shaded areas indicate that the protocol meets the SAM Tier III definition of laboratory testing for the analyte/sample type combination.

1.3 Results described in this protocol are based on use of the procedures in a single laboratory and may contain high levels of uncertainty. Care should be taken by each laboratory using the procedures to ensure that a sufficient initial demonstration of competence is performed by each analyst and that adequate QC acceptance criteria are established before any results are reported.

2.0 SUMMARY OF PROTOCOL

2.1 This analytical protocol involves solvent extraction of the sample followed by gas chromatography/mass spectrometry analysis to determine SVOCs. The protocol describes procedures and provides data for analyses using a mass selective detector (MSD) in both full scan and selected ion monitoring (SIM) modes. The technique used will depend on the data quality objectives. The user should keep in mind that, while SIM offers greater sensitivity, SIM tends to be more affected by interferences than full scan.

2.2 Prior to analysis, aqueous, soil and wipe samples are prepared by microscale solvent

extraction (MSE). Appendix A provides information regarding additional extraction procedures that have not been fully tested (solid phase extraction for aqueous samples, automated Soxhlet extraction for soils, and pressurized fluid extraction (PFE) for soils and wipes). Sample extracts may require concentration to achieve appropriate detection and quantitation.

3.0 ACRONYMS, ABBREVIATIONS and DEFINITIONS

3.1 Acronyms and Abbreviations

%Recovery	Percent recovery
ACS	American Chemical Society
ASE	Accelerated Solvent Extraction
ASTM	ASTM International
amu	Atomic mass unit
CAS RN	Chemical Abstract Service Registry Number
CCV	Continuing calibration verification
DCM	Dichloromethane (methylene chloride)
DF	Dilution factor
DFTPP	Decafluorotriphenylphosphine
DVB	Divinylbenzene
EI	Electron ionization
EICP	Extracted ion current profile
EPA	U.S. Environmental Protection Agency
FC-43	Perfluoro-tri-*n*-butylamine
GC	Gas chromatograph
GC/MS	Gas chromatograph/Mass spectrometer
GPC	Gel permeation chromatography
ID	Internal diameter
IDC	Initial demonstration of capability
IDL	Instrument detection limit
IPR	Initial precision and recovery
IS	Internal standard
LCS	Laboratory control sample
LFB	Laboratory fortified blank
LRB	Laboratory reagent blank
MDL	Method detection limit
mEq	Milliequivalent(s)
MS	Mass spectrometer
MS/MSD	Matrix spike/Matrix spike duplicate
MSD	Mass selective detector
MSE	Microscale solvent extraction
NHSRC	National Homeland Security Research Center
NIST	National Institute of Standards and Technology
OSHA	U.S. Occupational Safety and Health Administration
PD	Percent drift
PE	Performance evaluation
PFE	Pressurized fluid extraction
PFK	Perfluorokerosene
PTFE	Polytetrafluoroethylene (Teflon®)
PUF	Polyurethane foam

QA	Quality assurance
QC	Quality control
QL	Quantitation limit
RPD	Relative percent difference
RRF	Relative response factor
RRT	Relative retention time
RSD	Relative standard deviation
RT	Retention time
SAM	*Selected Analytical Methods for Environmental Remediation and Recovery*
SDS	Safety data sheet
SIM	Selected ion monitoring
S:N	Signal-to-noise ratio
SPE	Solid phase extraction
SVOC	Semivolatile organic compound
TEA	Triethylamine
TEPP	Tetraethyl pyrophosphate
TETS	Tetramethylenedisulfotetramine
VOA	Volatile organic analysis

3.2 Definitions

Aliquot – A measured portion of a field sample, standard or solution taken for sample preparation and/or analysis.

Analytical Batch – A set of samples that is analyzed on the same instrument during a 12-hour period of operation or after the analysis of 10 samples (whichever comes first). The analytical batch begins and ends with the analysis of the appropriate Continuing Calibration Verification (CCV) standards.

Calibration Standard – A solution prepared from the stock standard solution(s) and the internal standards and surrogate analytes. The calibration standards are used to calibrate instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV) Standard – A calibration standard containing the target analytes. It is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

Extracted Ion Current Profile (EICP) – A plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).

Extraction Batch – A set of up to 20 field samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of solid phase extraction devices, solvents, surrogate solution, and fortifying solutions.

Holding Time – The elapsed time from sample collection until sample extraction or analysis.

Initial Calibration – Analysis of calibration standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument for target analytes.

Initial Demonstration of Capability (IDC) – Procedures performed prior to using the method to analyze field samples. The IDC is used to demonstrate that the laboratory and analyst are capable of performing the analysis with acceptable precision, accuracy, sensitivity and specificity pertaining to that particular method.

Initial Precision and Recovery (IPR) – A set of four aliquots of a clean reference matrix (i.e., reagent water, Ottawa sand, clean wipe or air filter) to which known quantities of the target analytes are added. The IPR aliquots are processed and analyzed exactly like a sample and analyzed prior to the analysis of field samples as part of the IDC. Their purpose is to determine whether the laboratory is capable of making accurate and precise measurements.

Instrument Detection Limit (IDL) – The minimum concentration of an analyte that, when injected into the gas chromatograph/mass spectrometer (GC/MS), produces an average signal-to-noise ratio (S:N) between 3:1 and 5:1 for at least three replicate injections.

Instrument Performance Check Solution – A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Internal Standard – A pure analyte added to an extract or standard solution in a known amount and used to measure the relative responses of target analytes and surrogates. The internal standard must be an analyte that is not a sample component.

Laboratory Control Sample (LCS) – An aliquot of a clean reference matrix (i.e., reagent water, Ottawa sand, clean wipe or air filter) to which known quantities of the target analytes are added. The LCS, also called a laboratory fortified blank (LFB), is processed and analyzed exactly like a sample. Its purpose is to determine whether the analytical process is in control.

Matrix – The predominant material of which the sample to be analyzed is composed. For the purpose of this protocol, a sample matrix is either aqueous/water, soil/sediment/sand, wipe or small (e.g., 37 mm) air filter. Matrix is <u>not</u> synonymous with phase (e.g., liquid or solid).

Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Two aliquots of a field sample which is fortified, extracted and analyzed exactly like a sample. The purpose of the MS/MSD is to assess method precision and accuracy for analyses of the sample type and whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations. The purpose of the MS/MSD is to assess method precision and accuracy for analyses of the sample type.

Method Blank – An aliquot of a clean reference matrix (reagent water, Ottawa sand, clean wipe or clean air filter) that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, sample preservatives, internal standards, and surrogates that are used in the extraction batch. The method blank, also called a laboratory reagent blank (LRB), is used to determine whether target analytes or interferences are present in the laboratory environment, reagents or equipment.

Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99 percent confidence that the analyte concentration is greater than zero. The MDL is a statistical determination (Section 9.7), and accurate quantitation is not expected at this level.

Percent Difference – The difference between two values divided by one of the values. Used in this protocol to compare two relative response factor (RRF) values.

Percent Drift (PD) – The difference between the calculated and theoretical value divided by the theoretical value. Used in this protocol to compare calculated and theoretical values for calibration by regression techniques.

Quantitation Limit (QL) – The minimum level of quantitation. This concentration must meet the criteria defined in Section 9.8.

Reagent Water – Water in which an interferent is not observed at or above the low-level calibration standard for each analyte of interest. The purity of this water must be equivalent to ASTM International (ASTM) Type II reagent water of Specification D1193-06, "Standard Specification for Reagent Water" (Reference 16.9).

Relative Percent Difference (RPD) – The difference between two values divided by the mean of the values. RPD is reported as an absolute value (i.e., always expressed as a positive number or zero).

Relative Response Factor (RRF) – A measure of the relative mass spectral response of an analyte compared to its internal standard. RRFs are determined by analysis of standards and are used in calculating the concentrations of analytes in samples.

Retention Time (RT) – The time an analyte is retained on a GC column before elution. The RT is dependent on the nature of the column's stationary phase, diameter, temperature, flow rate, and other parameters.

Relative Retention Time (RRT) – The ratio of the RT of a compound to the RT of a corresponding internal standard.

Safety Data Sheet (SDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, flammability, and reactivity data including storage, spill, and handling precautions.

Stock Standard Solution – A concentrated solution containing one or more target analytes prepared in the laboratory using assayed reference materials or materials purchased from a reputable commercial source.

Surrogate – A pure analyte that is unlikely to be found in any sample and that is added to a sample aliquot in a known amount before extraction or other processing. Surrogates are measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

Working Standard Solution – A solution containing target analytes prepared from stock standard solutions. Working standard solutions are diluted as needed to prepare calibration and spiking solutions.

4.0 INTERFERENCES

4.1 Contaminants in solvents, reagents, glassware, and other sample processing hardware can cause interferences such as discrete artifacts and/or elevated baselines in the Extracted Ion Current Profiles (EICPs). All of the materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences can be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences can vary considerably depending on the sample source.

4.2 For solid samples containing significant matrix interferences, gel permeation chromatography (GPC) cleanup following the procedures in SW-846 Method 3640 (Reference 16.10) may help improve chromatography. Preliminary evaluation during a single-laboratory study showed that analyte recoveries in solid sample extracts having undergone GPC cleanup were comparable with analyte recoveries in sample extracts having no GPC cleanup (see Appendix A). If GPC is used, a thorough demonstration of capability is performed for each target analyte before results are reported.

4.3 Laboratory results indicate that improved recovery of alkaline compounds (e.g., strychnine, nicotine, crimidine, and phencyclidine) from water may result when extracting samples under acidic conditions (e.g., pH <2) during the first extraction, followed by back extraction under basic conditions (Reference 16.11).

4.4 This protocol includes conditions for collecting mass spectral data using selected ion monitoring (SIM) operating conditions. Although SIM may be used in cases when there is a need to address low concentration levels, the procedure is, as with any scan analysis technique, prone to matrix interference effects with the analyte of interest and may cause suppression/enhancement of ionization signal relative to the analyte eluting in the absence of the matrix component. Laboratories should give special attention to all calibration and quality assurance/quality control (QA/QC) data requirements.

5.0 SAFETY

This protocol does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of U.S. Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals listed in this method. Analysts should wear safety glasses, gloves, and laboratory coats when working in the laboratory. Analysts also should review the Safety Data Sheets (SDSs) for all reagents used in this method. A reference file of SDSs must be available to all personnel involved in these analyses, chemical handling, and contaminated area cleaning, or who might potentially come in contact with the materials in their workplace.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified in this protocol. Demonstration of equivalent performance meeting the requirements of this analytical protocol is the responsibility of the laboratory.

6.1 Microscale Extraction (MSE) Apparatus

6.1.1 General

6.1.1.1 Glass vials – 40- or 60-mL (Fisher Scientific Catalog No. 05-719-400, Westminster, MD, or equivalent) capacity with polytetrafluoroethylene (PTFE)-lined screw caps (Fisher Scientific Catalog No. 05-719-400, Westminster, MD, or equivalent) OR 50- or 60-mL glass conical bottom vials or centrifuge tubes (Fisher Scientific Catalog No. 0553841A, Westminster, MD, or equivalent) with screw caps.

Note: Tubes with conical ends may facilitate the removal of the bottom methylene chloride layer.

6.1.1.2 Vials – amber glass, 2-mL, with PTFE-lined screw or crimp top (Sigma Aldrich Catalog No.SU860033, St. Louis, MO, or equivalent)

6.1.1.3 Vortexer – VWR® or equivalent

6.1.1.4 Water bath – heated, capable of temperature control (± 5 °C). The bath should be used in a hood.

6.1.1.5 Pasteur glass pipettes – 1 mL, disposable (Fisher Scientific Catalog No. NC0541803, Westminster, MD, or equivalent)

6.1.1.6 Centrifuge – capable of at least 500 G force units (4900 m/s^2) and accommodating 40-mL or 60-mL vials. Accuspin™ Model 400 or equivalent. CAUTION: Different centrifuge makes and models have different maximum centrifuge speeds for safe operation. The maximum safe handling speed of each centrifuge will depend, in part, on the vials used and should be determined prior to use.

6.1.2 Soil, Wipes and Air Filter Samples

6.1.2.1 Glass powder funnel with glass wool plugging the bottom, used in filtering soil samples that fail to settle out with centrifugation (Fisher Scientific Catalog No. CG172305, Westminster, MD, or equivalent)

6.1.2.2 Sonicator – Branson 3510 Ultrasonic Cleaner (Branson Ultrasonic Corp., Danbury, CT, or equivalent)

6.1.2.3 Rotator/Shaker – Glas-Col® Rotator (Part # 099A-RD50, Glas-Col Inc., Terre Haute, IN), Glas-Col Shaker (Part # 099A LC1012, Glas-Col Inc., Terre Haute, IN), Glas-Col Digital Pulse Mixer (Part # 099A DPM12, Glas-Col Inc., Terre Haute, IN, or equivalent). Model used must be adequately sized to accommodate sample batch.

Note: The Digital Pulse Mixer requires a foam pad for 40-mL volatile organic analysis (VOA) vials (Part #099A VC0614, Glas-Col Inc., Terre Haute, IN, or equivalent).

6.1.2.4 Syringes – gastight, contaminant-free, 500 µL and 25 µL

(Thermoscientific Part No. NS600911 and NS600511, ThermoFisher Scientific, Westminster, MD, or equivalent)

6.1.2.5 Glass beads – solvent-rinsed with acetone:methylene chloride:ethyl acetate (1:2:1 v:v:v) and baked in 400 °C oven for approximately one hour (Fisher Scientific Catalog No. S80024, Westminster, MD, or equivalent)

6.1.3 Water Samples

6.1.3.1 Syringes – gastight, contaminant-free, 2.0 mL, 1.0 mL (BD Medical Part No. 512019, 512027, Becton Dickinson, Franklin Lakes, NJ, or equivalent) and , 10 µL (Thermoscientific Part No. NS142404 or equivalent)

6.1.3.2 Class A volumetric pipette – 2 mL (Corning Part No. 7103C-2, Corning, NY, or equivalent)

6.1.3.3 Beakers – 400 mL

6.1.3.4 Syringes – 2 µL, 10 µL, 0.1 mL, 0.2 mL, 0.5 mL, 1 mL, 5 mL, and 10 mL with Luer-lok® fitting (Hamilton Gas-tight Luer-lok® syringes, Hamilton Robotics, Reno, NV, or equivalent)

6.1.3.5 Graduated cylinder – Class A, 100 mL

6.1.3.6 Volumetric flasks – Class A, 10 mL

6.2 General Equipment

6.2.1 Spatula - Stainless steel or PTFE

6.2.2 Balances - Analytical, capable of accurately weighing ±0.0001 gram, and one balance capable of weighing 100 grams (±0.01 gram). The balances must be calibrated with Class S weights at a minimum of once per month. The balances also must be calibrated with Class S weights or known reference weights once per each 12-hour work shift, and be checked annually by a certified technician.

6.2.3 Vacuum Filtration Apparatus

6.2.3.1 Büchner funnel (porcelain or Pyrex®)

6.2.3.2 Filter paper - Whatman® No. 41, Whatman, Maidstone, UK, or equivalent

6.2.4 Borosilicate glass wool - rinsed with dichloromethane (DCM)

6.2.5 Test Tube Rack

6.2.6 Silicon carbide boiling chips (Troemner Hengar Boiling Granules, Sigma-Aldrich Catalog No. 902100, St. Louis, MO, or equivalent) - approximately 10/40 mesh. Heat to 400 °C for 30 minutes or clean using DCM and Soxhlet extraction. PTFE boiling chips that are solvent-rinsed prior to use are acceptable.

6.2.7 Water bath - with concentric ring cover, capable of heating to 80 °C and

maintaining a temperature control (±5 °C). The bath should be used in a hood.

6.2.8 Nitrogen evaporation device - Equipped with a water bath that can be maintained at 35 – 40 °C, a RapidVap® (Labconco Corporation, Kansas City, MO, or equivalent). To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.2.9 pH indicator paper - capable of covering a wide pH range (i.e., 1 – 14)

6.2.10 pH meter - with a combination glass electrode. Calibrate prior to each use according to manufacturer's instructions.

6.2.11 Apparatus for determining percent dry weight

6.2.11.1 Drying oven – capable of maintaining 105 °C

6.2.11.2 Desiccator

6.2.11.3 Crucibles – disposable aluminum or porcelain

6.2.12 Clean cloth or wipes – Kimwipe® (Kimberly-Clark Professional, Roswell, GA) or equivalent

6.2.13 Air filters – Consisting of glass fiber filter (Pallflex®, Pall Corp., Timonium, MD, or equivalent) and XAD resin (Supelpak™ 2SV, Sigma Aldrich, St. Louis, MO, or equivalent)

6.3 Gas chromatograph/mass spectrometer (GC/MS) System

Note: The single-laboratory study was performed using an Agilent® 6890/5973 with Agilent 7683 Autosampler and a Zebron™ ZB-5MS capillary column from Phenomenex.

6.3.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, regulators, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.3.2 Gas Chromatography Column - Minimum length 30 m x 0.25 mm internal diameter (ID) (or 0.32 mm) bonded phase silicon coated fused silica capillary column DB-5 (J&W Scientific, Agilent Technologies, Santa Clara, CA); RTX-5, RTX-5Sil MS (Restek Corp., Bellefonte, PA); Zebron™ ZB-5 (Phenomenex, Phenomenex, Inc., Torrance, CA); Zebron™ ZB-5MS (Phenomenex, Phenomenex, Inc., Torrance, CA), SPB®-5 (Supelco, Sigma-Aldrich, St. Louis, MO); AT™-5 (Alltech, Grace, Columbia, MD); HP®-5 (Agilent, Agilent Technologies, Santa Clara, CA); CP™-Sil 8 CB (Chrompack, Raritan, NJ); 007-2 (Quadrex®, Quadrex, Corp., Bethany, CT); BP-5 (SGE, Trajan Scientific Americas, Inc., Austin, TX) or equivalent.

Note: This is a minimum requirement for column length. Longer columns may be used. Although a film thickness of 1.0 micron may be desirable because of its larger capacity, a film thickness of 0.25 micron also may be used.

A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantification of the compounds listed in Section 1.2.
- The analytical results generated using the column meet the initial and continuing calibration verification (CCV) technical acceptance criteria and the quantitation limits listed in Tables 11a, 11b, 12a and 12b.
- The column can accept up to 80 ng of each compound without becoming overloaded.
- The column provides equal or better resolution of the compounds.

6.3.3 Mass Spectrometer - Must be capable of scanning from 35 to 500 atomic mass unit (amu) every 1 second or less, using 70 volts (nominal) electron energy in the electron ionization (EI) mode, and producing a mass spectrum that meets the tuning acceptance criteria (Section 10.2.4) when 50 ng of decafluorotriphenyl-phosphine (DFTPP) is injected through the GC inlet. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.4 GC/MS Interface - The laboratory may use any GC/MS interface that provides acceptable sensitivity and QC. However, direct insertion of the GC column into the mass spectrometer source is the recommended interface.

6.3.5 Helium Carrier Gas – Ultra high purity (99.995 % or higher)

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water - ASTM Type II reagent water of Specification D1193-06, "Standard Specification for Reagent Water," (Reference 16.9) or equivalent.

7.1.2 Acetone, DCM, Ethyl Acetate, Triethanolamine (TEA), and Toluene - Pesticide residue analysis grade or equivalent.

Note: Solvents should be dried prior to use with anhydrous sodium sulfate.

7.1.3 Drying Agent – Powdered or granular anhydrous sodium sulfate, American Chemical Society (ACS) reagent grade, heated at 400 °C for four hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle. See Appendix A for possible alternative drying agents.

7.1.4 Dechlorinating Agents

See Section 8.1.2 for dechlorinating agents recommended for specific analytes.

7.1.4.1 Ammonium chloride - ACS reagent grade

7.1.4.2 Sodium sulfite - ACS reagent grade

7.1.5 Anhydrous Sodium Chloride – ACS reagent, ≥99 %. Used to adjust the ionic strength during MSE of water samples.

7.1.6 Ottawa Sand (Fisher Scientific Catalog No. S25516 or equivalent) – Oven muffled in a 500-mL, wide mouthed amber bottle. (Oven is muffled to 450 °C and held for four hours, then ramped back to room temperature.)

7.2 Standards

7.2.1 Introduction

The laboratory must be able to verify that standards are certified. Manufacturers' certificates of analysis must be retained by the laboratory and presented upon request. Standard solutions purchased from a chemical supply house as extracts in sealed, glass ampules may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, general guidance for similar compounds suggests that unopened ampules of standard solutions may be retained and used up to two years from the preparation date (Reference 16.12). Based on this guidance, the expiration date of opened standards, upon breaking the glass seal, is six months (or sooner, if the standard has degraded or evaporated). Solutions used for calibration verification ideally are prepared from a separate source other than the source used to prepare calibration standards.

7.2.2 Stock Standard Solutions

Stock standard solutions are defined as standards that are used to produce working standards, and may be in the form of single compounds or mixtures. Stock standard solutions may be purchased or prepared from neat compounds in DCM or another suitable solvent.

Note: Combined stock standard solutions can be prepared for most of the target analytes listed in Section 1.2. Exceptions are tetraethyl pyrophosphate (TEPP) and strychnine, which are unstable when combined with other target analytes. If analysis of TEPP and strychnine are required, fresh standards should be prepared immediately prior to calibration.

7.2.3 Working Standards

7.2.3.1 Surrogate Standard Spiking Solution - Prepare a surrogate standard spiking solution that contains the appropriate surrogates for the target compounds (see Table 2). Surrogate standards are added to all samples and calibration solutions. Additional surrogates may be added at the laboratory's discretion. Surrogates are added to samples and blanks at a concentration that is approximately the midpoint of the calibration range.

Note: It is recommended that all surrogates in Table 2 be added to all samples and calibration standards. In cases where only certain analytes are to be measured and/or high throughput is necessary, the laboratory may add a subset of these surrogates.

7.2.3.2 Matrix Spiking Solution - The matrix spiking solution should consist of the target compounds prepared at a concentration that, when added to samples, results in a concentration near the midpoint of the calibration range for each target compound.

7.2.3.3 Instrument Performance Check Solution - Prepare a solution of DFTPP such that a 1-µL injection will contain 50 ng of DFTPP. The DFTPP may also be included in the calibration standards at this level.

7.2.3.4 Initial and Continuing Calibration Solutions

7.2.3.4.1 Prepare calibration standards at a minimum of five concentration levels. Each calibration standard should contain each target compound, associated surrogate, and internal standard. (See Section 17.0, Tables 10a and 10b for suggested concentrations for full scan and Selected Ion Monitoring (SIM), respectively.)

Note: 1.0 µL injections of all calibration standards should be used. All sample extracts must be injected at the same volume (1.0 µL) as the calibration standards.

Note: The concentrations listed in Section 17.0, Tables 10a and 10b were used during method evaluation in a single laboratory. For most analytes, the low calibration standard is set at the expected quantitation level (QL). The remaining calibration standards should be prepared at concentrations that meet the specifications in Section 10.3.5.

7.2.3.4.2 The continuing calibration standard is prepared at or near the midpoint of the calibration curve.

7.2.3.5 Internal Standard Solution - An internal standard solution is prepared by dissolving 100 mg of each of the following compounds in 100 mL of DCM: 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. It may be necessary to use 5 - 10 percent toluene in this solution and a few minutes of ultrasonic mixing to dissolve all constituents. A sufficient portion of this solution will be added to each sample extract just prior to analysis to result in a concentration of 10 ng/µL. Alternatively, internal standard solutions can be purchased from commercial sources (e.g., Supelco part number 861238 or equivalent).

7.2.4 Storage of Standard Solutions

7.2.4.1 Store the stock standard solutions at 4 °C (± 2 °C) in PTFE-lined screw-cap amber bottles. Prepare fresh standards every six months at a minimum (or sooner if the expiration date has elapsed).

7.2.4.2 Store the working standards at 4 °C (± 2 °C) or less in PTFE-sealed containers. Certain analytes (i.e., TEPP and strychnine) may degrade in as little as two weeks; calibrations for these analytes should be performed using separate, freshly prepared standard solutions. It is also recommended that working standard solutions for all analytes be checked at least weekly for stability. These solutions must be replaced after six months (or sooner if the stock standard solutions have expired), or if comparison with QC samples or standards indicates a problem.

7.2.4.3 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

7.2.4.4 The laboratory is responsible for maintaining and verifying the integrity of standard solutions prior to use. The standards must be brought to room temperature prior to use, checked for losses, and checked to ensure that all components have remained in solution.

8.0 SAMPLE PRESERVATION, STORAGE, AND TECHNICAL HOLDING TIMES

Preservation, storage, and holding times for drinking water samples were evaluated in a single-laboratory. Suggested sample preservation, storage, and holding times for all other sample types are based on EPA's SW-846 Method 8270D (Reference 16.1). SW-846 preservation techniques were not evaluated for solids, wipes or air filters.

8.1 Sample Preservation

8.1.1 All samples should be protected from light and cooled to 4 °C (±2 °C).

8.1.2 Water Samples

Existing EPA methods for determination of SVOCs use sodium thiosulfate or sodium sulfite for dechlorination of water samples. Laboratory results evaluating the procedures described in this protocol, however, indicated improved analyte recovery and stability when using ammonium chloride (NH_4Cl) for sample dechlorination. Results also indicated improved stability when using sodium sulfite (Na_2SO_3) for sample dechlorination along with hydrochloric acid (HCl) for sample preservation. This dechlorination/preservation procedure was also used during a multi-laboratory exercise for three analytes (dichlorvos, mevinphos and TETS). Recommended dechlorinating agents and preservatives based on single-laboratory results are provided in the table below (entitled "Recommended Preservatives/Dechlorinating Agents"). Recommended procedures using ammonium chloride are provided in Section 8.1.2.1. Recommended procedures using sodium sulfite, with and without HCl, are provided in Section 8.1.2.2.

Note: Due to low recoveries of nicotine and strychnine, results of this evaluation could not be used to determine an appropriate treatment for drinking water samples containing these analytes.

Recommended Preservatives/Dechlorinating Agents

NH_4Cl	Na_2SO_3	Na_2SO_3 and HCl	No treatment
Chlorfenvinphos	Crimidine	Dichlorvos	Chlorfenvinphos
Chloropicrin	Dicrotophos	Dicrotophos	Chloropicrin
Crimidine	Mevinphos	1,4-Dithiane	Crimidine
Chlorpyrifos	Phencyclidine	Methyl parathion	Fenamiphos
Dichlorvos	Phosphamidon	Mevinphos	Dicrotophos
Dicrotophos	TETS	Phencyclidine	Disulfoton
Disulfoton		Phosphamidon	Fenamiphos
1,4-Dithiane		TEPP	Mevinphos
Methyl parathion		TETS	Parathion
Mevinphos		1,4-Thioxane	Phencyclidine
Parathion			Phorate
Phencyclidine			Phosphamidon
Phorate			TEPP
Phosphamidon			TETS
TEPP			
TETS			
1,4-Thioxane			

Acronyms:
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

8.1.2.1 NH_4Cl – To each water sample, add a sufficient amount of ammonium chloride to achieve a concentration of 40 – 50 mg/L (this may be added as a solid with stirring or shaking until dissolved). Do NOT add HCl preservative, as this will decrease the effectiveness of ammonium chloride as a dechlorinating agent.

8.1.2.2 Na_2SO_3/HCl – To each water sample, add a sufficient amount of sodium sulfite to achieve a concentration of 40 – 50 mg/L (this may be added as a solid with stirring or shaking until dissolved). If preservative is required, adjust the pH of the sample with 6 N hydrochloric acid (HCl) until the pH is ~2.

8.2 Sample Storage

8.2.1 Samples must be protected from light and refrigerated at 4 °C (±2 °C).

8.2.2 Samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at ≤6 °C.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Technical Holding Times

It is recommended that samples be extracted within 14 days from the time of collection and that extracts be analyzed within 40 days following extraction.

Note: Laboratory results indicate that water samples to be analyzed for TEPP or fenamiphos should be extracted and/or analyzed immediately upon receipt. The holding times for samples containing nicotine and strychnine have not been determined. Until additional holding time data are available, laboratories are advised to extract all samples as soon as possible after receipt and to evaluate analyte holding times in matrices typically analyzed by the laboratory.

9.0 QUALITY CONTROL (QC)

QC requirements for this protocol include the following:

Quality Control (QC) Analyses

Requirement	Section	Frequency
Instrument Detection Limit (IDL) Determination	Section 9.6	Optional. Performed prior to Method Detection Limit (MDL) Study
Method Detection Limit (MDL) Determination	Section 9.7	Performed once, prior to first performing the method and with each significant change as part of the Initial Demonstration of Capability (IDC)
Initial Precision and Recovery (IPR) Determination	Section 9.2	
Quantitation Limit (QL) Determination	Section 9.8	
Method Blanks	Section 9.3	At least one per extraction batch
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	Section 9.4	One per each batch of 20 samples of the same matrix or within 24 hours or less
Laboratory Control Sample (LCS)	Section 9.5	At least one per extraction batch
Continuing Calibration Verification (CCV)	Section 10.4	Prior to the analysis of samples, and after instrument performance check. Analyzed once per analytical batch (every 12 hours or after 10 samples, whichever comes first)

Precision and bias criteria for data generated using this method are currently set at 50 – 150 % recovery and ≤ 30 % precision (as relative standard deviation [RSD] or relative percent difference [RPD]). These criteria may change as more laboratory data become available. In cases where analyses of difficult sample matrices generate results outside these criteria, data should be flagged, and laboratories should collect additional data to support development of laboratory- and matrix-specific criteria. Example precision and bias results obtained from laboratories analyzing spiked reference matrix samples (reagent water, Ottawa sand, and wipes) and field samples (water and soil) are provided in Section 17.

9.1 Initial Demonstration of Capability (IDC)

An IDC is performed prior to the analysis of any samples and with each significant change in instrument type, detection technique, personnel or method. An IDC consists of the following:

- An demonstration of initial precision and recovery (IPR) determination (Section 9.2)
- A method detection limit (MDL) study (Section 9.7)
- A QL determination (Section 9.8) on a clean matrix (reagent water, Ottawa sand, pre-cleaned wipe, air filter)

The IPR consists of four replicate samples of a clean matrix spiked with the target analytes around the midpoint of the calibration curve and carried through the entire analytical process. Prior to performing the IDC, a valid initial calibration (Section 10.3) should be established.

9.2 Initial Precision and Recovery (IPR) Determination

9.2.1 Preparation and analysis of IPR samples

9.2.1.1 Water Samples

Prepare four replicate samples consisting of 35 mL of reagent water. Add a sufficient amount of surrogate standard spiking solution to result in a surrogate concentration at approximately the calibration midpoint. Extract, concentrate, and analyze according to the procedures for water samples (Section 11.2). The total volume of dichloromethane (DCM) added will be slightly greater than the 2 mL needed for extraction and includes the volumes added for spiking target compounds, surrogates, and internal standards.

9.2.1.2 Ottawa Sand

Prepare four replicate samples consisting of 10 grams of Ottawa sand and 2.5 grams of sodium sulfate. Add a sufficient amount of the surrogate standard spiking solution to result in a surrogate concentration at approximately the calibration midpoint and follow the appropriate extraction procedure in Section 11.3. Extract, concentrate and analyze according to procedures for solid samples.

9.2.1.3 Wipes

Prepare four replicate samples of wipes (Section 6.2.14). Add a sufficient amount of the surrogate standard spiking solution to result in a surrogate concentration at approximately the calibration midpoint, and follow the appropriate extraction procedure in Section 11.5. Extract, concentrate and analyze according to procedures for wipe samples.

9.2.1.4 Air Filters

Prepare four replicate samples of air filters (Section 6.2.15). Add a sufficient amount of the surrogate standard spiking solution to result in a surrogate concentration at approximately the calibration midpoint, and follow the appropriate extraction procedure in Section 11.4. Extract, concentrate and analyze according to procedures for air filter samples.

9.2.2 Calculations for IPR

9.2.2.1 Calculate the percent recovery of each compound in each IPR sample using Equation 11 (Section 12.2.9.1). Calculate an average percent recovery for each compound.

9.2.2.2 Calculate a percent relative standard deviation (%RSD) for each compound in the IPR samples.

9.2.3 Technical Acceptance Criteria for IPR

9.2.3.1 The average percent recovery of each compound in the IPR should be within 50 – 150 %.

9.2.3.2 The %RSD of each compound in the IPR should be less than or equal to 20 %.

9.2.4 Corrective Action for IPR

If the technical acceptance criteria in Section 9.2.3 are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

Note: The technical acceptance criteria are based on results obtained in a single laboratory. Until criteria are developed based on multi-laboratory data, laboratory-specific criteria may be developed and used.

9.3 Method Blanks

A method blank is a volume of a clean reference matrix (e.g., reagent water for water samples, Ottawa sand for soil/sediment samples, clean sorbent for air samples, or clean wipe for wipe samples) spiked with a sufficient amount of surrogate standard spiking solution (Section 7.2.3.1) so that each surrogate is added at a concentration expected to be at approximately the midpoint of the calibration range. The blank is carried through the entire analytical procedure used to analyze associated samples. Internal standard solution is added just prior to full scan analysis by GC/MS to give a concentration of 10 ng/µL for each internal standard. The volume or weight of the reference matrix must be approximately equal to the volume or weight of the samples associated with the blank.

9.3.1 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank should not exceed 20 field samples (excluding Matrix Spike and Matrix Spike Duplicates [MS/MSDs] and Performance Evaluation [PE] samples). In addition, a method blank is:

- Extracted by the same procedure used to extract samples
- Analyzed on each GC/MS system used to analyze associated samples and conditions (i.e., GC/MS settings)

9.3.2 Method Blank Preparation

9.3.2.1 A method blank for water samples consists of an aliquot of reagent water, of the same volume as the corresponding field samples spiked with a sufficient amount of the surrogate standard spiking solution to result in the addition of 10 µg of each surrogate (Section 7.2.3.1). For soil/sediment samples, a method blank consists of an aliquot of Ottawa sand, of the same weight as the corresponding field samples, spiked with sufficient amount of the surrogate spiking solution to result in the addition of 10 µg of each surrogate. A method blank for gas-phase samples consists of a clean unused polyurethane foam (PUF) cartridge (or XAD-2) and filter spiked with a sufficient amount of the surrogate standard spiking solution to result in the addition of 10 µg of each surrogate. A method blank for wipe samples consists of a clean, unused wipe spiked with a sufficient amount of the surrogate standard spiking solution to result in the addition of 10 µg of each surrogate. Extract, concentrate, and analyze the blank according to procedure.

9.3.2.2 Under no circumstances should method blanks be analyzed at a dilution.

9.3.3 Technical Acceptance Criteria for Method Blank Analysis

9.3.3.1 All blanks should be extracted and analyzed at the frequency described in Section 9.3.1 on a GC/MS system meeting the DFTPP (Section 10.2.4), initial calibration (Section 10.3.5), and CCV (Section 10.4.5) technical acceptance criteria.

9.3.3.2 The recovery of each of the surrogates in the blank must be within 50 – 150 %.

9.3.3.3 The blank must meet the internal standard acceptance criteria listed in Sections 12.3.5 through 12.3.6.

9.3.3.4 A method blank for soil, water, air, and wipe samples must not contain analytes at concentrations at or above the low-level calibration standard for each analyte of interest.

9.3.4 Corrective Action for Method Blanks

9.3.4.1 If a method blank does not meet the technical acceptance criteria for method blank analysis, the analytical system is considered to be out of control.

9.3.4.2 If contamination is the problem, the source of the contamination should be investigated and appropriate corrective measures taken before further sample analysis proceeds. It is the laboratory's responsibility to ensure that interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS have been eliminated. If possible, samples associated with the contaminated blank should be re-extracted and reanalyzed.

9.3.4.3 If surrogate recoveries in the method blank do not meet the acceptance criteria Section 9.3.3.2, reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank should be re-extracted if possible, and reanalyzed.

9.3.4.4 If the method blank does not meet internal standard response requirements listed in Section 12.3.5, follow the corrective action procedure outlined in Section 12.4.4.1. Resolve the problem before proceeding with sample analysis.

9.3.4.5 If the method blank does not meet the retention time (RT) requirements for internal standards (Section 12.3.6), check the GC/MS instrument for malfunction and recalibrate. Reanalyze the method blank. Sample analyses cannot proceed until the method blank meets these requirements.

9.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

9.4.1 Summary of MS/MSD - To evaluate the effects of the sample matrix, a mixture of target compounds is spiked into two aliquots of a water or soil sample and analyzed in accordance with the appropriate method. MS/MSDs are not performed on air or wipe samples.

9.4.2 Frequency of MS/MSD Analyses

9.4.2.1 An MS/MSD pair is analyzed with each batch of ≤20 samples of each water or solid matrix type. MS/MSDs are not performed on wipe or air samples.

9.4.2.2 For QA/QC purposes, water rinsate samples and/or field/trip blanks (field QC) or PE samples may accompany samples that are delivered to the laboratory for analysis. These field QC or PE samples are not used for MS/MSD analyses.

9.4.2.3 If the agency requesting the analyses designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory should choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory should notify the agency that insufficient sample was received and identify the sample selected for the MS/MSD analysis.

9.4.2.4 If there is insufficient sample remaining in any of the samples in a batch to perform the requested MS/MSD, then the laboratory must immediately contact the agency to inform them of the problem. The agency will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis.

9.4.3 Procedure for Preparing MS/MSD

9.4.3.1 Water Samples

Prepare two additional aliquots of the sample chosen for spiking. The volume chosen should be equal to that of the associated samples. Add a sufficient amount of the surrogate standard spiking solution and the matrix spiking solution to each aliquot to result in a concentration that is expected to be at approximately the midpoint of the calibration range. Extract, concentrate, clean up, and analyze the MS/MSD according to the procedures for water samples (Section 11.2).

9.4.3.2 Soil/Sediment Samples

Prepare two additional aliquots of the sample chosen for spiking in the two 400 mL beakers. The amount chosen should be equal to that of the associated samples. Add twice the weight of anhydrous powdered sodium sulfate to each aliquot (relative to sample). Mix well. Add a sufficient amount of the surrogate standard spiking solution and the matrix spiking solution to each aliquot to result in a concentration that is expected to be at approximately the midpoint of the calibration range, and then follow the appropriate extraction procedure in Section 11.3. Extract, concentrate, clean up, and analyze the MS/MSD according to the procedures for soil/sediment samples (Section 11.3).

9.4.4 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported.

9.4.5 Calculations for MS/MSD

9.4.5.1 Calculate the recovery of each MS/MSD compound in the MS/MSD sample.

9.4.5.2 Calculate the relative percent difference (RPD) of the recoveries of each compound in the MS/MSD (Equation 12). Concentrations of the MS/MSD compounds are calculated using the same equations as are used for target compounds (Equations 5 through 8).

9.4.6 Technical Acceptance Criteria for MS/MSD

9.4.6.1 All MS/MSDs must be prepared and analyzed at the frequency described in Section 9.4.2. All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial and CCV technical acceptance criteria and the method blank technical acceptance criteria.

9.4.6.2 The MS/MSD must have an associated method blank meeting the blank technical acceptance criteria.

9.4.6.3 The MS/MSD must be extracted and analyzed within the technical holding time.

9.4.6.4 The RT shift for each of the internal standards must be within ± 30 seconds between the MS/MSD sample and the most recent CCV standard analysis.

9.4.6.5 MS/MSD compound recovery and RPD limits are 50 – 150 % and ≤30 %, respectively. These limits are based on SW-846 methods and will be updated following method validation in multiple laboratories.

9.4.7 Corrective Action for MS/MSD

If recovery or RPD limits are not met and the LCS, CCV and method blank are within acceptable limits, this might be an indication of matrix interferences. If recovery or RPD limits are not met and the LCS, CCV or method blank are not within acceptable limits, then the MS/MSD samples should be reanalyzed along with all appropriate QC samples. If, after reanalysis, MS/MSD recovery limits cannot be met, flag the results of the associated sample.

9.5 Laboratory Control Sample (LCS)

An LCS consists of an aliquot of clean reference matrix, of the same weight or volume as the corresponding field samples, and spiked with the same compounds at the same concentrations used to spike the MS/MSD. When the results of the MS/MSD analysis indicate a matrix interference might be present, the LCS results are used to verify that the interferences are due to the sample matrix and not from artifacts introduced in the laboratory.

9.5.1 Preparation of LCS

An LCS is prepared by spiking reagent water (when analyzing water samples), clean sand (when analyzing soils), a clean sorbent and filter (when analyzing air samples), or a clean wipe (when analyzing wipe samples) at a concentration that is expected to be at approximately the midpoint of the calibration range. The same spiking levels that are used for the MS/MSD samples should be used for the LCS. Extract and analyze the LCS according to the procedure(s) in Section 11.2 for water samples, 11.3 for soil/sediment samples, 11.4 for air filter samples, or 11.5 for wipe samples.

Note: Air filters and wipes used for the LCS and method blank should come from the same manufacturing lot as those used for samples.

9.5.2 Frequency of LCS Analyses

One LCS should be prepared, extracted, analyzed, and reported for every 20 field samples or fewer extracted in a batch of a similar matrix. The LCS must be extracted and analyzed concurrently with the samples, using the same extraction protocol, cleanup procedure (if required), and instrumentation.

9.5.3 Calculations for LCS

Calculate the recovery of each target and surrogate compound in the LCS.

9.5.4 Technical Acceptance Criteria for LCS Analysis

9.5.4.1 All LCSs should be extracted and analyzed at the frequency described in Section 9.5.2 on a GC/MS system meeting the tuning, initial and CCV, and the method blank technical acceptance criteria.

9.5.4.2 LCS compound recovery limits will be established following laboratory validation of these procedures. Recovery limits of 50–150 % are applied as guidance until laboratory limits are established.

9.6 Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed, laboratories may determine an IDL for each target compound on each instrument used for analysis. While determining IDLs is not required, IDL results can be helpful in determining an appropriate spike level for use in determining the MDL (Section 9.7). It is recommended that IDLs be verified annually thereafter or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters, or electron multiplier; or installing a different GC column type. An IDL is instrument-specified and independent of sample matrices. An IDL is determined for each compound as the concentration that produces an average signal-to-noise ratio (S:N) between 3:1 and 5:1 for at least three replicate injections.

9.7 Method Detection Limit (MDL) Determination

Before any field samples are analyzed, laboratory MDLs should be determined for each target analyte in appropriate reference matrices (i.e., reagent water, Ottawa sand, clean wipes or air filters), using the sample preparation and analytical procedures described in this analytical protocol for each specific matrix (see also 40 CFR Part 136, Appendix B).

9.7.1 The laboratory must use full method procedures to prepare and analyze at least seven replicates.

9.7.2 Spike each replicate sample at concentrations of 1 – 5 times the IDL concentration for each analyte and analyze the samples following analytical protocol procedures.

9.7.3 To determine analyte MDLs, the following equation is applied to the analytical results (Student's t-factor is dependent on the number of replicates used; 3.14 assumes seven replicates):

EQ. 1. Method Detection Limit Calculation

$$MDL = 3.14 \times sd$$

where:
sd = standard deviation for the analytical results, and
3.14 = the Student's t-value for seven replicate samples

9.7.4 The MDL results calculated using Equation 1 in Section 9.7.3 must meet the following requirements as well as all other requirements specified in 40 CFR Part 136, Appendix B:

- MDL result must not be greater than the spiking level used for the MDL determination.
- MDL result must not be less than 0.10 times the spiking level used for the MDL determination.

If either requirement is not met, the laboratory must adjust the spiking level appropriately and repeat the MDL determination.

9.8 Quantitation Limit (QL) Determination

A QL determination is recommended for each laboratory/technician performing the method for the first time, or in cases where new or repaired instrumentation is being used. Laboratory QLs are determined by first assessing at least four samples containing concentrations of target analytes at the levels of the lowest calibration standard, against the criteria listed below. If any of these criteria are not met, samples are assessed at concentrations of the next (second lowest) calibration standard. These criteria are provided as guidance. If the criteria cannot be met, the laboratory should consult project managers to determine if the QL is sufficient to address project needs.

- Results from spikes at the QL should be above the MDL.
- The QL should be at or above the lowest calibration level.
- The QL should be at least two times the MDL.
- The RSD of results from spikes at the QL should be less than 30 %.
- The mean recovery of spikes at the QL should be within 50 – 150 %.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operating Conditions

10.1.1 Gas Chromatograph (GC)

10.1.1.1 The following are suggested GC conditions when using an Agilent 6890/5973 mass selective detector (MSD) or equivalent. These conditions were used during the single-laboratory evaluation of this protocol, using a Zebron™ ZB-5MS column. Instrument conditions are the same for SIM and full scan analysis modes. Analyte RTs using the conditions below are provided in Section 17, Table 4.

Injector Temperature:	250 °C
Injection Volume:	1.0 µL
Injector Type:	Grob-type, Splitless
Column:	Zebron™ ZB-5MS (95 % dimethyl, 5 % diphenylpolysiloxane), 30 m, 0.25 mm I.D., 0.25µm
Oven Temperature	35 °C for 5.5 minutes

Program:	35 - 270 °C at 10 ºC/minute, hold for 2 minutes. 270 - 320 °C at 30 °C/minute, hold for 5 minutes.
Carrier Gas:	1.0 mL/minute, helium (7.07 psi, 36 cm/second)

10.1.1.2 The conditions below were used during the single-laboratory evaluation of this analytical protocol, using an Agilent Programmed Temperature Vaporization injector. These conditions may be necessary when using a programmed temperature vaporization injection GC/MS.

Oven Temperature Program:	40 °C for 4 minutes. 40 - 270 °C at 10 °C/minute, hold for 4 minutes. 270 - 320 °C at 10 °C/minutes, hold for 2 minutes.
Front Inlet Program:	40 °C for 0.10 minute. 40 - 340 °C at 600 °C/minute, hold for 10 minutes. 340 - 170 °C at 10 °C/minute.

10.1.2 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy	70 electron volts (nominal)
Mass Range	35 to 500 daltons
Ionization Mode	Electron ionization (EI)
Scan Time	Not to exceed 1 second per scan

For SIM ion groupings and dwell times, see Table 5 (Section 17).

10.2 GC/MS Mass Calibration (Tuning) and Ion Abundance

10.2.1 Summary of GC/MS Instrument Performance Check

The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibration such as perfluoro-tri-*n*-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.3.3). Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution (Table 1) containing DFTPP.

10.2.2 Frequency of GC/MS Instrument Performance Check

10.2.2.1 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed.

10.2.2.2 The 12-hour period for the instrument performance check and initial or CCV begins at the moment of injection of the DFTPP.

10.2.3 GC/MS Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of 50 ng or less of DFTPP into the GC/MS or by adding a sufficient amount of DFTPP to the calibration standards to result in an on-column amount of 50 ng or less of DFTPP (Section 7.2.3.3) and analyzing the calibration standard.

10.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

10.2.4.1 The GC/MS system tune must be verified or the instrument must be tuned at the frequency described in Section 10.2.2.

10.2.4.2 The abundance criteria listed in Table 1 must be met. The mass spectrum of DFTPP must be acquired using an average of three scans (the peak apex scan and the scans immediately preceding and following the apex). Background subtraction is required and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be used only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

Note: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical GC/MS instrument run conditions.

10.2.5 Corrective Action for GC/MS Instrument Performance Check

10.2.5.1 If the GC/MS instrument performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to perform maintenance to achieve the criteria.

10.2.5.2 The instrument performance check technical acceptance criteria in Section 10.2.4 must be met before any standards, samples (including QC samples), or required blanks are analyzed.

10.2.6 Selected Ion Monitoring (SIM)

SIM analysis can be used to achieve lower detection and quantitation levels. Instrument conditions for SIM analysis are the same as those for full scan. Analyte-specific dwell times and ion groupings are provided in Table 5.

10.3 Initial Calibration

10.3.1 Summary of Initial Calibration

Prior to the analysis of samples and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.3.4.1 and Tables 10a

and 10b) to determine instrument sensitivity and the linearity of the GC/MS response for the target and surrogate compounds.

10.3.2 Frequency of Initial Calibration

10.3.2.1 Each GC/MS system should be calibrated whenever the laboratory takes corrective action that might change or affect the initial calibration criteria, or if the CCV technical acceptance criteria have not been met.

10.3.2.2 If time remains in the 12-hour period that defines an analysis batch after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period.

10.3.3 Procedure for Initial Calibration

10.3.3.1 Prepare calibration standards containing the target compounds and associated surrogates at the concentrations described in Tables 10a (full scan) and 10b (SIM).

10.3.3.2 Add a sufficient amount of internal standard solution (Section 7.2.3.5) to aliquots of calibration standards to result in 10 ng/µL of each internal standard. Standards specified in Section 7.2.3.5 should permit most of the target compounds to have relative retention times (RRTs) of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

10.3.3.3 Analyze each calibration standard by injecting 1.0 µL of standard.

10.3.4 Calculations for Initial Calibration

10.3.4.1 Calculate the relative response factors (RRFs) for each target compound and surrogate using Equation 2 and the primary characteristic ions found in Table 4. Assign the target compounds and surrogates to the internal standard according to Table 2. For internal standards, use the primary ion listed in Table 4 unless interferences are present. Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 2. Relative Response Factor (RRF) Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:
A_x = Area of the characteristic ion for the compound to be measured (Table 4)
A_{is} = Area of the characteristic ion for specific internal standard (Table 4)
C_{is} = Amount of the internal standard injected (ng)

C_x = Amount of the target compound or surrogate injected (ng)

Note: Phosphamidon and chlorfenvinphos exist as two and three isomers, respectively; therefore, RRF for these analytes is calculated as the sum of the peak areas of the individual isomers.

10.3.4.2 The Mean Relative Response Factor ($\overline{RRF}$) for the Initial Calibration

$\overline{RRF}$ must be calculated for all compounds. Calculate the %RSD of the RRF values for the initial calibration. If linear regression or quadratic curve fitting is needed, consult SW-846 Method 8000C (Reference 16.13) for guidance on the appropriate calculations.

10.3.5 Technical Acceptance Criteria for Initial Calibration

10.3.5.1 All initial calibration standards should be analyzed at the concentration levels described in Section 7.2.3.4.1 and at the frequency described in Section 10.3.2 on a GC/MS system meeting the instrument performance technical acceptance criteria.

10.3.5.2 The RRF for each target compound and surrogate should be greater than or equal to 0.01.

10.3.5.3 The %RSD of the RRFs over the initial calibration range for each target compound and surrogate should be less than or equal to 20. If %RSD for a target analyte or surrogate cannot meet the acceptance criteria, curve fitting by linear or quadratic regression may be used, provided the R^2 value is greater than or equal to 0.99 (linear) or 0.995 (quadratic). Single-laboratory calibration results are provided in Table 6a (full scan) and Table 6b (SIM).

Note: Percent drift (PD) criteria may be added to the initial calibration following a multi-laboratory study and/or updates to SW-846 Method 8000C (Reference 16.13).

10.3.5.4 Excluding those ions in the solvent front, no quantitation ion may saturate the detector.

10.3.6 Corrective Action for Initial Calibration

10.3.6.1 If any technical acceptance criteria for initial calibration are not met, inspect the system for problems and take corrective actions to achieve the acceptance criteria.

10.3.6.2 Initial calibration technical acceptance criteria must be met before any samples or required blanks are analyzed.

10.4 Continuing Calibration Verification (CCV)

10.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples, and after instrument performance check technical acceptance criteria and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements. The CCV standard contains all the target compounds, surrogates, and internal standards. The same injection volume must be used for all standards, samples, and blanks.

10.4.2 Frequency of Continuing Calibration Verification – Each GC/MS used for analysis must be checked once per analytical batch for every 12-hour period of operation or after the analysis of 10 samples, whichever comes first. The 12-hour period of operation begins with the injection of DFTPP for full scan or the analysis of the CCV.

10.4.3 Procedure for Continuing Calibration Verification

10.4.3.1 Add a sufficient amount of internal standard solution (Section 7.2.3.5) to an aliquot of CCV standard to result in a concentration of 0.5 ng/µL for SIM analyses, and 10 ng/µL for full scan analyses. The concentration of the CCV should fall near the mid-point of the calibration curve.

Note: The laboratory should analyze a CCV standard at a concentration near the mid-point of the calibration range. It is recommended that the laboratory also analyze a CCV standard at the low end of the calibration range. For example, analyze a mid-point CCV at the beginning of an analytical batch and a low-point CCV at the end of the analytical batch.

10.4.3.2 Analyze the CCV standard by injecting 1.0 µL of standard.

10.4.4 Calculations for CCV

10.4.4.1 Calculate an RRF for each target compound and surrogate using Equation 2 and the primary characteristic ions found in Table 4.

10.4.4.2 Calculate the Percent Difference (%Difference) between the $\overline{RRF_i}$ from the most recent initial calibration and the continuing calibration verification RRF for each target compound and surrogate using Equation 3a.

EQ. 3a. Relative Response Factor Percent Difference Calculation

$$\%\text{Difference}_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where:
RRF_i = Mean Relative Response Factor from the most recent initial calibration meeting technical acceptance criteria
RRF_c = Relative Response Factor from CCV standard

10.4.5 Technical Acceptance Criteria for CCV

10.4.5.1 The CCV standard should be analyzed at the frequency described in Section 10.4.2, on a GC/MS system meeting the instrument performance check and the initial calibration technical acceptance criteria.

10.4.5.2 The RRF for each target compound and surrogate should be ≥ 0.01.

10.4.5.3 The RRF percent difference for each target compound should be within the range of ±50 %.

Note: This range may be updated following additional laboratory testing of the method.

If regression techniques are used for the initial calibration, the CCV should be evaluated in terms of PD using concentrations (see Equation 3b). The PD for each target compound should be within the range of ±50 %.

EQ. 3b. Percent Drift (PD) Calculation for CCV

$$PD = \frac{\text{Calculated Concentration} - \text{Theoretical Concentration}}{\text{Theoretical Concentration}} \text{x} 100\%$$

10.4.5.4 Excluding those ions in the solvent front, no quantitation ion may saturate the detector.

10.4.6 Corrective Action for CCV

10.4.6.1 If the CCV technical acceptance criteria in Section 10.4.5 are not met, recalibrate the GC/MS instrument according to Section 10.3.

10.4.6.2 CCV technical acceptance criteria should be met before any samples, MS/MSDs, or required blanks are analyzed. If CCV criteria are not met, flag associated samples and blanks accordingly.

11.0 ANALYTICAL PROCEDURE

11.1 Sample Preparation – General

11.1.1 If an insufficient sample amount (less than 90 % of the required amount) is received to perform the analyses, use a reduced amount and adjust calculations accordingly.

11.1.2 If multi-phase samples (e.g., a two-phase liquid sample, oily sludge/sandy soil sample) are received, the laboratory should contact the agency requesting the analyses. If some or all phases of the sample are amenable to analysis, the agency may require the laboratory to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample

- Separate the phases of the sample and analyze each phase separately
- Separate the phases and analyze one or more but not all of the phases
- Do not analyze the sample

11.2 Preparation of Water Samples

Microscale extraction (MSE) has been evaluated for precision and bias in a single-laboratory and is the suggested procedure for preparing water samples. Single-laboratory data are provided in Section 17.0, Table 7a and 8a. See Appendix A for alternative preparation techniques, such as solid phase extraction (SPE).

11.2.1 Approximately 35 mL of a water sample is required for this extraction. If extraction is to be performed in the sample receipt vial, remove any excess sample so that a total sample volume of 35 mL is retained and recap the vial. Weigh the capped vial. Record the weight to the nearest 0.1 gram. Alternatively, 35 mL of sample can be transferred by pipette into the vial and the weighing step eliminated.

Note: The conical bottoms of centrifuge vials may allow the DCM layer to be removed more easily than from VOA vials.

11.2.2 Add a sufficient volume of each surrogate to the sample to yield a concentration approximating the mid-calibration level in the VOA vial.

11.2.3 Add 2.0 mL of DCM using a Class A volumetric pipette or gastight syringe (or equivalent) and approximately 12 grams of anhydrous sodium chloride to the sample. Replace the vial cap.

Note: During a multi-laboratory exercise using this protocol for analysis of dichlorvos, mevinphos and TETS in water, two laboratories used less salt (8.8 and 10 grams) and one laboratory found it was easier to dissolve the salt if it was added prior to adding the DCM. These modifications, as well as other solvent delivery systems, such as a repeating solvent dispenser, may be used provided that equivalent performance can be demonstrated.

11.2.4 Shake the vial vigorously or vortex for approximately 2 minutes or until the sodium chloride dissolves completely.

11.2.5 Briefly allow the phases to settle. If the phases do not separate, then centrifuge at 500 times the force of gravity (500 G force units) for 5 – 15 minutes. CAUTION: The maximum safe handling speed of each centrifuge will depend, in part, on the vials used and should be determined prior to use. Adding an additional volume of DCM may also help separate the phases.

Note: If additional DCM is used, calculations must be adjusted to account for the additional volume.

11.2.6 Using a 2.0-mL gastight syringe, transfer approximately 1.5 mL of the lower (DCM) layer to a 2-mL vial with a PTFE-lined screw cap, taking precautions to

exclude any water from the syringe. Add a small amount (~50 mg) of anhydrous sodium sulfate to the vial, then cap, and shake for 2 minutes.

11.2.7 Using a 1.0-mL gastight syringe, transfer 1.0 mL of the dried extract to a 2-mL vial with a PTFE-lined screw cap.

11.2.8 Discard the remaining contents of the VOA vial according to laboratory waste disposal guidelines. Shake off the last few drops with short, brisk movements. If needed, rinse the vial with a water-soluble solvent to ensure the extraction solvent is removed. If the vial was pre-weighed (i.e., exact sample volume used in Section 11.2.1 is unknown), reweigh the capped vial, and record the weight to the nearest 0.1 grams. The difference between this weight and the weight determined in Section 11.2.1 is equal to the volume of water extracted in milliliters. As the density of water is 1.00 g/mL (at 20 °C), the volume of water extracted may be assumed to be equal to the weight of water extracted.

11.2.9 Proceed to Section 11.6.

11.3 Preparation of Soil/Sediment Samples - General

MSE was evaluated for precision and bias in a single-laboratory and is recommended for analysis of soil or sediment samples. Laboratory results are provided in Tables 7b and 8b. See Appendix A for alternative techniques.

11.3.1 Soil/Sediment Samples - Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

11.3.2 pH Determination – If pH determination is requested, transfer a 1:1 (w:w) ratio of sample:water to a 100-mL beaker and stir for one hour. Determine the pH of the sample with a pH meter or wide-range pH paper, and document this value in the data narrative. Discard this portion of the sample.

11.3.3 Percent Moisture Determination

If percent moisture determination is requested, immediately after weighing the sample for extraction, weigh 5 - 10 grams of the soil/sediment into a tared crucible. Determine the Percent Moisture (%Moisture) by drying overnight at 103-105 °C. Allow the sample to cool in a desiccator before weighing.

EQ. 4. Percent Moisture Calculation

$$\%Moisture = \frac{grams\ of\ \ wet\ sample - grams\ of\ \ dry\ sample}{grams\ of\ \ wet\ sample} \times 100$$

11.3.4 Perform the following steps rapidly to avoid loss of the more volatile compounds. Weigh 10 grams of sample to the nearest 0.1 gram, and place in a 400-mL beaker. Add double the weight (relative to the sample) of anhydrous powdered or granulated sodium sulfate and mix well.

11.3.5 Microscale Solvent Extraction (MSE)

Note: The extraction solvent of choice is dependent on the analyte that is to be measured. For most target analytes, the extraction solvent that gave the best results in a single-laboratory was acetone:DCM:ethyl acetate (1:2:1 v:v:v). If nicotine, crimidine, phencyclidine, or strychnine is to be measured, the extraction solvent giving the best results was 5 % TEA in ethyl acetate. Results of a single-laboratory preliminary evaluation of alternate solvent mixtures are provided in Appendix A.

11.3.5.1 Add approximately 2.5 grams of anhydrous sodium sulfate to a pre-cleaned extraction tube (e.g., 40-mL VOA vial with PTFE screw cap). Also add 5 - 10 pre-cleaned glass beads (Section 6.1.2.5).

11.3.5.2 Weigh 10 grams of sample into the tared extraction tube. Wipe the lip and threads of the tube with a clean cloth (e.g., Kimwipe®, Kimberly-Clark Professional, Roswell, GA, or equivalent). Cap tightly, and record the weight to the nearest 0.01g.

11.3.5.3 Add 10 µg of the surrogate standard compounds in DCM directly to the sample. If the surrogate compounds in the spiking solution are at a concentration of 100 µg/mL, add 0.1 mL of the spiking solution.

11.3.5.4 Add 15 mL of the extraction solvent (see Note in Section 11.3.5 for solvent choice) to the tube, and cap tightly. For certain sample types, 15 mL of solvent will not be sufficient to completely immerse the sample. For these situations, add the minimal amount of solvent so that the sample is completely immersed. The additional volume of solvent should be reported in the narrative.

11.3.5.5 Shake the tubes vigorously until the slurry is free-flowing. Break up any chunks with a metal spatula, working quickly but gently. Cap immediately when finished. Add more sodium sulfate and manually mix as necessary to produce a free-flowing, finely divided slurry.

11.3.5.6 Extract the samples by rotating end-over-end for at least 1 hour or by sonicating, in a water bath, for at least 30 minutes.

11.3.5.7 Vortex each sample for 30 seconds. Add ~ 1g anhydrous, sodium sulfate to each sample. Cap and shake briefly or vortex to ensure thorough mixing. Allow the solids to settle or centrifuge for 1–2 minutes at 1000 rpm. If the solid is still unsettled, repeat the centrifuge step, but increase speed to 2500 rpm. CAUTION: Different centrifuge makes and models have different maximum centrifuge speeds that are recommended for safe operation. The maximum safe handling speed of each centrifuge will depend, in part, on the vials used and should be determined prior to centrifuging samples. Repeat until the solid is completely settled. If after repeating the centrifuging steps several times the solid is still unsettled, proceed to Section 11.3.5.8. Once the solid has settled, decant or pipette the solvent layer into a pre-cleaned, 40-mL VOA vial with PTFE-lined screw cap and proceed to Section 11.3.5.9.

Note: For solids that have difficulty settling, pipetting is recommended.

11.3.5.8 If solids are not settled out by centrifugation (Section 11.3.5.7), filter by placing a small plug of glass wool into a small glass funnel. Add anhydrous sodium sulfate to cover the glass wool plug. Wet the sodium sulfate thoroughly with DCM. Decant the sample solvent layer into the funnel. Rinse the sodium sulfate with 2-3 mL of DCM as soon as the surface is exposed, not allowing it to dry.

Note: Due to the potential for analyte loss, filtration should be used only as a last resort in cases where centrifugation does not work.

11.3.5.9 Extract the sample twice more by adding approximately 10 mL of the extraction solvent to the sample, capping the extraction tube tightly, and shaking vigorously by hand for 2 minutes. Be certain to wipe the lip and threads of the extraction tube clean before capping each time. More sodium sulfate can be added as necessary to dry the extract and break up any clumps that may have formed.

Note: Less than three extractions may be needed and can be used provided all surrogate and MS/MSD performance criteria are met.

11.3.5.10 After each extraction, repeat procedures in Section 11.3.5.6 – 11.3.5.8.

11.3.5.11 If a sample requires extraction by both solvent systems, repeat procedures in Sections 11.3.5.3 – 11.3.5.9, using the other extraction solvent. Extracts are not combined and are analyzed separately.

11.3.5.12 Proceed to Section 11.6.

11.4 Preparation of Air Samples

MSE of spiked air filters has been evaluated in a single-laboratory and is the suggested procedure. Data characterizing pressurized fluid extraction (PFE) efficiency is limited and the procedure is provided as a possible alternative for analytes exhibiting poor results by MSE. Follow the procedure in Section 11.3.5 replacing the soil sample with the air filter and using the acetone:DCM:ethyl acetate (1:2:1 v:v:v) solvent system. Once extraction is complete, proceed to Section 11.6.

Note: If PUF is the sorbent, the extraction solvent is 10 % diethyl ether in hexane. If XAD-2 resin is the sorbent, the extraction solvent is DCM.

11.5 Preparation of Wipe Samples

MSE of spiked wipe samples was evaluated in a single-laboratory and is the suggested procedure for preparing wipe samples. Laboratory results are provided in Table 8c. See Appendix A for alternative preparation techniques. Follow the procedure in Section

11.3.5 replacing the soil sample with a surface wipe and using the acetone:DCM:ethyl acetate (1:2:1 v:v:v) solvent system. Once extraction is complete, proceed to Section 11.6.

11.6 Final Concentration of Extract by Nitrogen Evaporation Technique

11.6.1 Place the concentrator tube in a warm water bath (30 - 35 °C recommended) and evaporate the solvent volume to just below 1 mL by blowing a gentle stream of clean dry nitrogen (filtered through a column of activated carbon) above the extract. CAUTION: Gas lines from the gas source to the evaporation apparatus should be stainless steel, copper, or PTFE tubing. Plastic tubing must not be used between the carbon trap and the sample since plastic tubing may introduce interferences. The internal wall of the concentrator tube must be rinsed down several times with DCM. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

11.6.2 Final Extract Volumes

The final extract volumes in Sections 11.6.2.1 through 11.6.2.4 are recommended volumes. If more sensitive GC/MS systems are used, the larger extract volumes (less concentrated extracts) may be used provided that the QLs for all target compounds can be achieved, and that all surrogates and internal standards have an expected extract concentration that is at the mid-point of the calibration curve. Once extract volumes are obtained, transfer the extract to a PTFE-sealed screw-cap vial (approximately 2.0 mL). Label the vial and store at 6 °C or less.

11.6.2.1 Water - As concentration of the sample extract is not needed for these sample matrices, no adjustment of the final extract volume is required. The nominal volume of DCM added to water samples is 2.0 mL. Target compound and surrogate spiking solutions also contain DCM; therefore, the total volume of DCM added may be slightly greater than 2.0 mL. The actual total volume of DCM added should be used in the calculations in Section 12.2.

11.6.2.2 Solids - Adjust the final volume for solid samples to a final volume of 1.0 mL with DCM or another appropriate solvent.

11.6.2.3 Air Filters - Adjust the final volume for air filter samples to a final volume of 1.0 mL with DCM or another appropriate solvent.

11.6.2.4 Wipes - Adjust the final volume for wipe samples to 1.0 mL with DCM or another appropriate solvent.

11.7 Sample Analysis by Gas Chromatograph/Mass Spectrometer (GC/MS)

11.7.1 Analyze extracts only after the GC/MS system has met the instrument performance check (Section 10.2.4), initial calibration (Section 10.3.5), and CCV requirements (10.4.5). The same instrument conditions used for calibration must be used for the analysis of samples.

11.7.2 Add a sufficient amount of the internal standard solution (Section 7.2.3.5) to each accurately measured aliquot of sample extract to result in 10 ng/µL concentration of each internal standard in the extract volume. If sample extracts are to be diluted, add internal standards after dilution.

11.7.3 Inject 1.0 µL of the sample extract into the GC/MS.

Note: The injection volume used for sample extracts must be the same as the injection volume used for the calibration standards.

11.7.4 Sample Dilutions

11.7.4.1 If the response of any target compound in any sample exceeds the response of the same target compound in the high standard of the initial calibration, that sample extract must be diluted. Add the internal standard solution to the diluted extract for a concentration of 10 ng/µL of each internal standard, and analyze the diluted extract.

11.7.4.2 Use the results of the original analysis to determine the approximate Dilution Factor (DF) required to achieve the largest analyte peak within the calibration range. The DF chosen must keep the response of the largest peak for a target compound in the upper half of the calibration range of the instrument.

12.0 CALCULATIONS AND DATA ANALYSIS

12.1 Qualitative Identification of Target Compounds

12.1.1 Target compounds should be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample analyte within the Gas Chromatograph (GC) RRT unit window established from the 12-hour calibration standard
- Correspondence of the sample analyte and calibration standard component mass spectra

12.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the analyte RTs to those from the midpoint initial calibration standard. Otherwise, use the corresponding CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using EICPs for ions unique to the component of interest.

12.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on the laboratory's GC/Mass Spectrometer (GC/MS) meeting the daily instrument performance requirements for DFTPP are required. Once obtained, these standard spectra may be used for identification

purposes only if the laboratory's GC/MS meets the DFTPP daily instrument performance requirements.

12.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectrum at a relative intensity greater than 10 % (most abundant ion in the spectrum equals 100 %) must be present in the sample spectrum. The relative intensities of ions must agree within ±20 % between the standard and sample spectra (e.g., for an ion with an abundance of 50 % in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 %). Ions greater than 10 % in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are below QLs but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the QL is 5.0 µg/L and concentration of 3.0 µg/L is calculated, report as "3.0J."

12.1.5 If a compound cannot be verified by all of the spectral identification criteria in Sections 12.1.1 – 12.1.4, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory should report the identification and proceed with quantitation.

12.2 Data Analysis and Calculations of Target Compounds

12.2.1 Target compounds identified are quantitated by the internal standard method. The internal standard used should be the one assigned to that analyte for quantitation (Table 2). The EICP area of primary characteristic ions of analytes listed in Table 4 are used for quantitation.

12.2.2 It is expected that situations will arise when the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interference. In these circumstances, the laboratory should perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration includes only the area attributable to the specific target compound. The area integrated must not include baseline background noise, and must not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

12.2.3 In some instances, the data system report may have been edited or manual integration or quantitation may have been performed. In all such instances, the GC/MS operator should identify such edits or manual procedures by initialing and dating the changes made to the report, and include the integration scan range. The GC/MS operator should also mark each integrated area on the quantitation report.

12.2.4 The requirements listed in Sections 12.2.1 - 12.2.3 apply to all standards, samples, and blanks.

12.2.5 The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration is used to calculate the concentration in the sample. Secondary ion quantitation is allowed ONLY when there are sample interferences with the primary ion. If linear regression is used, a regression curve must be used to calculate the concentration in samples. Refer to Section 12.2.7 for calculating sample concentration using linear regression techniques.

12.2.6 Calculate the concentration in the sample using the $\overline{RRF}$ and Equations 5 − 8.

12.2.6.1 Water

EQ. 5. Concentration of Water Sample

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(\overline{RRF})(V_o)(V_i)}$$

where:
A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in ng
V_o = Volume of water extracted in mL
V_i = Volume of extract injected in µL
V_t = Volume of the concentrated extract in µL
$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard
DF = Dilution Factor

The DF for analysis of water samples is defined as follows:

$$DF = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

12.2.6.2 Soil/Sediment

EQ. 6. Concentration of Soil/Sediment Sample

Eq. 6 includes a %moisture factor (D) for those cases when data are to be reported on the basis of dry sample weight. In cases where results are reported in terms of sample weight, this factor is deleted from the equation.

$$\text{Concentration mg/Kg (Dry weight basis)} = \frac{(A_x)(I_s)(V_t)(DF)}{1000(A_{is})(V_i)(\overline{RRF})(W_s)(D)}$$

where:
A_x, I_s, A_{is}, V_i, V_t are as given for water, above.

$$D = \frac{100 - \%Moisture}{100}$$

%Moisture is as given in EQ. 4
W_s = Weight of sample extracted in grams
$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard
DF = Dilution Factor

12.2.6.3 Air

EQ. 7. Concentration of Gas Phase Sample

$$Concentration\ \mu g / m^3 = \frac{(A_x)(I_s)(V_t)(DF)}{1000(A_{is})(V_o)(V_i)(\overline{RRF})}$$

where:
A_x = area response for the compound to be measured, counts
A_{is} = area response for the internal standard, counts
I_s = amount of internal standard, ng
$\overline{RRF}$ = the mean RRF from the most recent initial calibration, dimensionless
V_o = volume of air sampled, std m^3
V_t = volume of final extract, µL
V_i = volume of extract injected, µL
DF = dilution factor for the extract. If there was no dilution, DF equals 1. If the sample was diluted, the DF is greater than 1.

12.2.6.4 Wipes

EQ. 8. Concentration of Wipe Sample

$$Concentration\ \mu g / cm^2 = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(Area)(V_i)(\overline{RRF})}$$

where:
A_x = area response for the compound to be measured, counts
A_{is} = area response for the internal standard, counts
I_s = amount of internal standard, µg
$\overline{RRF}$ = mean RRF from the most recent initial calibration, dimensionless
Area = area of surface wiped, cm^2. If concentration is reported as µg/wipe, area = 1 wipe.
V_t = volume of final extract, µL
V_i = volume of extract injected, µL
DF = dilution factor for the extract. If there was no dilution, DF equals 1. If the sample was diluted, the DF is greater than 1.

12.2.7 Calculate the concentration in the sample using linear regression. Refer to SW-846 Method 8000C (Reference 16.13) if calibration curves were determined

using quadratic equations.

12.2.7.1 Set y = (Peak Area of Target/Peak Area of Internal Standard) and x = (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

12.2.7.2 Plot (Peak Area of Target/Peak Area of Internal Standard [Y-axis]) vs. (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

12.2.7.3 Determine the slope of the line (m) and the y-intercept (b).

12.2.7.4 Rearrange the line equation to solve for x: x = (y-b)/m.

12.2.7.5 Multiply x by the concentration of the internal standard to get concentration of target in extract.

12.2.7.6 Multiply the concentration of target analyte in the extract by the extract volume and divide by the sample volume to get the concentration of target analyte in the sample.

12.2.8 QL Calculations

12.2.8.1 Water Samples

EQ. 9. Aqueous Adjusted QL

$$\text{Adjusted QL} = \text{Method QL} \times \frac{(V_x)(V_t)(DF)}{(V_o)(V_c)}$$

where:
V_t, DF, and V_o are as given in Equation 5.
V_x = Method sample volume (35 mL).
V_c = Method concentrated extract volume.

12.2.8.2 Soil/Sediment Samples

EQ. 10. Soil/Sediment Adjusted QL

$$\text{Adjusted QL} = \text{Method QL} \times \frac{(W_x)(V_t)(DF)}{(W_s)(V_c)(D)}$$

where:
V_t and DF are as given in Equation 5
W_s and D are as given in Equation 6
W_x = Method sample weight (10 grams for soil/sediment samples)
V_c = Method concentrated extract volume

12.2.9 Surrogate Recoveries

12.2.9.1 Calculate surrogate recoveries for all samples, blanks, and MS/MSDs using Equation 11.

EQ. 11. Percent Recovery

$$Recovery = \%R = \frac{C_S}{C_n} \times 100$$

where:
C_s = Measured concentration of the spiked sample aliquot.
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS).

12.2.9.2 Calculate the RPD of the concentrations of each compound in the MS/MSD using Equation 12. Concentrations of the MS/MSD compounds are calculated using the same equations used for target compounds (Equation 5 for water samples and Equation 6 for solid samples in Section 12.2.6).

EQ. 12. Relative Percent Difference (RPD) Calculation

$$\text{RPD} = \frac{|\,C_1 - C_2\,|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:
C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot
Note: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.9.3 Calculate the concentrations of the surrogates using the same equations as used for the target compounds. Calculate the recovery of each surrogate.

12.3 Technical Acceptance Criteria for Sample Analysis

12.3.1 Samples must be analyzed on a GC/MS system meeting the instrument performance check, initial calibration, CCV, and blank technical acceptance criteria.

12.3.2 The sample must be extracted and analyzed within the technical holding times.

12.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

12.3.4 Percent recoveries of the surrogates in a sample must be within the recovery limits of 50–150 % .

Note: Surrogate recovery requirements do not apply to samples that have been diluted.

12.3.5 The instrumental response (EICP area) for each of the internal standards in the sample must be within the range of 50.0 % - 200 % of the response of the

internal standard in the most recent CCV standard analysis.

12.3.6 The RT shift for each of the internal standards must be within ±0.50 minutes (30 seconds) between the sample and the most recent CCV standard analysis.

12.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 11.7.4.

12.4 Corrective Action for Sample Analysis

12.4.1 The sample technical acceptance criteria must be met before data are reported.

12.4.2 Corrective action for failure to meet instrument performance checks and initial calibration and CCV must be completed before the analysis of samples.

12.4.3 Corrective Action for Surrogate Recoveries that Fail to Meet Their Acceptance Criteria (Section 9.3.3.2).

12.4.3.1 If the surrogate recoveries in a sample fail to meet the acceptance criteria, check calculations, sample preparation logs, surrogate standard spiking solutions, and the instrument operation.

- If the calculations were incorrect, correct them and verify that the surrogate recoveries meet their acceptance criteria.
- If the sample preparation logs indicate that the incorrect amount of surrogate standard spiking solution was added to the sample, then re-extract (if possible) and reanalyze the sample after adding the correct amount of surrogate standard spiking solution.
- If the surrogate standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution, and re-extract the sample (if possible) and re-analyze the samples.
- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the surrogate recoveries meet their acceptance criteria.
- If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

12.4.3.2 If the above actions do not correct the problem, then the problem might be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.3.2.1 Re-extract (if possible) and reanalyze the sample.

Note: Samples with corresponding MS and MSDs should be re-extracted and reanalyzed only if surrogate recoveries in a sample were considered

unacceptable, and the surrogate recoveries met the acceptance criteria in both the corresponding MS and MSD.

12.4.3.2.2 If the surrogate recoveries meet acceptance criteria in the re-extracted/reanalyzed sample, then the problem was within the laboratory's control.

12.4.3.2.3 Submit data from both analyses. Distinguish between the initial analysis and the extraction/reanalysis on all data.

12.4.4 Corrective Action for Internal Standard Compound Responses that Fail to Meet Their Acceptance Criteria (Sections 12.3.5 and 12.3.6).

12.4.4.1 If the internal standards in a sample fail to meet their acceptance criteria, check calculations, internal standard solutions, and instrument operation.

- If the calculations were incorrect, correct them, and verify that the internal standard responses meet their acceptance criteria.
- If the internal standard solution was improperly prepared, concentrated, or degraded, re-prepare solutions and reanalyze another aliquot of the sample extract (if possible) after adding the correct amount of the freshly prepared internal standard solution.
- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract.
- If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

12.4.4.2 If the above actions do not correct the problem, then the problem might be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.4.2.1 Reanalyze the sample extract.

Note: Samples with corresponding MS and MSDs should be re-extracted and reanalyzed only if internal standard recoveries in a sample were considered unacceptable, and the internal standard recoveries met the acceptance criteria in both the corresponding MS and MSD.

12.4.4.2.2 If the internal standard compound recoveries meet acceptance criteria in the reanalyzed sample extract, then the problem was within the laboratory's control.

12.4.4.2.3 Submit data from both analyses. Distinguish

between the initial analysis and the reanalysis on all data.

12.4.5 Corrective Action for Internal Standard Compound RTs Outside Acceptance Criteria (Section 12.3.6)

12.4.5.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

12.4.5.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.5.2.1 Reanalyze the sample extract.

Note: Samples with corresponding MS and MSDs should be re-extracted and reanalyzed only if internal standard RTs in a sample were considered unacceptable, and the internal standard RTs met the acceptance criteria in both the corresponding MS and MSD.

12.4.5.2.2 If the internal standard compound RTs are within the acceptance criteria in the reanalyzed sample extract, then the problem was within the laboratory's control.

12.4.5.2.3 Submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables.

13.0 ANALYTICAL PROCEDURE PERFORMANCE

Performance of this protocol was evaluated in a single laboratory for all analyte/matrix combinations listed in the table in Section 1.2 (except those labeled “Not a concern”). Reagent water and Ottawa sand were used as reference matrices throughout the study. Surface and tap water were obtained by the laboratory from Germany Creek, Washington, and from the tap at ALS Environmental (formerly Columbia Analytical Services [CAS] in Kelso Washington), respectively. Pre-characterized EPA Georgia Bt2 and EPA Nebraska Ap soils were provided to the laboratory for use as environmental soil matrices, and the laboratory procured Clinisorb 2-inch x 2-inch (CliniMed, Ltd., Buckinghamshire, UK), non-woven sterile sponges and XAD-2 (Sigma-Aldrich, St. Louis, MO) polymeric adsorbent resin for use in evaluation of precision and bias in wipes and air collection material, respectively. MSE was used to extract analytes from the reagent, surface and laboratory tap water, Ottawa sand, Georgia Bt2 red clay and Nebraska Ap soil, surface wipes, and spiked air sorbents and filters. Resulting detection and quantitation levels are listed in Tables 3, 11a, 11b, 12a and 12b. Resulting precision and recovery for target analytes

are listed in Tables 7a, 7b and 8a - 8d. Surrogate recovery ranges are listed in Tables 9a and 9b. Figure 1 shows an example chromatogram of the analysis of a midpoint calibration standard. Figures 2 − 5 show the chromatograms and mass spectra for analytes that required manual integration. Characterization information for the water and soils is provided in Tables 13a and 14, respectively.

Performance of this protocol was evaluated in nine laboratories for dichlorvos, mevinphos, and TETS in reagent water and drinking water. Characterization information for the water samples used is provided in Table 13b. Characterization of the drinking water used in this evaluation is listed in Table 13b. Drinking water was spiked with the three analytes and dechlorinated and preserved with Na_2SO_3 and HCl. Resulting precision and recovery for target analytes and surrogates are listed in Tables 15 and 16, respectively.

13.1 Instrument Detection Limit (IDL), Method Detection Limit (MDL) and Quantitation Limit (QL)

Table 4 lists single-laboratory estimated IDLs (Section 9.6), RTs, and quantitation ions for all target analytes. The mass spectra generated from full scan analyses for the analytes were verified by comparison with the spectra in the National Institute of Standards and Technology (NIST) 98 library (http://www.nist.gov/srd/nist1a.cfm).

For SIM mode, only a few selected ions were monitored, therefore the NIST library was not applied. RTs and quantitation ions were established using the instrument conditions listed in Section 10.1. MDLs listed in Table 3 were established using the procedures outlined in Section 9.7. Single-laboratory QLs listed in Tables 11a and 11b (reagent water) and Tables 12a and 12b (Ottawa sand) were established using the procedures and criteria provided in Section 9.8.

13.2 Precision and Recovery in Samples

Single-laboratory study samples were spiked at 1, 2, 5 and/or 10 times the QL with either 2, 3 or 4 replicates at each concentration level. Results of precision and recovery for clean reference sample types (reagent water, Ottawa sand, and clean wipes) and non-reference sample types (tap water, surface water, and Nebraska Ap and Georgia Bt2 soils) are presented in Section 17.0, Tables, 7a, 7b, and 8a – 8d. Reagent water samples in the multi-laboratory exercise were spiked with dichlorvos, mevinphos, and TETS at 28.6 and 571 µg/L, with seven and four replicates prepared at each concentration level, respectively. The drinking water samples in the exercise were spiked at 114 and 571 µg/L in drinking water, with four replicates prepared at each concentration level. Multi-laboratory precision and bias results are presented in Section 17.0, Tables 15 and 16.

13.3 Problem Analytes

13.3.1 During the single-laboratory study, TEPP and strychnine showed instability when combined with other analytes in standard solutions and exhibited improved linearity and coefficients of determination when run separately. For this reason, separate standards are prepared for these analytes (see Section 7.2.2).

13.3.2 Dimethylphosphite was not recovered from spiked water samples using any of the extraction procedures that were evaluated (i.e., SPE at pH = 4 and pH = 8, or MSE at pH = 4).

13.3.3 Nicotine had low recoveries (<50 %) and poor precision (RSDs > 20 %) in reagent and non-reference waters when using MSE. Preliminary results using SPE at pH = 8 gave higher recoveries (see Appendix A).

13.3.4 Chloropicrin and TEPP had consistently low recoveries and poor precision in Ottawa sand, non-reference soils and wipes. None of the extraction procedures evaluated resulted in recoveries between 50 – 150 % and RSD of less than 20 %.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that might be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

EPA requires that laboratory waste management practices be conducted in a manner consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

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16.2 U.S. Environmental Protection Agency. *Polychlorinated Dibenzo-p-Dioxins (PCDDS) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)*. SW-846 Method 8290A, Revision 1. February 2007. Washington DC: U.S. Environmental Protection Agency, Office of Land and Emergency Management.

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16.10 U.S. Environmental Protection Agency. *Gel-Permeation Cleanup*. SW-846 Method 3640A, Revision 1. September 1994. Washington DC: U.S. Environmental Protection Agency, Office of Land and Emergency Management.

16.11 Patnaik, P. *Handbook of Environmental Analysis. Chemical Pollutants in Air, Water, Soil, and Solid Wastes*, Second Edition. 2010. CRC Press, Boca Raton, FL, pp. 593-594.

16.12 U.S. Environmental Protection Agency. *EPA Contract Laboratory Program Statement of Work for Organic Superfund Methods Multi-Media, Multi-Concentration SOM02.3. Exhibit D–Semivolatile Organic Compounds Analysis.* September 2015. http://www.epa.gov/clp/epa-contract-laboratory-program-statement-work-organic-superfund-methods-multi-media-multi-0 (accessed 05/31/2016)

16.13 U.S. Environmental Protection Agency. *Determinative Chromatographic Separations.* SW-846 Method 8000C, Revision 3. March 2003. Washington DC: U.S. Environmental Protection Agency, Office of Land and Emergency Management.

17.0 TABLES and FIGURES

Table 1
Decafluorotriphenylphosphine (DFTPP) Key Ions and Ion Abundance Criteria

Note: All ion abundances MUST be normalized to m/z of base peak (either 198 or 442).

Mass	Ion Abundance Criteria
51	10.0 – 80.0 % of mass 198
68	Less than 2.0 % of mass 69
69	Present
70	Less than 2.0 % of mass 69
127	10.0 – 80.0 % of mass 198
197	Less than 2.0 % of mass 198
198	Present (see Note, above)
199	5.0 – 9.0 % of mass 198
275	10.0 – 60.0 % of mass 198
365	Greater than 1.0 % of base peak (198 or 442)
441	Present but less than mass 443
442	Present (see Note)
443	15.0 – 24.0 % of mass 442

Table 2
Internal Standards (IS) with Corresponding Target and Surrogate (S) Compounds Assigned for Quantitation

Note: Not all target compounds have been assigned to an internal standard.
(S) = Surrogate

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Chloropicrin Dimethylphosphite 1,4-Dithiane 1,4-Thioxane Bromoform-d_1 **(S)** Nitrobenzene-d_5 **(S)**	Dichlorvos	Crimidine Mevinphos Nicotine TEPP 2-Fluorobiphenyl **(S)** Nicotine-d_4 **(S)**
Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
Chlorfenvinphos Chlorpyrifos Dicrotophos Disulfoton Methyl parathion Parathion Phencyclidine Phorate Phosphamidon Tetramethylenedisulfotetramine (TETS) Phencyclidine-d_5 **(S)** Triphenyl phosphate **(S)** Terphenyl-d_{14} **(S)**	Fenamiphos	Strychnine

Table 3
Single-Laboratory Method Detection Limits (MDLs) for Target Compounds in Reagent Water and Ottawa Sand

Note: Parenthetical data represent cases where the spike level used is greater than 10 times the resulting MDL.
D = Dropped from matrix due to poor performance (see Section 1.2).

Analyte	Full Scan		Selected Ion Monitoring (SIM)	
	Reagent Water (µg/L)	Ottawa Sand (µg/kg)	Reagent Water (µg/L)	Ottawa Sand (µg/kg)
	MDL	MDL	MDL	MDL
Chlorfenvinphos	(0.79)	1.6	0.36	0.63
Chloropicrin	3.6	(18)	0.512	7.0
Chlorpyrifos	0.89	3.8	0.107	0.107
Crimidine	(0.91)	2.1	0.141	0.34
Dichlorvos	0.79	3.2	0.032	0.31
Dicrotophos	(2.2)	9.9	0.086	2.86
Dimethylphosphite	D	93.5	D	12
Disulfoton	0.92	(1.9)	0.100	0.172
1,4-Dithiane	0.79	1.9	0.089	0.180
Fenamiphos	(0.92)	(3.0)	0.141	0.70
Methyl parathion	(1.4)	3.4	0.45	0.63
Mevinphos	(0.92)	2.3	0.165	0.65
Nicotine	4.1	10.0	1.09	15.4
Parathion	(1.3)	3.4	0.34	0.94
Phencyclidine	1.2	3.2	0.091	0.32
Phorate	0.79	1.6	0.031	0.42
Phosphamidon	(1.4)	9.6	0.081	0.047
Strychnine	(9.0)	(32.1)	0.97	1.02
TEPP	2.2	D	1.45	D
TETS	0.89	2.5	0.030	0.058
1,4-Thioxane	0.89	3.9	0.138	0.180

Acronyms:
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

Table 4
Single-Laboratory Estimated Instrument Detection Limits (IDL), Retention Times (RT), and Characteristic Ions for Target Compounds, Surrogates (S) and Internal Standards (IS)

Analyte	Quant Ions	Qualifier Ions	Full Scan			Selected Ion Monitoring (SIM)		
			Retention Time (RT)	IDL[(1)] (ppm)	Signal: Noise (S:N)	RT	IDL[(1)] (ppm)	S:N
Chlorfenvinphos	267	269, 323, 295	25.57	0.15	6.17	25.55	0.02	4.13
Chloropicrin	117	119, 82, 47	6.04	0.20	4.17	6.02	0.01	5.16
Chlorpyrifos	197	314, 97, 258	24.72	0.09	5.10	24.70	0.01	4.53
Crimidine	142	156, 171, 120	19.58	0.13	3.83	19.60	0.02	4.27
Dichlorvos	109	185, 79, 145	16.01	0.09	3.77	16.09	0.01	4.70
Dicrotophos	127	67, 109, 193	21.43	0.30	5.30	21.50	0.02	3.97
Dimethylphosphite	79	80, 95	7.88	2.00	4.40	9.72	0.1	4.13
Disulfoton	88	97, 142, 186	23.03	0.15	4.13	23.02	.005	4.13
1,4-Dithiane	120	61, 46	13.18	0.05	4.63	13.16	0.003	4.10
Fenamiphos	303	154, 288, 217	26.36	0.30	4.50	26.37	0.02	3.67
Methyl parathion	109	125, 263, 79	23.91	0.25	4.10	23.91	.02	4.40
Mevinphos	127	192, 109, 67	18.52	0.20	6.43	18.58	0.02	4.23
Nicotine	162	161, 133	17.66	0.20	6.20	17.65	0.04	4.27
Parathion	109	97, 291, 139	24.88	0.20	3.97	24.86	0.02	3.73
Phencyclidine	200	242, 186, 91	24.20	0.09	6.30	24.21	0.005	4.43
Phorate	75	260, 121	21.76	0.13	6.33	21.75	0.005	5.10
Phosphamidon	127	264, 72, 109	23.60	0.25	5.33	23.60	0.02	4.57
Strychnine	334	120, 130, 162	34.84	3.00	5.10	34.83	0.1	4.07
TEPP	161	263, 179, 235	20.20	0.30	4.50	20.19	0.05	3.50
TETS	212	240, 132, 121	22.09	0.10	5.53	22.08	0.002	4.67
1,4-Thioxane	104	46, 61	9.33	0.09	4.93	9.34	0.005	3.60
Bromoform-d_1 (S)	174	93	9.29	NA	NA	9.31	NA	NA
Nitrobenzene-d_5 (S)	82	128, 54, 70	13.41	NA	NA	13.41	NA	NA
Nicotine-d_4 (S)	166	165,136	17.52	NA	NA	17.52	NA	NA
2-Fluorobiphenyl (S)	172	171, 170, 85	17.74	NA	NA	17.74	NA	NA
Phencyclidine-d_5 (S)	205	171	24.13	NA	NA	24.12	NA	NA
Terphenyl-d_{14} (S)	244	212, 182	26.76	NA	NA	26.76	NA	NA
Triphenyl phosphate (S)	326	122	28.50	NA	NA	28.47	NA	NA
1,4-Dichlorobenzene-d_4 (IS)	152	150	12.08	NA	NA	12.08	NA	NA
Naphthalene-d_8 (IS)	136	68	15.09	NA	NA	15.08	NA	NA
Acenaphthene-d_{10} (IS)	164	162	19.28	NA	NA	19.27	NA	NA
Phenanthrene-d_{10} (IS)	188	94	22.83	NA	NA	22.81	NA	NA
Chrysene-d_{12} (IS)	240	120,236	29.18	NA	NA	29.15	NA	NA
Perylene-d_{12} (IS)	264	260,265	32.69	NA	NA	32.66	NA	NA

Acronyms:
NA = Not available
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

(1) Estimated instrument detection limits (IDLs) were determined in a single laboratory based on concentrations producing a signal-to-noise (S:N) ratio of at least 3:1.

Table 5
Analyte-specific Dwell Times and Ion Grouping for Selected Ion Monitoring (SIM) Analysis

Ion Group	Plot Ion	Scan Rate (cycles/second)	Ions	Dwell Time (milliseconds)
1	117.0	2.33	61.0, 66.0, 71.0, 79.0, 80.0, 82.0, 93.0, 94.0, 99.0, 104.0, 117.0, 119.0, 120.0, 128.0, 150.0, 152.0, 174.0	10
2	136.0	4	61.0, 67.0, 68.0, 94.0, 109.0, 136.0, 185.0	20
3	162.0	2.63	67.0, 94.0, 127.0, 133.0, 136.0, 142.0, 156.0, 161.0, 162.0, 164.0, 166.0, 171.0, 172.0, 192.0, 263.0	10
4	127.0	2.17	67.0, 75.0, 94.0, 121.0, 127.0, 212.0, 240.0	50
5	188.0	2.33	88.0, 94.0, 97.0, 109.0, 127.0, 188.0, 197.0, 200.0, 205.0, 242.0, 246.0, 263.0, 264.0, 267.0, 291.0, 314.0, 232.0	10
6	326.0	3.51	120.0, 122.0, 217.0, 240.0, 244.0, 303.0, 325.0, 326.0	20
7	264.0	3.03	120.0, 130.0, 260.0, 264.0, 334.0	50

Table 6a
Relative Response Factors (RRF) and Percent RSDs for Initial Calibration of Target Compounds and Surrogates in Full Scan Mode from a Single-Laboratory Evaluation

Analyte	Calibration Range (ppm)	Mean RRF [1]	%RSD [2]	R^2 [3]	Mean RT
Chlorfenvinphos	3.0 – 20.0	0.182	18.4	0.998	28.02
Chloropicrin	0.5 – 20.0	0.191	10.0	-	6.01
Chlorpyrifos	0.5 – 20.0	0.090	14.8	-	24.71
Crimidine	0.5 – 20.0	0.169	10.4	-	19.57
Dichlorvos	0.5 – 20.0	0.347	16.1	0.999	15.97
Dicrotophos	3.0 – 20.0	0.347	20.0	0.998	21.40
Dimethylphosphite	6.0 – 40.0	0.703	12.2	-	7.28
Disulfoton	0.5 – 20.0	0.347	16.0	-	23.02
1,4-Dithiane	0.5 – 20.0	0.596	4.9	-	13.17
Fenamiphos	7.0 – 20.0	0.172	18.1	0.999	26.36
Methyl parathion	2.0 – 20.0	0.057	23.0	0.997	23.89
Mevinphos	0.5 – 20.0	0.117	21.6	0.999	18.49
Nicotine	0.5 – 20.0	0.084	19.2	0.999	17.51
Parathion	3.0 – 20.0	0.084	20.9	0.998	24.87
Phencyclidine	0.5 – 20.0	0.457	16.8	-	24.18
Phorate	0.5 – 20.0	0.423	16.5	-	21.75
Phosphamidon	3.0 – 20.0	0.210	21.8	0.997	23.58
Strychnine	10.0 – 60.0	0.176	13.5	-	34.82
TEPP	1.0 – 20.0	0.237	20.7	0.998	20.19
TETS	0.5 – 12.0	0.233	6.9	-	22.08
1,4-Thioxane	0.5 – 20.0	0.551	7.2	-	9.31
Bromoform-d_1 (S)	0.5 – 20.0	0.646	8.6	-	9.83
Nitrobenzene-d_5 (S)	0.5 – 20.0	1.08	7.2	-	13.89
Nicotine-d_4 (S)	0.5 – 20.0	0.090	19.6	-	18.01
2-Fluorobiphenyl (S)	0.5 – 20.0	1.383	5.5	-	18.22
Phencyclidine-d_5 (S)	0.5 – 20.0	0.457	12.4	-	24.63
Terphenyl-d_4 (S)	0.5 – 20.0	0.930	7.6	-	27.27
Triphenyl phosphate (S)	0.5 – 20.0	0.349	20.4	0.999	29.00

Acronyms:
RSD – relative standard deviation
RT – retention time
S – surrogate
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

[1] Mean RRF values calculated as the average of the RRFs for the calibration levels listed in Table 10a. The RRFs were generated using EQ. 2.
[2] %RSD values are based on single initial calibration (using non-shaded calibration points in Table 10a).
[3] Coefficient of determination or R^2 values were calculated by linear regression (see Method 8000C for guidance based on single replicate analyses across the calibration range) using all shaded and non-shaded calibration points in Table 10a.

Table 6b
Relative Response Factors (RRF) and Percent RSDs for Initial Calibration of Target Compounds and Surrogates in SIM Mode from a Single-Laboratory Evaluation

Analyte	Calibration Range (ppm)	Mean RRF (1)	%RSD (2)	Mean RT
Chlorfenvinphos	0.02 – 1.4	0.116	9.3	25.77
Chloropicrin	0.1 – 1.4	0.051	14.9	6.19
Chlorpyrifos	0.02 – 1.4	0.078	6.6	24.92
Crimidine	0.01 – 1.4	0.152	9.5	19.77
Dichlorvos	0.01 – 1.4	0.270	9.6	16.20
Dicrotophos	0.05 – 1.4	0.149	11.6	21.61
Dimethylphosphite	0.8 – 5.0	0.293	12.4	10.82
Disulfoton	0.01 – 1.4	0.252	8.7	23.32
1,4-Dithiane	0.01 – 1.4	0.588	5.9	13.38
Fenamiphos	0.02 – 1.4	0.072	7.8	26.57
Methyl parathion	0.02 – 1.4	0.048	8.3	24.10
Mevinphos	0.05 – 1.4	0.398	13.8	18.73
Nicotine	0.05 – 1.4	0.092	10.7	17.77
Parathion	0.02 – 1.4	0.038	11.7	25.07
Phencyclidine	0.01 – 1.4	0.432	9.1	24.40
Phorate	0.02 – 1.4	0.316	12.9	21.96
Phosphamidon	0.02 – 1.4	0.123	8.9	23.69
Strychnine	2.0 – 15.0	0.110	16.3	34.81
Tetraethyl pyrophosphate (TEPP)	0.2 – 1.2	0.081	19.9	20.17
Tetramethylenedisulfotetramine (TETS)	0.004 – 0.8	0.276	6.0	22.29
1,4-Thioxane	0.01 – 1.4	0.530	1.9	9.57
Bromoform-d_1 (S)	0.01 – 1.4	0.585	6.9	9.56
Nitrobenzene-d_5 (S)	0.01 – 1.4	0.905	5.1	13.64
Nicotine-d_4 (S)	0.1 – 1.4	0.066	13.6	17.75
2-Fluorobiphenyl (S)	0.01 – 1.4	1.597	4.3	17.97
Phencyclidine-d_5 (S)	0.01 – 1.4	0.423	5.7	24.38
Terphenyl-d_4 (S)	0.01 – 1.4	0.907	6.8	27.02
Triphenyl phosphate (S)	0.01 – 1.4	0.324	10.6	28.74

Acronyms:
RSD – relative standard deviation
RT – retention time
S – surrogate
SIM – selected ion monitoring

(1) Mean RRF values calculated as the average of the RRFs for the non-shaded calibration levels listed in Table 10b. The RRFs were generated using EQ. 2.
(2) %RSD values are based on single replicate analyses across the calibration range (using non-shaded calibration points in Table 10b).

Table 7a
Single-Laboratory Matrix Spike Recovery and Relative Percent Difference (RPD) in Surface and Drinking Water Samples

Note: Matrix spike %recovery and relative percent difference (RPD) ranges are based on the results of 8 samples of each water type (two replicates at each of two concentration levels in surface and drinking waters).

Analyte	Non-Reference Waters					
	Full Scan			Selected Ion Monitoring (SIM)		
	Spike Level (µg/L)	% Recovery Range	% RPD Range	Spike Level (µg/L)	% Recovery Range	% RPD Range
Chlorfenvinphos	172/200	33.3 – 146	3.1 – 48.6	2.86/5.7	61.5 – 81.1	4.5 – 27.5
Chloropicrin	28.6/57.1	66.1 – 127	8.4 – 38.8	2.86/11.4	62.9 – 126	10.5 – 41.5
Chlorpyrifos	28.6/57.1	0 – 154	6.8 – 21.7	2.86/5.7	42.7 – 79.3	0.6 – 43.1
Crimidine	28.6/57.1	52.1 – 105	9.0 – 20.5	5.7/11.4	75.5 – 98.2	5.2 – 10.3
Dichlorvos	28.6/57.1	42.0 – 93.0	3.8 – 22.0	2.86/5.7	58.7 – 77.6	1.8 – 12.3
Dicrotophos	172/286	22.0 – 123	7.4 – 20.6	2.86/5.7	37.8 – 72.5	0.3 – 22.1
Disulfoton	28.6/57.1	38.0 – 112	3.9 – 57.9	2.86/5.7	54.9 – 74.5	5.6 – 17.3
1,4-Dithiane	28.6/57.1	69.9 – 108	2.8 – 16.1	0.46/0.9	91.3 – 104	0 – 9.1
Fenamiphos	572/686	37.8 – 109	1.8 – 24.3	2.86/5.7	48.6 – 71.1	1.1 – 15.4
Methyl parathion	114/286	30.2 – 141	0.6 37.4	2.86/5.7	55.9 – 85.1	3.0 – 22.3
Mevinphos	57.2/114	46.0 – 104	6.0 – 27.9	5.7/11.4	56.4 – 87.4	4.6 – 14.2
Nicotine	28.6/114	3.5 – 55.9	3.5 – 120	5.7/11.4	0 – 47.1	17.5 – 56.8
Parathion	286/400	30.3 – 128	1.3 – 60.9	2.86/5.7	42.7 – 78.6	8.0 – 25.7
Phencyclidine	28.6/57.1	77.1 – 128	3.0 – 7.4	5.7/11.4	69.6 – 101	3.0 – 19.4
Phorate	28.6/57.1	35.0 – 102	1.9 – 55.6	2.86/5.7	53.5 – 76.2	1.2 – 16.8
Phosphamidon	172/286	36.7 – 130	0 – 21.9	2.86/5.7	76.7 – 140	4.9 – 24.3
Strychnine	172/343	41.7 – 210	2.5 – 28.7	114/229	32.8 – 108	0.9 – 41.3
TEPP	57.2/114	0 – 150	0 – 9.4	11.5/22.9	0 – 157	0.3
TETS	28.6/57.1	45.5 – 150	7.9 – 67.5	0.23/0.5	54.7 – 96.1	6.8 – 16.2
1,4-Thioxane	28.6/57.1	52.1 – 101	3.0 – 20.6	2.86/11.4	70.9 – 84.6	3.3 – 13.2

Acronyms:
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

Table 7b
Single-Laboratory Matrix Spike Recovery and Relative Percent Difference (RPD) in Soils

Note: Matrix spike %recovery and relative percent difference (RPD) ranges are based on the results of 8 samples of each soil type (two replicates at each of two concentration levels in EPA Nebraska AP and EPA Georgia Bt2 soils).

Analyte	Non-Reference Soils					
	Full Scan			Selected Ion Monitoring (SIM)		
	Spike Level (mg/kg)	%Recovery Range	%RPD Range	Spike Level (µg/kg)	%Recovery Range	%RPD Range
Chlorfenvinphos	0.3/0.5	90.8 – 125	0 – 1.4	5/10	107 – 294	5.4 – 25.3
Chloropicrin	5.0/10	11.8 – 34.5	4.4 – 47.4	40/80	0 – 81.5	20.6 – 200
Chlorpyrifos	0.05/0.1	75.4 – 107	1.7 – 12.8	5/10	100 – 314	0.8 – 39.2
Crimidine[(1)]	0.05/0.1	58.9 – 77.2	1.2 – 14.2	10/20	49.9 – 78.0	7.9 – 9.6
Dichlorvos	0.3/0.5	15.4 – 87.6	3.1 – 17.0	5/10	26.4 – 112	4.6 – 32.9
Dicrotophos	10.0/12.0	0 – 30.8	0 – 5.4	5/10	32.3 – 218	0.3 – 87.8
Dimethylphosphite	0.3/0.5	4.4 – 86.7	0.8 – 15.9	40/80	0	0
Disulfoton	0.01/0.02	59.7 – 201	0 – 7.0	5/10	74.2 – 302	1.5 – 116
1,4-Dithiane	0.05/0.1	58.5 – 73.1	1.9 – 12.6	5/10	87.5 – 122	3.8 – 33.0
Fenamiphos	1.0/1.2	63.3 – 87.5	0.4 – 8.8	5/10	90.8 – 216	0.9 – 29.3
Methyl parathion	0.3/0.5	95.7 – 137	1.7 – 6.8	50/60	110 – 348	0.9 – 84.0
Mevinphos	0.1/0.2	51.5 – 89.5	2.6 – 7.1	10/20	57.5 – 140	5.5 – 17.1
Nicotine[(1)]	0.05/0.1	22.8 – 84.8	1.9 – 7.4	5/10	66.6 – 151	0.3 – 7.6
Parathion	0.3/0.5	72.0 – 117	0.5 – 3.7	10/20	141 – 221	4.9 – 15.1
Phencyclidine[(1)]	0.3/0.5	8.2 – 63.5	3.8 – 22.0	5/10	20.5 – 75.0	2.0 – 17.4
Phorate	0.05/0.1	59.8 – 85.4	1.0 – 9.5	5/10	301 – 838	5.7 – 20.0
Phosphamidon	0.3/0.5	44.1 – 153	0.2 – 10.1	5/10	57.8 – 194	6.5 – 83.0
Strychnine[(1)]	2.0/3.0	0 – 26.8	0 – 5.0	300/600	0 – 59.8	0.8 – 19.2
TETS	0.05/0.1	64.4 – 92.0	0.5 – 13.8	0.4/1.0	0 – 69.5	6.9 – 10.6
1,4-Thioxane	0.05/0.1	43.8 – 58.8	2.1 – 10.6	5/10	47.7 – 58.6	3.6 – 4.9

Acronyms:
TETS – tetramethylenedisulfotetramine

[(1)] Determined using 2-solvent system (5 % TEA in ethyl acetate).

Table 8a
Single-Laboratory Recovery and Precision in Reagent Water

Analyte	Reagent Water					
	Full Scan (n=8)			Selected Ion Monitoring (SIM) (n=8)		
	Spike Level (µg/L)	%Recovery Range	%RSD	Spike Level (µg/L)	%Recovery Range	%RSD
Chlorfenvinphos	172/200	68.2 – 140	5.5 – 7.3	2.86/5.7	58.5 – 94.4	8.8 – 19.3
Chloropicrin	28.6/57.1	44.1 – 107	15.2 – 25.9	2.86/11.4	42.2 – 158	13.0 – 18.1
Chlorpyrifos	28.6/57.1	66.0 – 108	2.6 – 19.6	2.86/5.7	68.5 – 101	6.1 – 9.9
Crimidine	28.6/57.1	67.8 – 105	4.1 – 7.4	5.7/11.4	84.0 – 116	9.0 – 9.2
Dichlorvos	28.6/57.1	64.0 – 98.1	5.3 – 7.6	2.86/5.7	71.1 – 86.3	6.6 – 8.5
Dicrotophos	172/286	47.3 – 110	3.0 – 6.0	2.86/5.7	48.5 – 133	5.1 – 19.5
Disulfoton	28.6/57.1	75.1 – 101	3.5 – 12.4	2.86/5.7	70.3 – 95.3	5.4 – 7.2
1,4-Dithiane	28.6/57.1	84.0 – 108	2.2 – 2.7	0.46/0.9	99.1 – 119	3.5 – 10.8
Fenamiphos	572/686	91.8 – 114	4.0 – 9.8	2.86/5.7	63.6 – 88.9	4.9 – 11.0
Methyl parathion	114/286	116 – 136	1.4 – 6.8	2.86/5.7	77.4 – 147	4.8 – 8.4
Mevinphos	57.2/114	59.0 – 109	5.3 – 7.3	5.7/11.4	54.8 – 132	5.8 – 19.2
Nicotine	28.6/114	40.5 – 168	3.9 – 11.6	5.7/11.4	29.2 – 71.8	14.2 –1 6.5
Parathion	286/400	71.0 – 120	4.4 – 10.3	2.86/5.7	69.0 – 177	5.2 – 9.1
Phencyclidine	28.6/57.1	112 – 164	3.3 – 6.9	5.7/11.4	84.5 – 103	5.0 – 9.1
Phorate	28.6/57.1	72.0 – 102	7.1 – 13.2	2.86/5.7	69.6 – 101	4.9 – 10.3
Phosphamidon	172/286	70.5 – 129	3.9 – 5.9	2.86/5.7	51.0 – 101	6.2 – 25.3
Strychnine	172/343	56.9 – 132	3.3 – 3.4	114/229	23.1 – 59.2	7.8 – 11.2
TEPP	57.2/114	96.7 – 152	1.5 – 4.0	11.5/22.9	175 – 200	1.2 – 2.0
TETS	28.6/57.1	85.0 – 133	4.8 – 11.1	0.23/0.5	30.2 – 52.8	1.9 – 11.1
1,4-Thioxane	28.6/57.1	58.0 – 98.1	4.2 – 5.4	2.86/11.4	42.8 – 88.8	4.6 – 4.6

Acronyms:
RSD – relative standard deviation
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

Table 8b
Single-Laboratory Recovery and Precision in Ottawa Sand

Analyte	Ottawa Sand					
	Full Scan (n=8)			Selected Ion Monitoring (SIM) (n=8)		
	Spike Level (mg/kg)	%Recovery Range	%RSD	Spike Level (µg/kg)	%Recovery Range	%RSD
Chlorfenvinphos	0.3/0.5	71.7 – 110	2.9 – 15.0	5/10	93.0 – 111	4.6 – 5.8
Chloropicrin	5.0/10	13.0 – 25.5	20.7 – 26.0	40/50	35.5 – 57.4	10.3 – 19.5
Chlorpyrifos	0.05/0.1	69.0 – 78.0	3.5 – 5.2	5/10	77.2 – 87.8	2.5 – 5.3
Crimidine[(1)]	0.05/0.1	73.0 – 96.0	3.9 – 5.2	5/10	70.5 – 95.8	7.5 – 11.1
Dichlorvos	0.3/0.5	77.0 – 89.2	3.6 – 6.2	5/10	71.8 – 86.4	3.1 – 4.7
Dicrotophos	0.3/0.5	43.0 – 90.6	8.3 – 15.0	40/80	53.2 – 94.2	7.1 – 10.4
Dimethylphosphite	10.0/12.0	91.7 – 159	6.8 – 9.5	5/10	41.8 – 88.1	18.5 – 19.2
Disulfoton	0.01/0.02	130 – 210	1.9 – 2.8	5/10	60.6 – 69.4	4.6 – 5.8
1,4-Dithiane	0.05/0.1	66.0 – 78.0	5.0 – 5.6	5/10	64.2 – 74.2	1.8 – 5.7
Fenamiphos	1.0/1.2	67.4 – 81.0	3.4 – 5.2	5/10	52.4 – 76.0	6.2 – 8.7
Methyl parathion	0.3/0.5	46.7 – 71.8	9.7 – 15.7	50/60	60.6 – 92.3	7.4 – 7.6
Mevinphos	0.1/0.2	62.0 – 77.0	5.8 – 8.9	10/20	67.6 – 89.5	3.9 – 8.9
Nicotine[(1)]	0.05/0.1	73.0 – 110	2.4 – 4.0	5/10	78.9 – 170	13.9 – 23.7
Parathion	0.3/0.5	67.3 – 95.0	5.4 – 10.6	10/20	66.8 – 88.0	8.1 – 8.6
Phencyclidine[(1)]	0.3/0.5	64.0 – 77.0	2.6 – 5.3	5/10	67.1 – 98.6	5.7 – 6.1
Phorate	0.05/0.1	62.0 – 70.0	4.4 – 4.9	5/10	56.0 – 61.2	2.5 – 4.3
Phosphamidon	0.3/0.5	33.7 – 63.0	8.0 – 13.0	5/10	62.4 – 103	4.8 – 18.3
Strychnine[(1)]	2.0/3.0	1.0 – 4.3	15.5 – 26.1	300/600	27.1 – 51.3	18.0 – 21.5
TETS	0.05/0.1	74.0 – 91.0	4.3 – 8.6	0.4/1.0	76.2 – 95.3	4.1 – 7.1
1,4-Thioxane	0.05/0.1	54.0 – 67.0	5.2 – 6.4	5/10	52.4 – 60.2	3.2 – 6.3

Acronyms:
RSD – relative standard deviation
TETS – tetramethylenedisulfotetramine

[(1)] Determined using 2-solvent system (5 % TEA in ethyl acetate).

Table 8c
Single-Laboratory Recovery and Precision in Wipes

Note: Four replicates were analyzed at each of two concentration levels. Ranges of recovery and RSD reflect evaluations at both concentration levels.

Analyte	Full Scan			Selected Ion Monitoring (SIM)		
	Spike Levels (mg/kg)	%Recovery Range	RSD	Spike Levels (µg/kg)	%Recovery Range	RSD
Chlorfenvinphos	3.0/5.0	77 – 121	2.5 – 3.0	0.05/0.10	121 – 159	8.8 – 13.2
Chlorpyrifos	1.0 /2.0	83.0 – 111	1.5 – 3.4	0.05/0.10	82.0 – 99.5	2.8 – 7.8
Crimidine	0.5/1.0	74.0 – 84.0	3.7 – 4.1	0.10/0.20	81.5 – 105	6.7 – 10.7
Dichlorvos	0.5/1.0	79.0 – 84.0	1.2 – 3.0	0.05/0.10	85.8 – 103	6.7 – 8.0
Dicrotophos	3.0/5.0	75.3 – 116	4.1 4.1	0.05/0.10	94.6 – 134	5.1 – 17.1
Dimethylphosphite	100/150	72.8 – 149	3.5 – 4.2	0.4/0.8	48.6 – 90.3	10.6 – 24.4
Disulfoton	0.1/0.5	70.0 – 80.0	2.2 – 7.7	0.05/0.10	65.6 – 77.5	3.4 – 6.9
1,4-Dithiane	0.5/1.0	72.0 – 80.0	1.9 – 3.0	0.05/0.10	75.5 – 92.8	2.9 – 6.1
Fenamiphos	10/12.0	87.5 – 103	1.6 – 1.9	0.05/0.10	89.6 – 124	5.6 – 17.0
Methyl parathion	0.5/1.0	75.0 – 176	2.4 – 4.4	0.50/0.60	77.2 – 107	5.9 – 16.8
Mevinphos	1.0/2.0	77.0 – 86.5	1.8 – 4.2	0.10/0.20	93.1 – 118	8.2 – 12.3
Nicotine	0.5/1.0	73.0 – 210	3.0 – 6.2	0.05/0.10	87.9 – 118	5.4 – 11.8
Parathion	3.0/5.0	70.0 – 104	2.9 – 4.3	0.10/0.20	73.8 – 114	6.9 – 20.3
Phencyclidine	0.5/1.0	80.0 – 140	0.0 – 1.0	0.05/0.10	84.6 – 101	5.0 – 8.7
Phorate	0.5/1.0	73.0 – 78.0	1.5 – 2.9	0.05/0.10	59.6 – 72.6	4.1 – 5.2
Phosphamidon	3.0/5.0	78.3 – 104	3.9 – 4.3	0.05/0.10	119 – 168	5.6 – 11.9
Strychnine	5.0/40.0	73.0 – 131	2.8 – 3.6	3.00/6.00	78.7 – 117	8.9 – 16.4
TETS	0.5/1.0	90.0 – 199	8.5 – 12.2	0.004/0.010	61.8 – 81.5	1.8 – 11.5
1,4-Thioxane	0.5/1.0	58.0 – 62.0	2.1 – 3.8	50/100	53.5 – 89.6	12.5 – 18.6

Acronyms:
RSD – relative standard deviation
TETS – tetramethylenedisulfotetramine

Table 8d
Single-Laboratory Recovery and Precision in Air Filters

Note: Four replicates were analyzed at each of two concentration levels. Ranges of recovery and RSD reflect evaluations at both concentration levels.

Analyte	Full Scan			Selected Ion Monitoring (SIM)		
	Spike Levels (mg/kg)	%Recovery Range	RSD	Spike Levels (µg/kg)	%Recovery Range	RSD
Chlorfenvinphos	3.0/5.0	69.7 – 122	6.6 – 13.6	0.05/0.10	86.0 – 116	5.0 – 15.1
Chloropicrin	200/250	42.2 – 68.0	6.2 – 22.5	0.40/0.50	38.4 – 67.5	20.8 – 26.9
Chlorpyrifos	1.0/2.0	71.0 – 112	6.6 – 7.7	0.05/0.10	74.6 – 86.8	1.7 – 7.1
Dichlorvos	0.5/1.0	67.0 – 82.0	4.6 – 7.6	0.05/0.10	70.8 – 82.6	2.9 – 7.0
Dicrotophos	3.0/5.0	64.4 – 96.0	2.3 – 17.3	0.05/0.10	83.8 – 105	3.7 – 9.5
Dimethylphosphite	100/150	52.8 – 173	4.5 – 18.9	0.40/0.80	58.1 – 85.3	7.3 – 11.7
Disulfoton	0.1/0.5	48.0 – 60.0	5.1 – 10.5	0.05/0.10	45.4 – 54.8	2.1 – 5.1
Fenamiphos	10.0/12.0	66.3 – 93.4	2.6 – 7.3	0.05/0.10	56.4 – 76.5	4.1 – 11.0
Methyl parathion	0.5/1.0	45.0 – 166	2.4 – 15.4	0.50/0.60	73.6 – 92.3	2.3 – 9.4
Mevinphos	1.0/2.0	65.5 – 77.5	6.2 – 7.7	0.10/0.20	78.3 – 99.0	5.1 – 6.7
Parathion	3.0/5.0	61.0 – 86.8	7.5 – 14.2	0.10/0.20	67.9 – 86.0	2.6 – 10.0
Phencyclidine	0.5/1.0	60.0 – 144	4.8 – 5.5	0.05/0.10	54.8 – 78.8	4.2 –16.8
Phorate	0.5/1.0	52.0 – 86.0	3.8 – 12.8	0.05/0.10	52.8 – 60.8	1.3 – 3.5
Phosphamidon	3.0/5.0	57.4 – 99.0	15.1 – 16.3	0.05/0.10	95.8 – 109	3.3 – 4.7
TETS	0.5/1.0	92.0 – 221	6.6 – 9.3	0.004/0.010	73.8 – 87.3	3.1 – 7.3

Acronyms:
RSD – relative standard deviation
TETS – tetramethylenedisulfotetramine

Table 9a
Surrogate Recovery in a Single-Laboratory (reagent water and Ottawa sand)

Note: Percent recoveries in this table represent the range of recoveries achieved in a single laboratory for reagent water (n=8) and Ottawa sand (n=8) samples spiked near the midpoint of the calibration range.

Surrogate	Reagent Water (% Recovery)				Ottawa Sand (% Recovery)			
	Full Scan		Selected Ion Monitoring (SIM)		Full Scan		Selected Ion Monitoring (SIM)	
	Min	Max	Min	Max	Min	Max	Min	Max
Bromoform-d_1	84.8	93.2	72.4	88.4	60.2	73.7	46.2	54.9
Triphenyl phosphate	74.3	102	52.3	60.0	72.9	82.0	57.7	71.6
Phencyclidine-d_5	83.6	119	84.4	104	66.6(1)	82.2(1)	65.3(1)	98.6(1)
2-Fluorobiphenyl	76.4	89.6	70.0	80.4	70.0	80.1	67.9	79.9
Nitrobenzene-d_5	87.8	107	78.4	97.6	76.2	89.0	62.3	74.5
p-Terphenyl-d_{14}	60.0	109	60.8	90.4	76.4	80.4	71.7	81.2
Nicotine-d_4	35.6	98.6	42.9	76.4	76.0(1)	92.0(1)	104(1)	114(1)

(1) Determined using 2-solvent system (5 % TEA in ethyl acetate).

Table 9b
Surrogate Recovery in a Single-Laboratory (surface wipes and air filters)

Note: Percent recoveries in this table represent the range of recoveries achieved in a single laboratory for surface wipes (n=8) and air filters (n=8) samples spiked near the midpoint of the calibration range.

Surrogate	Surface Wipes (% Recovery)				Air Filters (% Recovery)			
	Full Scan		SIM		Full Scan		SIM	
	Min	Max	Min	Max	Min	Max	Min	Max
Bromoform-d_1	51.2	90.6	21.9	49.4	51.4	78.0	52.9	57.2
Triphenyl phosphate	77.3	95.7	74.6	89.6	71.7	88.3	60.6	78.5
Phencyclidine-d_5	81.3	98.9	76.0	103	64.2	77.9	54.6	76.1
2-Fluorobiphenyl	71.6	95.8	60.5	80.1	63.0	87.6	70.1	77.8
Nitrobenzene-d_5	79.6	92.4	56.6	79.1	65.5	78.4	62.3	70.6
p-Terphenyl-d_{14}	71.9	95.3	75.7	89.1	65.2	83.4	66.2	79.8
Nicotine-d_4	101	133	77.0	120	80.2	110	39.9	67.9

Table 10a
Calibration Standard Concentrations (ng/µL) for GC/MS Full Scan with Split-Splitless Injection

Notes: Shaded cells indicate calibration points that were removed to improve calibration linearity or due to a low S:N (<10:1). Linearity was achieved by linear regression using all calibration points (both shaded and unshaded cells).

Internal standards are added at a concentration of 10ppm to each calibration standard (see Table 2).

Analyte	Calibration Standard Concentrations (ppm)										
	1	2	3	4	5	6	7	8	9	10	11
Chlorfenvinphos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17	20.0
Chloropicrin	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Chlorpyrifos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Crimidine	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Dichlorvos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Dicrotophos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Dimethylphosphite	-	-	-	6.0	10.0	14.0	20.0	24.0	30.0	34.0	40.0
Disulfoton	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
1,4-Dithiane	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Fenamiphos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Methyl parathion	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Mevinphos	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Nicotine	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Parathion	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Phencyclidine	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Phorate	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Phosphamidon	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Strychnine	3.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0
TEPP	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
TETS	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	-	-
1,4-Thioxane	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Bromoform-d_1 (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Nitrobenzene-d_5 (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Nicotine-d_4 (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
2-Fluorobiphenyl (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Phencyclidine-d_5 (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Terphenyl-d_4 (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0
Triphenyl phosphate (S)	0.5	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0

Acronyms:
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine
(S) = Surrogate

Table 10b
Calibration Standard Concentrations (ng/µL) for GC/MS Selected Ion Monitoring (SIM) with Split-Splitless Injection

Notes: Shaded cells indicate calibration points that were removed to improve calibration linearity or due to a low Signal:Noise (S:N) (<10:1).

Internal standards are added at a concentration of 10ppm to each calibration standard (see Table 2).

Analyte	Calibration Standard Concentration (ppm)											
	1	2	3	4	5	6	7	8	9	10	11	12
Chlorfenvinphos	-	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Chloropicrin	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Chlorpyrifos	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Crimidine	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Dichlorvos	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Dicrotophos	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Dimethylphosphite	0.4	0.8	1.6	2.0	2.4	3.0	3.4	4.0	4.4	5.0	-	-
Disulfoton	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
1,4-Dithiane	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Fenamiphos	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Methyl parathion	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Mevinphos	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Nicotine	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Parathion	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Phencyclidine	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Phorate	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Phosphamidon	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Strychnine	0.5	1.0	2.0	4.0	6.0	8.0	10.0	12.0	15.0	-	-	-
TEPP	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	-	-	-
TETS	0.004	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.8	-
1,4-Thioxane	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Bromoform-d (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Nitrobenzene-d_5 (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Nicotine-d_4 (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
2-Fluorobiphenyl (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Phencyclidine-d_5 (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Terphenyl-d_4 (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4
Triphenyl phosphate (S)	0.01	0.02	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0	1.2	1.4

Acronyms:
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine
(S) – Surrogate

Table 11a
Single-Laboratory Quantitation Limit (QL) Results and Low Calibration Standard Concentrations in Reagent Water Using Full Scan Analysis

Analyte	Low Calibration Standard [1] (µg/L)	QL[2] (µg/L)	%Recovery Range at QL	Precision at QL (%RSD)
Chlorfenvinphos	171	171	68.2 – 77.5	5.5
Chloropicrin	28.6	57.1	57.1 – 107	25.9
Chlorpyrifos	28.6	28.6	99.8 – 106	2.6
Crimidine	28.6	28.6	67.8 – 80.1	7.4
Dichlorvos	28.6	28.6	64.0 – 75.9	7.6
Dicrotophos	171	286	47.3 – 54.0	6.0
Disulfoton	28.6	28.6	78.0 – 84.0	3.5
1,4-Dithiane	28.6	28.6	84.0 – 87.8	2.2
Fenamiphos	400	571	91.8 – 114	9.8
Methyl parathion	114	114	120 – 123	1.4
Mevinphos	28.6	57.1	59.0 – 68.9	7.3
Nicotine	28.6	ND	ND	ND
Parathion	171	286	71.0 – 78.7	4.4
Phencyclidine	28.6	57.1	112 – 120	3.3
Phorate	28.6	28.6	72.0 – 83.9	7.1
Phosphamidon	171	171	70.5 – 81.0	5.9
Strychnine	571	571	122 – 132[3]	3.3[3]
TEPP	57.1	57.2	96.7 – 99.0	1.5
TETS	28.6	28.6	105 – 133	11.1
1,4-Thioxane	28.6	28.6	58.0 – 64.0	4.2

Acronyms:
ND – not determined (at least one of the criteria described in Section 9.8 was not met)
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

[1] Low calibration standard adjusted to reflect sample concentration assuming 100 % extraction efficiency.
[2] QL meets all criteria described in Section 9.8.
[3] Precision and recovery correspond to 171 µg/L for strychnine. Strychnine showed good precision and recovery at this level; however, the level was well below the lowest calibration point used.

Table 11b
Single-Laboratory Quantitation Limit (QL) Results and Low Calibration Standard Concentrations in Reagent Water Using SIM Analysis

Analyte	Low Calibration Standard [1] (µg/L)	QL[2] (µg/L)	%Recovery Range at QL	Precision at QL (%RSD)
Chlorfenvinphos	1.14	2.86	81.8 – 94.4	8.8
Chloropicrin	5.71	ND	NA	NA
Chlorpyrifos	1.14	2.86	68.5 – 79.4	6.1
Crimidine	2.86	5.71	96.3 – 116	9.2
Dichlorvos	0.57	2.86	73.8 – 85.0	6.6
Dicrotophos	2.86	2.86	118 – 133	5.1
Disulfoton	0.57	2.86	70.3 – 82.5	7.2
1,4-Dithiane	0.57	0.57	99.1 – 124	10.8
Fenamiphos	1.14	2.86	63.6 – 80.1	11.0
Methyl parathion	1.14	2.86	132 – 147	4.8
Mevinphos	2.86	5.71	115 – 132	5.8
Nicotine	2.86	5.71	50.6 – 71.8	14.2
Parathion	1.14	5.71	69.0 – 85.3	9.1
Phencyclidine	0.57	5.71	87.7 – 99.1	5.0
Phorate	1.14	2.86	69.6 – 84.3	10.3
Phosphamidon	1.14	2.86	88.5 – 101	6.2
Strychnine	114	ND	ND	ND
Tetraethyl pyrophosphate (TEPP)	11.4	ND	ND	ND
Tetramethylenedisulfotetramine (TETS)	0.23	0.46	50.0 – 52.8	1.9
1,4-Thioxane	0.57	2.86	80.4 – 88.8	4.6

Acronyms:
ND – not determined (at least one of the criteria described in Section 9.8 was not met.)
RSD – relative standard deviation
SIM – selected ion monitoring

[1] Low calibration standard adjusted to reflect sample concentration assuming 100 % extraction efficiency.
[2] QL meets all criteria described in Section 9.8.

Table 12a
Single-Laboratory Quantitation Limit (QL) Results and Low Calibration Standard Concentrations in Ottawa Sand Using Full Scan Analysis

Analyte	Low Calibration Standard [1] (mg/kg)	QL[2] (mg/kg)	%Recovery Range at QL	Precision at QL (%RSD)
Chlorfenvinphos	0.3	0.3	71.7 – 96.7	15.0
Chloropicrin	0.05	ND	ND	ND
Chlorpyrifos	0.05	0.05	69.0 – 75.0	3.5
Crimidine	0.05	0.05[4]	86.0 – 96.0	5.2
Dichlorvos	0.05	0.3	80.7 – 87.7	3.6
Dicrotophos	0.3	0.5	74.8 – 90.6	8.3
Dimethylphosphite	0.6	12.0	91.7 – 108	6.8
Disulfoton	0.05	0.05	130 – 135[3]	1.9[3]
1,4-Dithiane	0.05	0.05	70.0 – 78.0	5.0
Fenamiphos	0.7	1.0	67.4 – 72.0	3.4
Methyl parathion	0.2	0.5	58.2 – 71.8	9.7
Mevinphos	0.05	0.1	65.0 – 69.0	5.8
Nicotine	0.05	0.05[4]	100 – 110	4.0
Parathion	0.3	0.3	67.3 – 83.7	10.6
Phencyclidine	0.05	0.3[4]	73.0 – 77.0	2.6
Phorate	0.05	0.05	62.0 – 70.0	4.9
Phosphamidon	0.3	0.5	52.8 – 63.0	8.0
Tetramethylenedisulfotetramine (TETS)	0.05	0.05	74.0 – 90.0	8.6
1,4-Thioxane	0.05	0.05	54.0 – 62.0	6.4

Acronyms:
ND – not determined (at least one of the criteria described in Section 9.8 was not met.)
RSD – relative standard deviation

[1] Low calibration standard adjusted to reflect sample concentration assuming 100 % extraction efficiency.
[2] QL meets all criteria described in Section 9.8.
[3] Precision and recovery correspond to 0.02 mg/kg. Disulfoton showed good precision and recovery at this level; however, the level was below the lowest calibration point used. The QL should be at or above the concentration of the lowest calibration standard. Recovery and precision at a spike of 0.02 mg/kg are shown for illustrative purposes.
[4] Determined using 2-solvent system (5 % TEA in ethyl acetate).

Table 12b
Single-Laboratory Quantitation Limit (QL) Results and Low Calibration Standard Concentrations in Ottawa Sand Using SIM Analysis

Analyte	Low Calibration Standard [1] (µg/kg)	QL[2] (µg/kg)	%Recovery Range at QL	Precision at QL (%RSD)
Chlorfenvinphos	2.0	5.0	93.0 – 105	5.8
Chloropicrin	1.0	ND	ND	ND
Chlorpyrifos	2.0	5.0	77.2 – 87.8	5.3
Crimidine	5.0	10[3]	82.5 – 95.8	7.5
Dichlorvos	1.0	5.0	71.8 – 77.2	3.1
Dicrotophos	5.0	5.0	53.2 – 67.0	10.4
Dimethylphosphite	80.0	80.0	60.4 – 88.1	18.5
Disulfoton	1.0	5.0	61.4 – 69.4	5.8
1,4-Dithiane	1.0	5.0	71.0 – 74.2	1.8
Fenamiphos	2.0	5.0	52.4 – 62.2	8.7
Methyl parathion	5.0	5.0	60.6 – 70.4	7.4
Mevinphos	5.0	50	67.6 – 80.8	8.9
Nicotine	5.0	10[3]	78.9 – 111	13.9
Parathion	2.0	10	66.8 – 79.8	8.6
Phencyclidine	5.0	5.0[3]	87.4 – 98.6	5.7
Phorate	2.0	5.0	56.0 – 59.2	2.5
Phosphamidon	2.0	5.0	62.4 – 96.0	18.3
Tetramethylenedisulfotetramine (TETS)	0.4	0.4	81.3 – 95.3	7.1
1,4-Thioxane	1.0	5.0	52.4 – 60.2	6.3

Acronyms:
ND – not determined (at least one of the criteria described in Section 9.8 was not met.)
RSD – relative standard deviation
SIM – selected ion monitoring

[1] Low calibration standard adjusted to reflect sample concentration assuming 100 % extraction efficiency.
[2] QL meets all criteria described in Section 9.8.
[3] Determined using 2-solvent system (5 % triethylamine [TEA] in ethyl acetate.

Table 13a
Single-Laboratory Study Water Matrix Characterization Data

Information	Matrix		
	Reagent Water	**Surface Water**	**Drinking Water**
Source Name	Deionized Water	Germany Creek, WA	Tap Water
Source Location	Columbia Analytical, WA	Germany Creek, WA	Columbia Analytical, WA
Collection Date	8/6/2009	8/6/2009	12/1/2009
Weight/Volume	500 mL	5 gallons	500 mL
pH	6.52	7.96	7.14
Total Organic Carbon (TOC) Content	<0.5 mg/L	1.5 mg/L	0.78 mg/L
Chlorine	<0.2 mg/L	5.7 mg/L (1)	0.9–1.1 mg/L (2)
Total Suspended Solids (TSS)	<5.0 mg/L	<5.0 mg/L	<5.0 mg/L

(1) High level of Cl^- reported for this matrix is possibly due to tidal effects.
(2) Range of Cl^- reported over a five-day period after study completion.

Table 13b
Multi-Laboratory Exercise Water Matrix Characterization Data

Information	Value
Source Name	Lab Tap Water
Source Location	ERA Laboratory, Golden, CO
Collection Date	6/19/2014
Alkalinity as $CaCO_3$	42.7 mg/L
Calcium Hardness as $CaCO_3$	49.3 mg/L
Specific Conductance at 25 ºC	209 mg/L
pH	7.84
Total Hardness as $CaCO_3$	68.0 mg/L
Total Organic Carbon (TOC)	2.68 mg/L
Total Residual Chlorine	0.04 mg/L

Table 14
Single-Laboratory Study Soil Matrix Characterization Data

Information	Matrix	
	Georgia Bt2 soil	**Nebraska Ap soil**
Calcium	NA	15.4 mEq/100g
Magnesium	NA	4.9 mEq/100g
Cation Exchange Capacity	NA	26.3 mEq/100g
pH	5.0	5.6
Total Organic Carbon (TOC)	0.2 %	2.1 %
Sand	46 %	6 %
Silt	22 %	60 %
Clay	32 %	34 %

Acronyms: NA – not available

Table 15
Multi-laboratory Reagent Water Results for Dichlorvos, Mevinphos, Tetramethylenedisulfotetramine (TETS) and Associated Surrogates

Analyte	Spike Concentration (µg/L)	n[1]	Avg Recovery (%)	Minimum Recovery (%)	Maximum Recovery (%)	Pooled RSD (%)
Low-Level Spike						
Dichlorvos	28.6	49	102	54.0	150	7.3
Mevinphos	28.6	48	112	65.9	161	9.7
TETS	28.6	49	101	76.9	140	8.0
Mid-Level Spike[2]						
Dichlorvos	571	40	106	70.6	140	5.0
Mevinphos	571	41	99.3	71.9	124	5.8
TETS	571	40	98.2	81.8	126	5.0
Surrogate	**Spike Concentration (µg/L)[3]**	**n[4]**	**Avg Recovery (%)**	**Minimum Recovery (%)**	**Maximum Recovery (%)**	**RSD (%)**
2-Fluorobiphenyl	571	80	102	61.6	137	20.9
Nitrobenzene-d_5	571	80	98.9	66.3	131	16.1
Terphenyl-d_{14}	571	81	110	64.3	140	19.3

[1] Number of analyte results used to develop performance data, after outlier removal.

[2] Four replicates from one laboratory were spiked at 286 µg/L.

[3] Surrogates were spiked at this level in all low- and mid-level samples.

[4] Number of surrogate results across both analyte spike levels, after outlier removal.

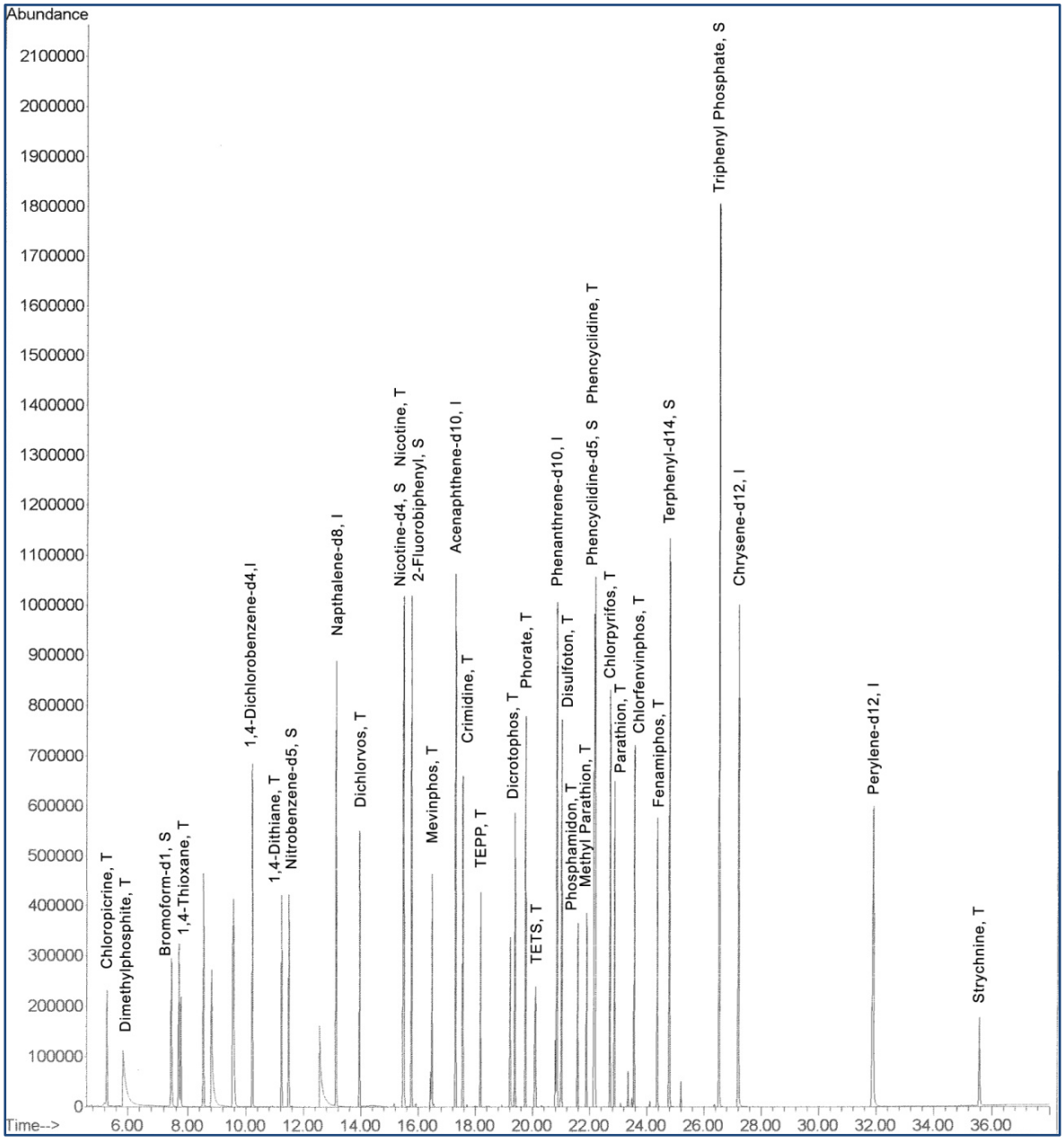
Table 16
Multi-laboratory Drinking Water Results for Dichlorvos, Mevinphos, Tetramethylenedisulfotetramine (TETS) and Associated Surrogates

Analyte	Spike Concentration (µg/L)	n[1]	Avg Recovery (%)	Minimum Recovery (%)	Maximum Recovery (%)	Pooled RSD (%)
Low-Level Spike						
Dichlorvos	114	32	59.0	38.6	83.1	10.6
Mevinphos	114	32	97.3	53.5	153	13.6
TETS	114	32	91.4	75.6	114	5.7
Mid-Level Spike						
Dichlorvos	571	31	62.1	44.0	83.5	14.1
Mevinphos	571	32	103	76.0	155	14.6
TETS	571	31	87.2	72.5	103	12.8
Surrogate	**Spike Concentration (µg/L)[2]**	**n[3]**	**Avg Recovery (%)**	**Minimum Recovery (%)**	**Maximum Recovery (%)**	**RSD (%)**
2-Fluorobiphenyl	571	80	106	73.7	131	10.9
Nitrobenzene-d_5	571	80	102	71.9	127	12.0
Terphenyl-d_{14}	571	80	113	81.4	158	10.2

[1] Number of analyte results used to develop performance data, after outlier removal.

[2] Surrogates were spiked at this level in all low- and mid-level samples.

[3] Number of surrogate results across both analyte spike levels, after outlier removal.



Acronyms:

T – Target

S – Surrogate

I – Internal standard

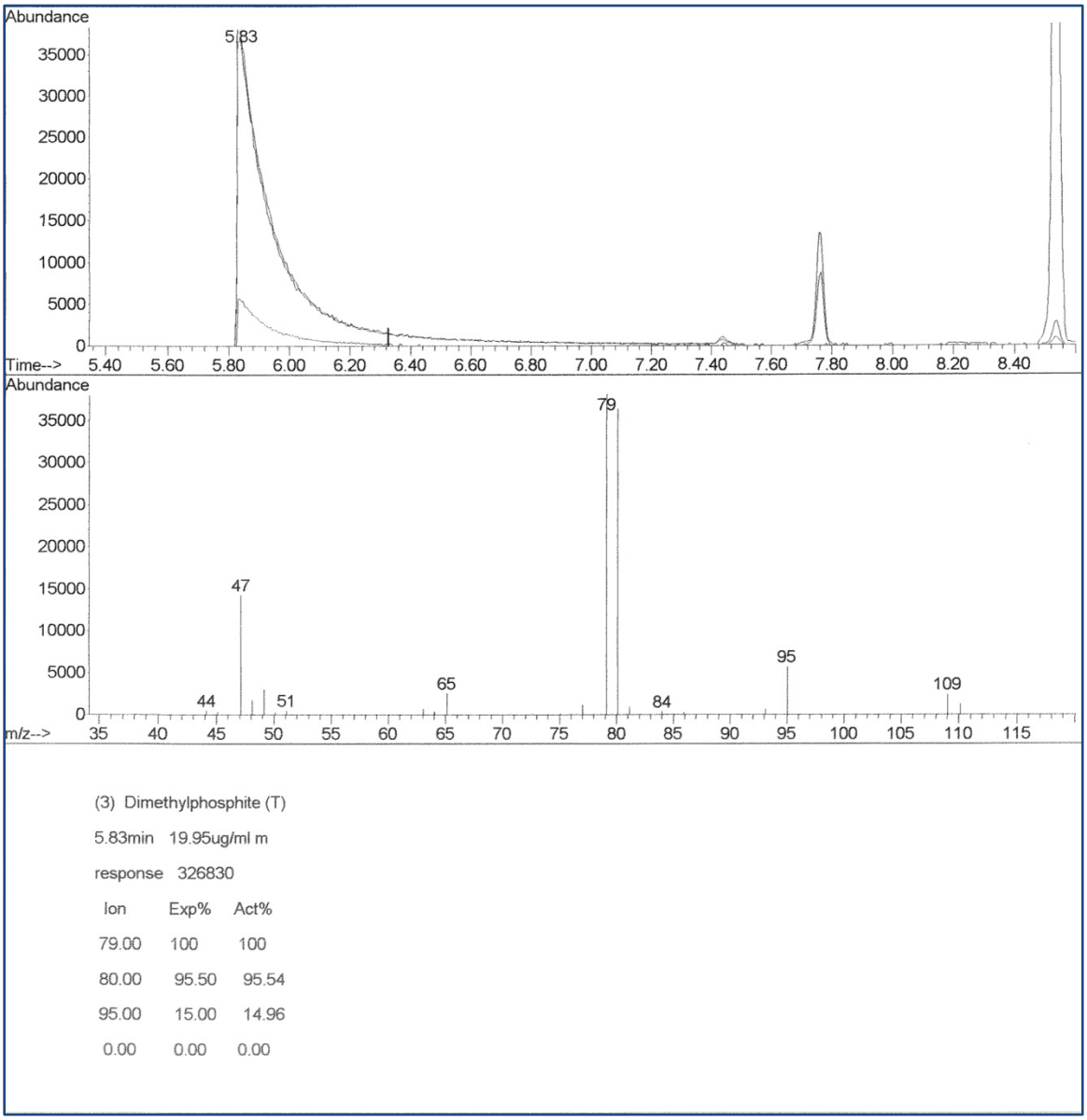
TETS – tetramethylenedisulfotetramine

TEPP – tetraethyl pyrophosphate

Concentrations of all analytes as described in Table 10a, Calibration Level 7.

Figure 1.

Gas chromatogram of a midpoint calibration standard.



(3) Dimethylphosphite (T)

5.83min 19.95ug/ml m

response 326830

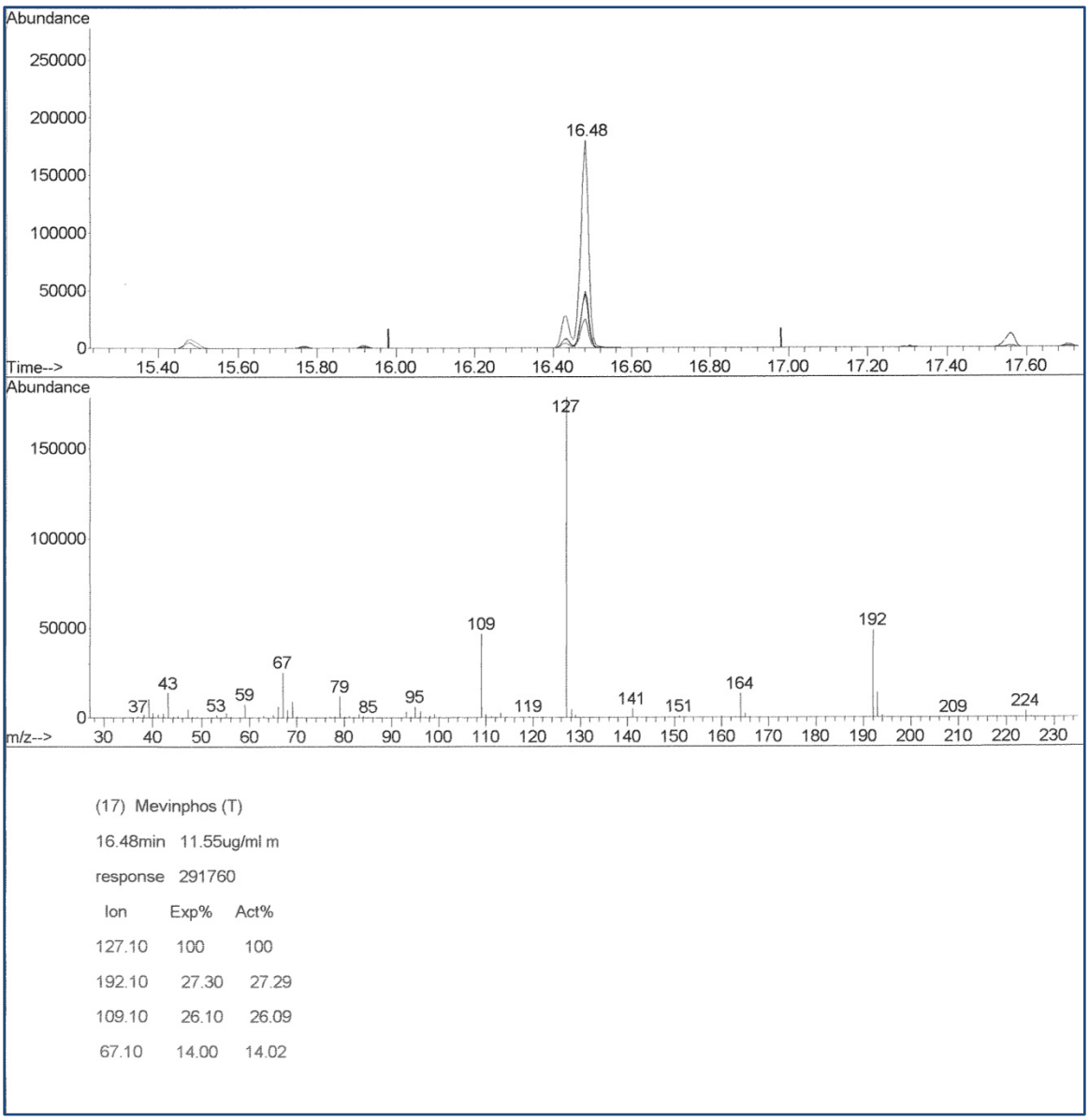
Ion	Exp%	Act%
79.00	100	100
80.00	95.50	95.54
95.00	15.00	14.96
0.00	0.00	0.00

Top image: Expanded view of DMP peak from chromatogram of Calibration Level 7 (see Table 10a), with DMP spiked at 20 µg/mL. Manual integration set from 5.80 to around 6.80 minutes.

Bottom image: Mass spectral fragmentation pattern for DMP, showing abundance ratios for quantitation ion (79 m/z) and qualifier ions (80 and 90 m/z). Exp% = Experimental ion abundance percentage based on NIST library data. Act% = Actual ion abundance percentage based on analysis of calibration standard.

Figure 2.

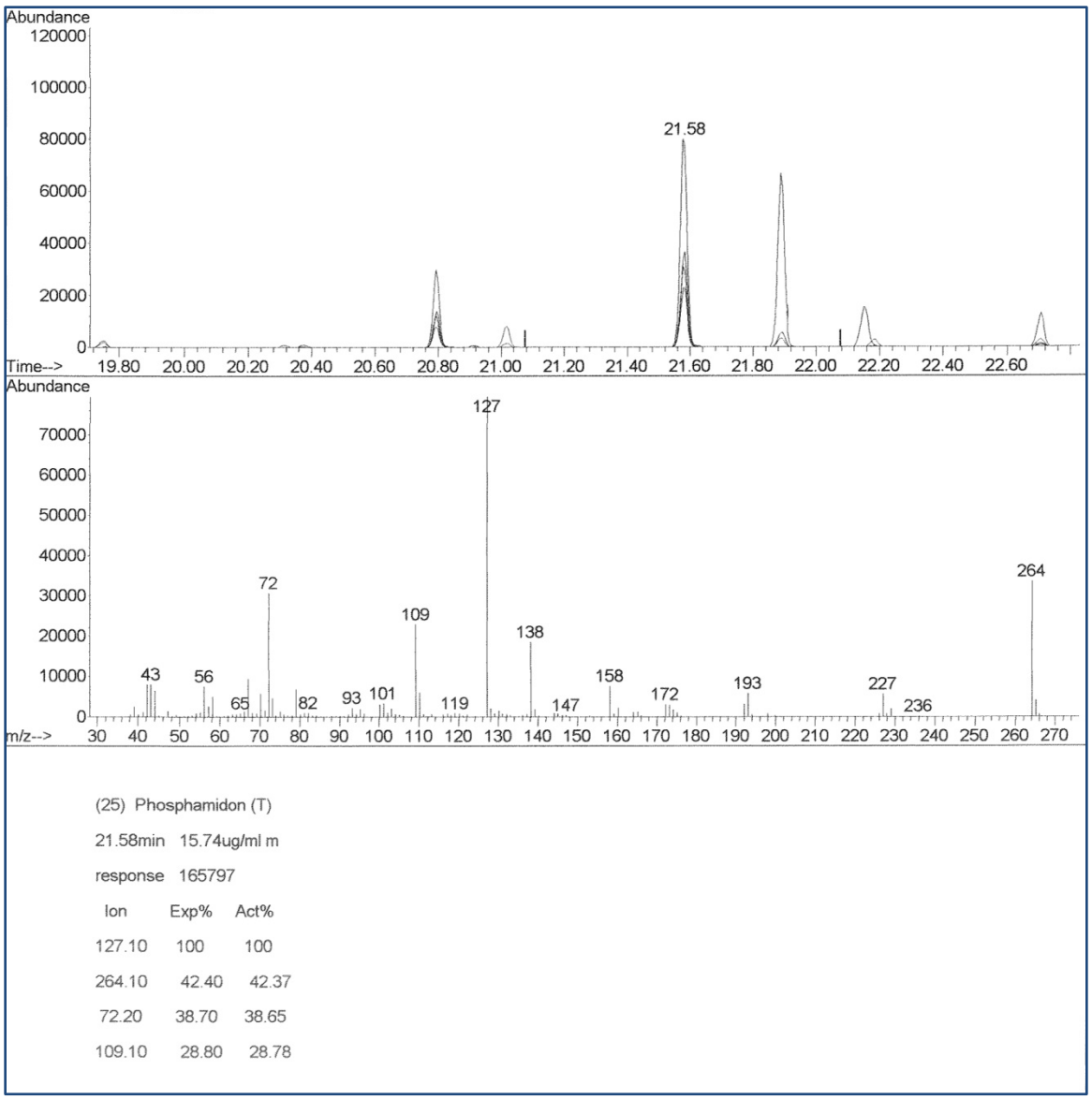
Peak requiring manual integration due to peak tailing – dimethylphosphite (DMP).



Top image: Expanded view of mevinphos peaks from chromatogram of Calibration Level 7 (see Table 10a), with mevinphos spiked at 10 µg/mL. Manual integration set from 15.98 to around 16.98 minutes combining two isomers of mevinphos (retention times of 16.43 and 16.48).

Bottom image: Mass spectral fragmentation pattern for mevinphos (both isomers), showing abundance ratios for quantitation ion (127.1 m/z) and qualifier ions (192.1, 109.1 and 67.1 m/z). Exp% = Experimental ion abundance percentage based on NIST library data. Act% = Actual ion abundance percentage based on analysis of calibration standard.

Figure 3.
Peak requiring manual integration due to closely eluting isomers – mevinphos.

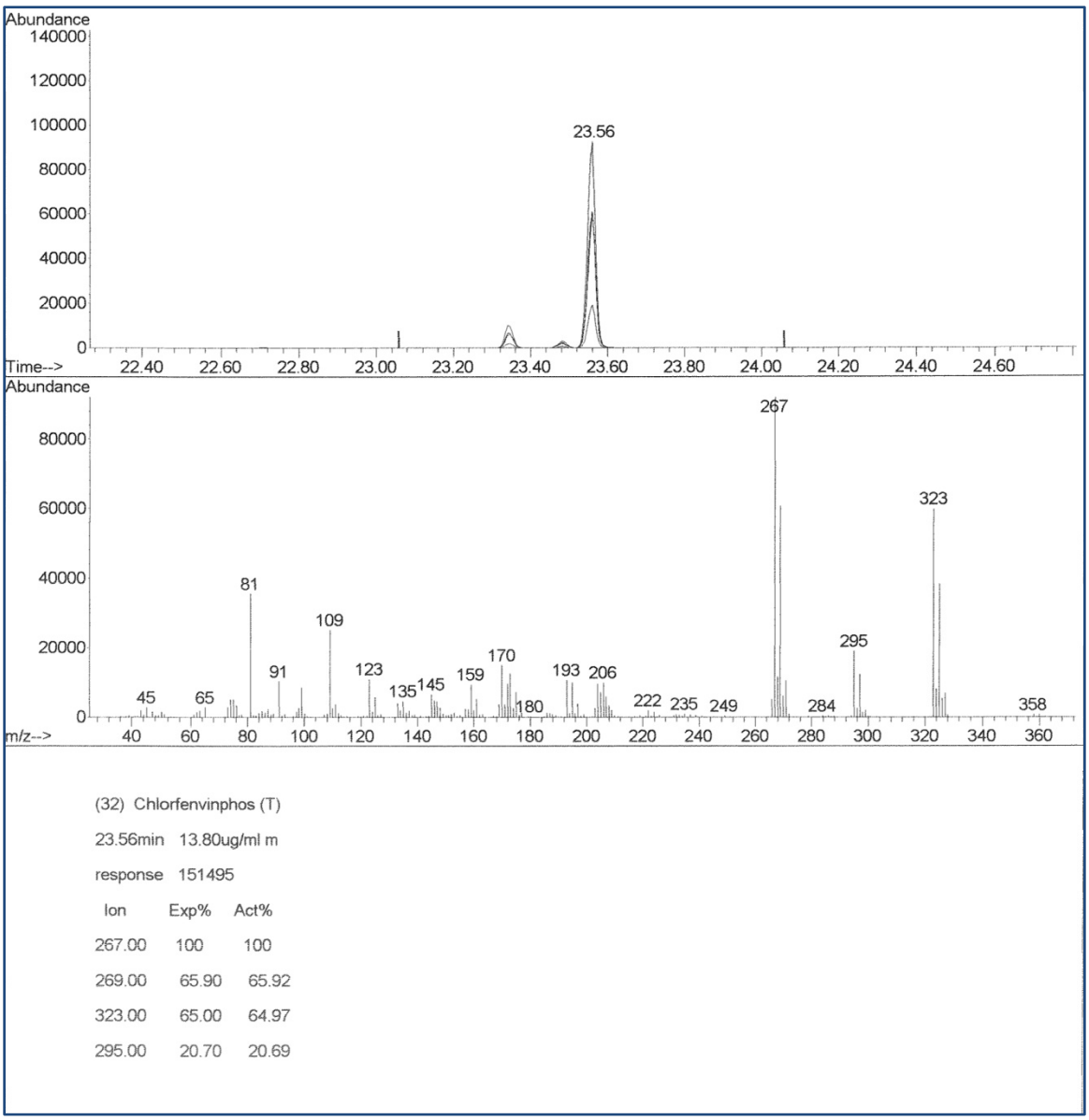


Top image: Expanded view of phosphamidon peaks from chromatogram of Calibration Level 7 (see Table 10a), with phosphamidon spiked at 10 µg/mL. Manual integration set from 21.08 to around 22.08 minutes combining two isomers of phosphamidon (retention times of 21.58 and 21.90).

Bottom image: Mass spectral fragmentation pattern for phosphamidon (both isomers), showing abundance ratios for quantitation ion (127.1 m/z) and qualifier ions (264.1, 72.2 and 109.1 m/z). Exp% = Experimental ion abundance percentage based on NIST library data. Act% = Actual ion abundance percentage based on analysis of calibration standard.

Figure 4.

Peak requiring manual integration due to closely eluting isomers – phosphamidon.



Top image: Expanded view of chlorfenvinphos peaks from chromatogram of Calibration Level 7 (see Table 10a), with chlorfenvinphos spiked at 10 µg/mL. Manual integration set from 23.06 to around 24.06 minutes combining three isomers of chlorfenvinphos (retention times of 23.35, 23.49 and 23.56).

Bottom image: Mass spectral fragmentation pattern for chlorfenvinphos (all three isomers), showing abundance ratios for quantitation ion (267.0 m/z) and qualifier ions (269.0, 323.0 and 295.0 m/z). Exp% = Experimental ion abundance percentage based on NIST library data. Act% = Actual ion abundance percentage based on analysis of calibration standard.

Figure 5.

Peak requiring manual integration due to closely eluting isomers – chlorfenvinphos.

APPENDIX: ALTERNATE SAMPLE PREPARATION PROCEDURES

Appendix A is provided as an addendum to the procedures and equipment described in the analytical protocol, and provides a description of alternative equipment and procedures that have undergone preliminary evaluation in a single laboratory or have not been evaluated at all, but may be appropriate for certain analytes, based on other methods or studies. Results using some of these procedures are provided for informational purposes.

A1.0 EQUIPMENT

Note: The equipment listed in Appendix A is needed specifically for the procedures described in the appendix, in addition to equipment listed in Section 6.0 of the protocol. Manufacturer instruction manuals should be consulted if using equipment other than the equipment specified in this appendix.

A1.1 Pressurized Fluid Extraction (PFE) Device for Soils, Wipes, and Air Filters - Dionex® Accelerated Solvent Extractor (ASE-300; Thermo Fisher Scientific Inc., Sunnyvale, CA) or equivalent, with appropriately sized extraction cells. Currently, 100-mL cells are available that will accommodate samples greater than 30 grams. Cells should be made of stainless steel or other material capable of withstanding the pressure environments (2000+ psi) necessary for this procedure. Other system designs may be used, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

A1.2 Automated Soxhlet Extraction System for Soils

A1.2.1 Automated Soxhlet extraction system with temperature controlled bath, such as Soxtec™ HT 6 (Foss, Eden Prairie, MN) or equivalent

A1.2.2 Cellulose or glass extraction thimble - 26 mm ID x 60 mm, contamination free

A1.2.3 Glass extraction cups (80 mL) - compatible with extraction system

A1.2.4 Thimble adapters - compatible with extraction system

A1.2.5 Viton seals - compatible with extraction system

A1.3 Solid-phase Extraction (SPE) for Water Samples

Note: A manual system with syringe adaptors that fit the top of the SPE tubes is recommended for accurate control of pressure (flow).

A1.3.1 Horizon SPE-DEX® 4790 Automated Solid Phase Extractor (Horizon Technology, Salem, NH) or equivalent

A1.3.2 SPE disks – JT Baker® divinylbenzene (DVB) (Avantor Performance Materials, Center Valley, PA) or equivalent

A1.3.3 Multilayer glass microfiber filter – Whatman GMF 150 or equivalent

A2.0 REAGENTS

Note: The reagents listed in Appendix A are needed specifically for the procedures described in the appendix, in addition to reagents listed in Section 7.0 of the protocol.

A2.1 Methanol (used in SPE Procedure)

A2.2 Solutions for adjusting the pH of samples before extraction

Note: Check the pH of water samples prior to adding acid or base solution as acid preservation may have been performed in the field.

A2.2.1 Sulfuric acid (H_2SO_4) solution (1:1 v/v) – Slowly add 50 mL of concentrated sulfuric acid (specific gravity 1.84) to 50 mL of organic-free reagent water.

A2.2.2 Sodium hydroxide (NaOH) solution (10N) - Dissolve 40 grams NaOH in organic-free reagent water and dilute to 100 mL.

A2.3 Hydromatrix™ (recommended drying agent for PFE) - Diatomaceous earth-based material rinsed with dichloromethane (DCM) and dried at 400 °C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle. (Hydromatrix is a product of Agilent Technologies, Santa Clara, CA.)

A-3.0 ALTERNATE WATER SAMPLE PREPARATION TECHNIQUES (i.e., SOLID-PHASE EXTRACTION [SPE])

A3.1 Preparation of Water Samples by Solid Phase Extraction (SPE)

Data characterizing the procedure described for SPE of water samples are limited. The procedure is provided as an alternative in the event that larger sample volumes are necessary to address lower concentrations.

Note: Preliminary evaluations showed poor extraction of chloropicrin, nicotine, phencyclidine, TEPP, and 1,4-thioxane. For this reason, SPE was not thoroughly evaluated during the single-laboratory study.

A3.1.1 Measure 1 L of sample and adjust the pH to ~4 using small amounts of H_2SO_4 (1:1 v/v in water) or 10N NaOH solution.

Note: Preliminary single-laboratory results have shown that adjusting the pH to 8 improves the recoveries for the following compounds: chloropicrin, nicotine, phencyclidine and tetraethyl pyrophosphate (TEPP). Therefore, it is recommended that the pH be adjusted to 8 if analyzing for these compounds.

A3.1.2 Place a Whatman® GMF 150 (Whatman, Maidstone, UK) on top of the divinylbenzene (DVB) disk prior to clamping the glass reservoir into the filter

apparatus. Wash the extraction apparatus and disk with 25 mL of each solvent (see Prep/Rinse program below) rinsing down the sides of the reservoir. Pull a small amount of solvent through the disk with a vacuum. Turn off the vacuum and allow the disk to soak for approximately one minute. Pull the remaining solvent through the disk and allow the disk to dry.

Sample Prep/Rinse Program:

Solvent	**Soak Time**	**Dry Time**
Prewet 1 - DCM	1:30 minutes	0:30 minute
Prewet 1 - DCM	1:30 minutes	0:30 minute
Prewet 2 - Acetone	1:30 minutes	0:30 minute
Prewet 3 - Methanol	1:30 minutes	0:30 minute
Prewet 4 - Deionized (DI) Water	0:10 minute	0:10 minute

A3.1.3 Add the sample to the reservoir. Under full vacuum, filter as quickly as the vacuum will allow, but for a minimum of 10 minutes. After the sample has passed through the disk, dry the disk by maintaining vacuum for an additional 5 minutes.

A3.1.4 Remove the entire filter assembly without dismantling from the manifold. Insert a collection tube with sufficient capacity to hold the elution solvents and prevent splattering when the vacuum is applied.

A3.1.5 Add 8.0 mL of acetone to the disk. Allow the acetone to spread evenly over the disk. Quickly turn the vacuum on and off to pull the first few drops of acetone through the disk. Allow the disk to soak for 15 to 20 seconds before proceeding. CAUTION: From this point until the extraction is completed, the surface of the disk should not be allowed to go dry.

A3.1.6 Add 8.0 mL of DCM to the sample bottle (or container used to measure sample volume). Rinse thoroughly, transferring the contents to the acetone soaked disk using a disposable pipette and rinsing down the sides of the reservoir in the process. Draw approximately one-half the solvent through the disk and then release the vacuum. Allow the remaining solvent to soak the disk and any particulate matter present for approximately one minute before applying a vacuum to draw the remaining solvent through the disk.

A3.1.7 Repeat Step A3.1.6 with an additional 8.0 mL of DCM, collecting the solvent in the same collection tube.

A3.1.8 Proceed to Section 11.6 for extract concentration.

A3.2 Single-laboratory Results for SPE

Table A1 provides a comparison of results for reagent water extraction using the procedures described in A3.1 (SPE at pH = 4 and pH = 8) and Section 11.2.1 (microscle solvent extraction [MSE]). For a majority of the analytes, MSE procedures gave the highest recoveries; however, SPE (pH = 4) gave better recoveries for chlorpyrifos, disulfoton, methyl parathion, parathion, and phorate. SPE (pH = 8) gave the best results for nicotine.

Table A1.
Mean Percent Recovery and Relative Percent Difference (RPD) Results of Duplicate Water Sample Extractions

Note: Bold entries indicate recovery was within 70-130 % and RPD was less than 25.

Analyte	SPE (pH = 4)			SPE (pH = 8)			MSE (pH = 4)		
	Spike (µg/L)	Mean % Recovery	RPD	Spike (µg/L)	Mean % Recovery	RPD	Spike (µg/L)	Mean % Recovery	RPD
4-Aminopyridine	25.0	Not detected		25.0	Not detected		714	Not detected	
Chlorfenvinphos	12.0	**79.5**	**7.9**	12.0	**72.8**	**5.8**	343	68	3
3-MCPD	20.0	Not detected		20.0	Not detected		571	Not detected	
Chloropicrin	10.0	Not detected		10.0	6.2	110	286	**71**	**1**
Chlorpyrifos	10.0	**96.0**	**6.8**	10.0	**78.6**	**6.9**	286	**80**	**5**
Crimidine	10.0	**78.6**	**2.4**	10.0	**74.8**	**9.9**	286	**93**	**10**
Dichlorvos	10.0	**77.4**	**5.9**	10.0	66.9	7.2	286	**92**	**10**
Dicrotophos	12.0	64.8	13.6	12.0	47.0	6.7	343	51	4
Dimethylphosphite	20.0	Not detected		20.0	Not detected		571	Not detected	
Disulfoton	10.0	**93.9**	**5.8**	10.0	**79.4**	**8.3**	286	**80**	**0**
1,4-Dithiane	10.0	69.9	1.4	10.0	61.1	11.3	286	**77**	**34**
Fenamiphos	15.0	**79.0**	**0.8**	15.0	68.7	5.8	429	**80**	**8**
Methyl parathion	10.0	**114**	**12.4**	10.0	64.9	7.7	571	62	0
Mevinphos	10.0	**85.0**	**2.7**	10.0	**72.2**	**15.5**	286	**87**	**12**
Nicotine	10.0	Not detected		10.0	60.3	0.8	286	49	8
Parathion	12.0	**90.8**	**11.0**	12.0	68.6	6.0	343	64	0
Phencyclidine	10.0	7.3	16.4	10.0	57.2	18.0	286	**102**	**6**
Phorate	10.0	**91.7**	**5.3**	10.0	**77.6**	**10.8**	286	**80**	**1**
Phosphamidon	12.0	**70.0**	**6.8**	12.0	**69.5**	**6.4**	343	**82**	**5**
Strychnine	50.0	Not detected		50.0	Not detected		1430	Not detected	
TEPP	20.0	16.0	34.6	20.0	31.2	10.6	571	**87**	**0**
TETS	5.0	**80.8**	**1.5**	5.0	**71.5**	**11.5**	143	**98**	**8**
1,4-Thioxane	10.0	13.2	33.3	10.0	12.4	15.4	286	**78**	**3**
All Analytes	53.0 ± 40.5			52.0 ± 28.7			69 ± 27		
Bromoform-d_1	10	67.0	4.0	10.0	1.0	6.9	286	**94**	**5**
Nitrobenzene-d_5	10	**98.0**	**5.1**	10.0	**83.4**	**10.0**	286	**122**	**8**
Nicotine-d_4	10	Not detected		10.0	68.8	4.9	286	57	4
2-Fluorobiphenyl	10	**88.3**	**4.4**	10.0	**75.4**	**8.1**	286	**91**	**0**
Phencylidine-d_5	10	Not detected		10.0	52.1	21.3	286	**97**	**4**
Terphenyl-d_{14}	10	**71.1**	**2.4**	10.0	35.7	3.4	286	**73**	**9**
Triphenyl phosphate	10	**75.1**	**3.6**	10.0	29.6	2.4	200	33	11
All Surrogates	68.6 ± 29.8			43.4 ± 31.9			77 ± 30		
Number of Target Analytes Within 70–130 % Recovery									
Target Recovery Range (70-130 %)	SPE (pH 4)			SPE (pH 8)			MSE (pH 4)		
	12			6			14		

Acronyms:

MSE – microscale solvent extraction
SPE – solid phase extraction
TEPP – tetraethyl pyrophosphate
TETS – tetramethylenedisulfotetramine

A4.0 ALTERNATE SOIL SAMPLE PREPARATION TECHNIQUES

A4.1 Preparation of Solid Samples by Automated Soxhlet Extraction

A4.1 1 The laboratory may use either automated or non-automated Soxhlet extraction. Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Open the cold water tap for the flux condensers and adjust the flow to prevent solvent loss through the condensers. Transfer the entire sample, including sodium sulfate drying agent (2:1 w/w drying agent:sample), to the thimble. Add a sufficient amount of the surrogate standard spiking solution to result in the addition of 10 µg of each surrogate to the sample.

A4.1.2 Immediately transfer the thimbles containing the weighed samples into the condensers. Adjust the heat to boil the solvent. Position the thimble just below the condenser valve. Insert the extraction cups containing boiling chips, and load each cup with appropriate volume of extraction solvent (1:1 v/v DCM/acetone). Clamp the cups into position.

Note: The Viton® seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

A4.1.3 Immerse the thimbles in DCM/acetone (1:1 v/v). Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time. Move the thimbles to rinsing position above the solvent surface. Set the timer for 60 minutes, leaving the condenser valves open. Extract for the preset time. After rinse time has elapsed, close the condenser valves. When all but 2 - 5 mL of the solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with DCM and add the rinsates to the glass tubes. Proceed to Section 11.6.

A4.2 Preparation of Solid Samples by Pressurized Fluid Extraction (PFE)

A4.2.1 Transfer the entire sample, including Hydromatrix drying agent (1:1 w/w drying agent: sample) (Section A2.3), to an extraction cell of the appropriate size for the aliquot. Add sufficient amount of the surrogate standard spiking solution to result in the addition of 10 µg of each surrogate to the sample.

A4.2.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer. Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrument and the extraction procedure recommended by the manufacturer, and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract. The following are recommended extraction conditions:

Oven temperature:	100 °C
Pressure:	1500 - 2000 psi

Nitrogen purge:	60 seconds at 150 psi (purge time may be extended for larger cells)
Flush volume:	60 % of the cell volume
Static cycles:	2
Static time:	10 minutes (after 5 minutes, pre-heat equilibration)

A4.2.3 Optimize the extraction conditions as needed, according to the manufacturer's instructions. An appropriate amount of 1:1 (v/v) acetone/DCM should be used to achieve the extraction conditions detailed in the preceding paragraph. Once established, the same pressure should be used for all samples in the same batch. Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 11.6.

A4.3 Single-Laboratory Results for Alternate Soil Preparation Techniques

Table A2 provides a comparison of results for Ottawa sand extractions by microscale solvent extraction (MSE; see protocol Section 11.3.5) and automated Soxhlet extraction (A4.1), each using two different solvent systems, and by PFE (A4.2). The procedure for MSE (2-solvent) involved extraction with only 5 % triethylamine (TEA)/ethyl acetate, while the procedure for MSE (3-solvent) involved extraction with acetone:DCM:ethyl acetate (1:2:1) followed by extraction with 5 % TEA/ethyl acetate. Note that the results for MSE (3-solvent) in Table A2 were generated using the procedure described in protocol Section 11.3.5 (triplicate extraction using the 3-solvent system, followed by single extraction using the 2-solvent system). The procedure for automated Soxhlet extraction using the 2-solvent system is described in A4.1. Automated Soxhlet extraction was also evaluated using this procedure with a 3-solvent system (acetone:DCM:ethyl acetate). The procedure used for PFE is described in A4.2. Automated Soxhlet extraction and PFE procedures are provided as possible alternatives for analytes that have demonstrated improved extraction efficiency as compared to MSE. Analytes with improved extraction efficiency using automated Soxhlet extraction include dicrotophos, phosphamidon, and strychnine; analytes with improved efficiency using PFE include dicrotophos, 1,4-dithiane, methyl parathion, and 1,4-thioxane.

Table A2. Mean Percent Recovery and Relative Percent Difference (RPD) Results of Duplicate Ottawa Sand Sample Extractions

Note: Bold entries indicate recovery was within 70-130 % and RPD was less than 25 %.

Analyte	Sample mg/kg	Microscale Solvent Extraction (MSE)				Automated Soxhlet Extraction				Pressurized Fluid Extraction (PFE)	
		2-solvent		3-solvent		2-solvent		3-solvent			
		Mean % Recovery	RPD	Mean % Recovery	RPD	Mean % Recovery	RPD	Mean % Recovery	RPD	Mean % Recovery	RPD
4-Aminopyridine	2.5	Not Detected		43.0	4.7	69.0	4.1	43.0	4.7	Not Detected	
Chlorfenvinphos	1.2	56.3	8.0	64.4	15.1	67.1	2.6	64.4	15.1	67.5	3.0
3-MCPD	2.0	Not Detected		44.0	6.0	24.8	108.9	44.0	6.0	Not Detected	
Chloropicrin	1.0	Not Detected				0.9	200	Not Detected			
Chlorpyrifos	1.0	**69.6**	**4.0**	**77.2**	**6.9**	**77.5**	**1.8**	**77.2**	**6.9**	**76.5**	**4.3**
Crimidine	1.0	64.8	4.3	**71.8**	**2.2**	**71.4**	**4.6**	**71.8**	**2.2**	**81.2**	**3.8**
Dichlorvos	1.0	27.0	27.4	61.9	4.8	52.0	61.5	61.9	4.8	36.7	37.6
Dicrotophos	1.2	56.0	7.0	56.3	24.1	**81.4**	**4.8**	56.3	24.1	**72.8**	**15.6**
Dimethylphosphite	2.0	Not Detected		27.0	15.9	18.0	200.0	27.0	15.9	Not Detected	
Disulfoton	1.0	**71.0**	**2.5**	**75.5**	**5.4**	**80.8**	**0.5**	**75.5**	**5.4**	**80.7**	**7.9**
1,4-Dithiane	1.0	41.9	1.0	46.0	12.4	32.0	200.0	46.0	12.4	69.5	5.9
Fenamiphos	1.5	68.0	2.0	69.4	9.5	**83.0**	**0.8**	69.4	9.5	**85.0**	**0.8**
Methyl parathion	1.0	14.1	86.8	68.5	1.5	**74.6**	**12.9**	68.5	1.5	**88.0**	**14.0**
Mevinphos	1.0	51.5	2.1	60.2	1.8	64.9	6.6	60.2	1.8	56.8	16.2
Nicotine	1.0	65.4	4.3	69.1	10.0	60.4	49.2	69.1	10.0	**80.9**	**18.2**
Parathion	1.2	63.6	0.0	**72.5**	**13.2**	**79.8**	**0.9**	**72.5**	**13.2**	**82.4**	**4.4**
Phencyclidine	1.0	**77.1**	**9.6**	69.4	1.2	**75.2**	**1.7**	69.4	1.2	**80.9**	**9.8**
Phorate	1.0	67.3	1.5	**72.2**	**4.3**	**79.5**	**3.5**	**72.2**	**4.3**	**80.4**	**7.6**
Phosphamidon	1.2	27.8	25.2	45.0	23.7	62.7	6.1	45.0	**23.7**	51.4	14.3
Strychnine	5.0	48.7	41.5	57.1	13.7	**82.6**	**41.6**	57.1	13.7	41.0	23.4
Tetraethyl pyrophosphate (TEPP)	2.0	13.9	6.8	Not Detected		4.9	109.9	Not Detected		1.1	200.0
Tetramethylenedisulfotetramine (TETS)	0.5	66.7	8.7	**86.0**	**2.3**	**80.8**	**1.5**	**86.0**	**2.3**	**84.8**	**7.1**
1,4-Thioxane	1.0	32.9	7.6	39.3	12.0	25.3	200.0	39.3	12.0	60.0	0.2
Mean Target Analyte Recovery		45.6 ± 25.7		56.1 ± 22.4		56.4 ± 22.2		56.1 ± 19.5		56.5 ± 32.5	
Bromoform-d_1	1.0	29.7	8.8	38.7	10.1	23.9	200.0	44.9	6.0	Not Detected	
Nitrobenzene-d_5	1.0	58.4	5.1	62.9	11.1	46.3	174.1	75.4	0.4	94.0	6.9
Nicotine-d_4	1.0	77.5	0.4	80.8	8.8	318.7	142.1	84.0	2.1	96.3	18.6
2-Fluorobiphenyl	1.0	54.0	7.0	60.5	6.1	202.9	124.4	66.9	2.4	87.2	10.0
Terphenyl-d_{14}	1.0	74.5	1.9	82.6	6.1	88.2	0.0	73.1	0.7	87.5	5.6
Triphenyl phosphate	0.8	55.3	6.7	63.9	6.3	71.6	2.4	54.6	1.3	215.1	4.1
Mean Surrogate Recovery		69.7 ± 16.2		64.9 ± 14.6		60.4 ± 21.0		67.2 ± 13.3		86 ± 6	
Number of Target Analytes Within 70–130 % Recovery											
Target Recovery Range (70 -130 %)		**MSE (2-solvent)**		**MSE (3-solvent)**		**ASE (3-solvent)**		**ASE**		**PFE**	
		3		9		11		6		12	

A5.0 ALTERNATE WIPE SAMPLES PREPARATION TECHNIQUES

Preparation of Wipe Samples by PFE – Follow the procedure in A4.2, replacing the soil sample with a surface wipe (Section 6.2.14). Once extraction is complete, proceed to Section 11.6.

A6.0 GEL PERMEATION CHROMATOGRAPHY (GPC) CLEANUP

The equipment, reagents and procedure for GPC cleanup can be found in EPA SW-846 Method 3640A (Reference 16.10). Prior to GPC cleanup, the soils were extracted by three different extraction procedures (solvent systems):

- (Extraction 1) 5 % TEA in ethyl acetate
- (Extraction 2) 1:2:1 (v:v:v) acetone:DCM:ethyl acetate
- (Extraction 3) Extraction 2 followed by Extraction 1, with extracts combined prior to analysis

Preliminary results in Georgia Bt2 soil showed no significant improvement in recoveries when GPC cleanup was performed; however, there is historical precedent that recoveries for analytes in certain soil types might be improved using this cleanup technique. Table A3 provides a comparison of results for duplicate Georgia Bt2 soil extractions using MSE with and without GPC cleanup.

Table A3. Effect of Gel Permeation Cleanup (GPC) on Microscale Solvent Extraction (MSE) of Georgia Bt2 Soil

Note: Bold entries indicate recovery was within 70−130 % and RPD was less than or equal to 25 %.

Analyte	Spike Level (mg/kg)	MSE with no GPC						MSE with GPC					
		Average % Recovery						Average % Recovery					
		Solvent[1] System	RPD	Solvent[2] System	RPD	Solvent[3] System	RPD	Solvent[1] System	RPD	Solvent[2] System	RPD	Solvent[3] System	RPD
Chloropicrin	0.5	ND											
Dimethylphosphite	1	ND											
1,4-Thioxane	0.5	26.4	19.7	40.0	14.0	36.7	0.5	30.2	41.1	45.4	0.9	42.2	23.7
1,4-Dithiane	0.5	34.2	29.2	56.3	6.0	46.5	12.5	40.0	36.0	57.4	0.7	56.4	25.5
Dichlorvos	0.5	ND		15.9	18.8	3.2	25.0	ND		14.5	21.3	3.2	50.0
Nicotine	0.5	59.2	9.5	ND		11.3	1.8	54.0	7.4	ND			
Mevinphos	0.5	17.7	28.2	48.4	5.8	36.0	1.1	16.8	42.9	36.4	13.2	36.2	12.2
Crimidine	0.5	50.5	2.8	1.9	10.5	7.0	11.4	45.4	0.9	1.0	40.0	6.0	0.0
Dicrotophos	0.5	2.1	47.6	8.2	0.0	15.9	3.8	1.2	66.7	3.2	25.0	14.0	11.4
Phorate	0.5	46.8	41.9	61.6	10.4	58.1	2.4	42.8	56.1	60.0	6.7	57.6	8.3
Tetramethylenedisulfotetramine (TETS)	0.1	**99.5**	**3.0**	**82.0**	**2.4**	**103**	**1.9**	**101**	**5.9**	**86.0**	**4.7**	**111**	**12.6**
Phosphamidon	0.6	30.0	61.1	**75.5**	**3.1**	50.8	11.5	27.2	57.7	60.5	0.6	47.8	0.7
Disulfoton	0.5	47.7	35.6	64.2	4.4	62.1	2.3	48.6	45.3	62.2	3.2	61.6	5.2
Methyl parathion	0.5	17.6	22.7	**74.4**	**0.5**	18.3	16.4	30.0	21.3	**74.0**	**6.5**	32.8	2.4
Phencyclidine	0.5	**82.6**	**6.8**	ND		19.2	2.1	**70.8**	**9.0**	ND		20.8	7.7
Chlorpyrifos	0.5	54.1	41.0	**76.9**	**2.9**	**71.7**	**3.1**	53.2	48.1	**74.0**	**2.2**	68.0	10.6
Parathion	0.6	39.1	54.2	61.5	1.1	52.5	5.1	33.0	60.6	51.0	3.9	45.0	5.9
Chlorfenvinphos	0.6	57.7	46.2	**83.3**	**0.6**	**84.2**	**4.0**	51.8	46.9	**78.7**	**0.8**	**83.5**	**7.6**
Fenamiphos	0.75	44.8	51.2	64.6	2.7	67.3	3.2	31.9	61.1	47.1	2.8	57.1	8.4
Strychnine	1.25	**89.7**	**16.1**	ND		32.3	6.9	**110**	**8.0**	ND		50.3	2.2
Bromoform-d_1	2.5	27.6	66.7	48.2	0.8	31.2	12.8	27.6	72.5	44.4	9.0	28.8	33.3
Nitrobenzene-d_5	2.5	29.2	57.5	45.6	5.3	40.8	31.4	29.2	79.5	38.4	12.5	44.8	39.3
Nicotine-d_4	2.5	69.6	17.2	ND		16.0	100	64.0	10.0	Not Detected			
2-Fluorobiphenyl	2.5	32.6	52.8	51.6	6.2	44.4	30.6	31.2	71.8	43.2	7.4	48.4	41.3
Phencyclidine-d_5	2.5	64.6	8.0	ND		11.4	10.5	54.8	1.5	Not Detected		6.8	11.8
Terphenyl-d_{14}	2.5	36.8	56.5	49.8	7.2	49.0	13.9	35.6	60.7	46.4	10.3	50.8	23.6
Triphenyl Phosphate	1.25	54.8	59.9	84.0	7.6	80.4	14.9	50.4	66.7	76.8	8.3	82.4	21.4
Number of Target Analytes Within 70–130 % Recovery													
Recovery Target Range (70-130 %)		Solvent System 3		Solvent System 5		Solvent System 3		Solvent System 3		Solvent System 4		Solvent System 2	

Acronyms:
RPD – relative percent difference
ND – not detected

[1] 5 % TEA in ethyl acetate [2] 1:2:1 (v:v:v) acetone:DCM:ethyl acetate [3] Extraction 2 followed by Extraction 1, with extracts combined prior to analysis.

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