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Determination of Semivolatile Organic Compounds and Polycyclic Aromatic Hydrocarbons in Solids by Gas Chromatography/Mass Spectrometry

Techniques and Methods 5–B3

U.S. Department of the Interior
U.S. Geological Survey

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Chapter 3
Section B, Methods of the National Water Quality Laboratory
Book 5, Laboratory Analysis

Techniques and Methods 5–B3

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Conversion Factors

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (gm)	3.53×10^{-2}	ounce, avoirdupois
kilogram (kg)	3.53×10^{1}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	3.38×10^{1}	ounce, fluid
meter (m)	3.281	foot
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
microliter (µL)	3.38×10^{-5}	ounce, fluid
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter	3.38×10^{-2}	ounce, fluid
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Abbreviated water-quality units used in this report

%	percent
°C	degree Celsius
°C/min	degree Celsius per minute
µg/kg	microgram per kilogram (parts per billion)
µg/mL	microgram per milliliter
mL/min	milliliter per minute
ng/µL	nanogram per microliter
amu	atomic mass unit
AD	average deviation
ASE	accelerated solvent extraction
ASMB	Alberta Sweet Mix Blend
BHT	butylated hydroxy toluene
CAS	Chemical Abstracts Service
CASRN	Chemical Abstracts Service registry number
CCV	continuing calibration verification solution
DCM	dichloromethane
DEE	diethyl ether
DFTPP	decafluorotriphenylphosphine
E	estimated remark code
EI	electron impact
dPAHIS	perdeuterated polycyclic aromatic hydrocarbon internal standard
eV	electron volts
FS	full-scan ion monitoring
GC	gas chromatography (or gas chromatograph)

Abbreviated water-quality units used in this report—Continued

GC/MS	gas chromatography/mass spectrometry
ID	identification number
IDL	instrument detection limit
IPA	isopropyl alcohol
IS	internal standard
Lab ID	laboratory identification number
LRB	laboratory reagent blank
LRS	laboratory reagent spike
LT–MDL	long-term method detection level
MDL	method detection limit
MRL	minimum reporting level
MS	mass spectrometry (or mass spectrometer)
m/z	mass-to-charge ratio
n	number of samples
NAWQA	National Water-Quality Assessment Program
N-evap	nitrogen gas evaporator
NIST	National Institute of Standards and Technology
ND	not determined
nd	not detected
no.	number
NPE	number of points excluded
NR	not reported
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OC	organic carbon
PAH	polycyclic aromatic hydrocarbon
PLE	pressurized liquid extraction
PLEHW	pressurized liquid extraction with subcritical heated water
QA/QC	quality assurance/quality control
QA	quality assurance
QC	quality control
r^2	correlation coefficient
RR	retention reference
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
sed	sediment
SOX	Soxhlet
SPE	solid-phase extraction
SRM	Standard Reference Material
TPC	third-party check solution

Abbreviated water-quality units used in this report—Continued

USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
±	plus or minus
<	less than
v/v	volume-to-volume ratio

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Abstract

A method for the determination of 38 polycyclic aromatic hydrocarbons (PAHs) and semivolatile organic compounds in solid samples is described. Samples are extracted using a pressurized solvent extraction system. The compounds of interest are extracted from the solid sample twice at 13,800 kilopascals; first at 120 degrees Celsius using a water/isopropyl alcohol mixture (50:50, volume-to-volume ratio), and then the sample is extracted at 200 degrees Celsius using a water/isopropyl alcohol mixture (80:20, volume-to-volume ratio). The compounds are isolated using disposable solid-phase extraction (SPE) cartridges containing divinylbenzene-vinylpyrrolidone copolymer resin. The cartridges are dried with nitrogen gas, and then sorbed compounds are eluted from the SPE material using a dichloromethane/diethyl ether mixture (80:20, volume-to-volume ratio) and through a sodium sulfate/Florisil SPE cartridge to remove residual water and to further clean up the extract. The concentrated extract is solvent exchanged into ethyl acetate and the solvent volume reduced to 0.5 milliliter. Internal standard compounds are added prior to analysis by capillary-column gas chromatography/mass spectrometry.

Comparisons of PAH data for 28 sediment samples extracted by Soxhlet and the accelerated solvent extraction (ASE) method described in this report produced similar results. Extraction of PAH compounds from standard reference material using this method also compared favorably with Soxhlet extraction. The recoveries of PAHs less than molecular weight 202 (pyrene or fluoranthene) are higher by up to 20 percent using this ASE method, whereas the recoveries of PAHs greater than or equal to molecular weight 202 are equivalent.

This ASE method of sample extraction of solids has advantages over conventional Soxhlet extraction by increasing automation of the extraction process, reducing extraction time, and using less solvent. Extract cleanup also is greatly simplified because SPE replaces commonly used gel permeation chromatography.

The performance of the method (as expressed by mean recoveries and mean precision) was determined using Ottawa sand, a commercially available topsoil, and an environmental stream sediment, fortified at 1.5 and 15 micrograms per compound. Recoveries of PAH and semivolatile compounds in Ottawa sand samples fortified at 1.5 micrograms averaged 88 percent ± 9.4 percent relative standard deviation, and calculated initial method detection limits per compound averaged 14 micrograms per kilogram, assuming a 25-gram sample size. The recovery for 1,2,4-trichlorobenzene is less than 60 percent; thus, the concentration of this compound will always be reported as estimated with the "E" remark code.

The analysis of 25 alkylated PAH homolog groups also can be determined with this method with extra data analysis and review, but because of the lack of authentic reference standard compounds, these results are considered to be semiquantitative. The PAH homolog groups are quantitated using the response factor of a parent PAH method compound, if available. Precision data for the alkylated PAH homologs detected in a marine sediment standard reference material (SRM 1944) also are presented to document and demonstrate method capability.

Introduction

Pressurized liquid extraction (PLE) of solid samples offers advantages for automated sample preparation and reduced extraction time, and it uses less solvent compared to conventional Soxhlet extraction. Recently, Hawthorne, Trembley, and others (2000) used PLE with subcritical heated water (PLEHW) at moderate temperatures (about 100ºC) for extracting polar to moderately polar organic compounds from sediments. The solubility of solutes in subcritical water increases dramatically (about a threefold increase with every 25ºC increase), which is largely a function of the decreasing dielectric constant of water (Hawthorne, Trembley, and others, 2000). Using PLEHW above 250ºC, they demonstrated that the extraction of nonpolar high molecular weight compounds, such as polycyclic aromatic hydrocarbons (PAHs) from environmental solids, is feasible.

Currently (2006), PLEHW above 250ºC has been performed using home-made instruments because of the lack of commercially available options. The ASE™ 200 is a commercially available PLE instrument produced by Dionex (Sunnyvale, Calif., USA), and the process, which also has been termed "accelerated solvent extraction" (ASE), generally uses conventional organic solvents at about 100ºC. The ASE™ 200 has an upper operating limit of 200ºC, which is too low to effectively extract nonpolar high molecular weight organic compounds, such as PAHs having molecular weights of 202 or higher, using only subcritical water. However, the addition of an organic cosolvent generally has a similar effect on increasing compound solubility as increasing temperature (Curren and King, 2001). Thus, a cosolvent is required to effectively extract high molecular weight PAH compounds. Even though temperature and cosolvents greatly affect solubility, pressure has little effect on solubility (U.S. Environmental Protection Agency, 2000) but must be high enough to maintain water in the liquid state. However, the elevated ASE™ 200 system pressure substantially increases solvent permeation into the sediment matrix and thereby greatly improves extraction efficiency.

The PLEHW of sediments provides more selectivity for analytes than conventional Soxhlet extraction using organic solvents as supported by a dramatic reduction in the extraction of the bulk organic nonpolar matrix and noticeable improvement in the quality of the extract (Hawthorne, Grabanski, and others, 2000). It is possible to gain some degree of selectivity using solvent modified PLEHW by varying the modifier concentration. However, the use of cosolvents produces somewhat dirtier extracts than if pure water could be used, and generally requires cleanup steps prior to analysis. In a production laboratory, extract quality (low matrix background) is desirable to facilitate a reproducible instrument response and minimize gas chromatography/mass spectrometry (GC/MS) maintenance.

Environmental sediment samples generally require extensive extract clean-up steps to provide a low matrix background amenable to analysis and yet retain the compounds of interest. Even though ASE extracts are noticeably cleaner than methylene chloride Soxhlet extracts, it is still advantageous to perform additional extract cleanup. Coupling PLE and SPE allows for complex matrices to be extracted, matrix interferences minimized, and full-scan GC/MS analysis to be performed.

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic compounds composed of two or more fused conjugated benzene rings that often have attached alkyl substituent(s), referred to as alkylated PAHs. These compounds commonly are associated with fossil fuels or combustion of fossil fuels. There are many possible environmental sources for PAHs (Walker and others, 2005) and many are considered to be toxic and carcinogenic (Nauss, 1995), thus indicating that long-term exposure poses a risk to aquatic and terrestrial organisms. The natural processes and combustion of fossil fuels that form alkylated PAHs normally can favor specific homolog groups according to the predominant conditions. The analysis of alkylated PAH homolog groups often can help deduce possible mechanisms or conditions required for their formation.

Alkylated PAHs are categorized by the total number of alkyl carbon atoms present, so that a particular homolog group includes all the isomers with the same number of carbon atoms in the substituents attached to the parent PAH. Thus, various combinations of parent PAHs and alkyl substituents can occur. For example, the possible substitutions for a C_3-PAH could include propyl- (*n*-propyl-, isopropyl-), trimethyl-, or ethylmethyl. Alkylated PAH homolog series from C_1 through C_5 substituent(s) having the same parent PAH are of particular interest. For example, an alkylated PAH homolog series for naphthalene follows: C_1-alkylated naphthalene, C_2-alkylated naphthalene, and so forth up to C_5-alkylated naphthalene.

If the parent PAH also is an isomer of another parent PAH, their homolog groups are combined for reporting purposes. The parent PAH compounds phenanthrene/anthracene, fluoranthene/pyrene, benz[*a*]anthracene/chrysene, and benzo[*a*]pyrene/perylene are isomers, so their alkyl homolog groups are combined and reported together, for example, as C_3-alkylated phenanthrene/anthracene.

Isomers within a homolog group have common physical properties, such as the same molecular weight and fragmentation patterns in a mass spectrometer. The fragment ions produced for each isomer within the same homolog group typically are identical, although the abundance ratios can be different. This results in a complex chromatographic pattern of partially resolved isomers. The total response of the isomers for a particular alkyl substituted PAH group is summed to calculate the relative response factor (RRF) from the calibration curve of a related method compound. The RRF, although from a related compound, may or may not reflect each individual isomer's response. Wang and others (1994) found that by using the RRF produced from the parent naphthalene standard's calibration curve, a quantitation error of 30 to 150 percent was typical for alkylated naphthalene homolog groups. For this reason, and because authentic standards are not available for every alkylated PAH isomer, the total concentration of each homolog group is reported by the NWQL as estimated as indicated by an "E" remark code. Reference standard compounds for the alkylated PAH homolog groups are not routinely available, and thus, they are set apart from the method compounds, whose concentrations are calculated using authentic reference standards.

The U.S. Geological Survey (USGS) National Water Quality Labotatory (NWQL) developed a method to determine 38 semivolatile organic compounds and polycyclic aromatic hydrocarbons (table 1) and 25 alkylated PAH homolog groups (table 2) in solids. The alkylated PAH homologs are qualitatively identified and semiquantitated using the response factor and calibration curve from a closely related reference compound within its homolog series or the appropriate parent PAH. Reference mass spectral agreement and isotopic patterns are used to qualitatively identify the alkylated PAH homolog groups, which then can be reported semiquantitatively as the

summed C_1-, C_2-, C_3-, C_4-, C_5-alkylated homolog groups of the parent PAH(s).

Purpose and Scope

This report describes all aspects of a method, from sample preparation through calculation and reporting of results, to determine semivolatile organic compounds and polycyclic aromatic hydrocarbons in solids by GC/MS using ASE. The new ASE method, USGS NWQL analytical method O-5506-06, has two schedules. NWQL schedule 5506 contains 38 semivolatile organic compounds and PAHs (table 1), and schedule 5507 contains all compounds in schedule 5506 plus 25 alkylated PAH homolog groups (table 2). This new ASE method is applicable for determining semivolatile organic compounds and PAHs in 25 g of solid sample (a minimum of 0.5 g of material is required). If it is difficult to obtain a minimum amount of material (as can be the case for collecting suspended sediment on glass-fiber filter paper), filtration of larger amounts of water using Teflon filters (Mahler and Van Metre, 2003) might be preferred and likely will yield sufficient material, which can then be easily removed from Teflon filter paper and weighed prior to analysis. The method is rapid, efficient, and was developed potentially to replace Soxhlet sample-preparation techniques, such as NWQL method 2502 (Furlong and others, 1996) and method 5505 (Olson and others, 2004). Because of the inherent complexity of sediment matrices, the NWQL strongly suggests that any sampling and analysis plan must include matrix spike QC samples for appropriate interpretation of the data. The method is designed so that sample extracts also may be used to determine other compounds in sediments simply by reprocessing the GC/MS data, without requiring additional sample preparation or analysis.

Table 1. Semivolatile and polycyclic aromatic hydrocarbon compounds determined using this method (schedule 5506).

[NWIS, National Water Information System; CAS, Chemical Abstracts Service Registry Number]

Compound name	NWIS parameter code	CAS number[1]
Acenaphthene	64108	83-32-9
Acenaphthylene	64109	208-96-8
Anthracene	63180	120-12-7
Anthraquinone	63181	84-65-1
Benz[*a*]anthracene	63610	56-55-3
Benzo[*b*]fluoranthene	64111	205-99-2
Benzo[*k*]fluoranthene	64114	207-08-9
Benzo[*g,h,i*]perylene	64113	191-24-2
Benzo[*a*]pyrene	63183	50-32-8
Benzo[*e*]pyrene	64112	192-97-2
Bis(2-ethylhexyl) phthalate	63187	117-81-7
9H-Carbazole	63194	86-74-8
Chrysene	64115	218-01-9
Dibenz[*a,h*]anthracene	64116	53-70-3
Dibenzothiophene	64117	132-65-0
Diethyl phthalate	63202	84-66-2
1,2-Dimethylnaphthalene	64097	573-98-8
1,6-Dimethylnaphthalene	64099	575-43-9
2,6-Dimethylnaphthalene	63167	581-42-0
2-Ethylnaphthalene	64104	939-27-5
Fluoranthene	63208	206-44-0
9H-Fluorene	64107	86-73-7
Hexachlorobenzene	63631	118-74-1
Indeno[1,2,3-*cd*]pyrene	64118	193-39-5
2-Methylanthracene	64105	613-12-7
1-Methyl-9H-fluorene	64100	1730-37-6
1-Methylphenanthrene	64101	832-69-9
1-Methylpyrene	64102	2381-21-7
4,5-Methylenephenanthrene	64106	203-64-5
Naphthalene	63220	91-20-3
Pentachloroanisole	64119	1825-21-4
Pentachloronitrobenzene	63650	82-68-8
Perylene	64120	198-55-0
Phenanthrene	63224	85-01-8
Phenanthridine	64121	229-87-8
Pyrene	63227	129-00-0
1,2,4-Trichlorobenzene	64095	120-82-1
2,3,6-Trimethylnaphthalene	64103	829-26-5
2-Fluorobiphenyl (method surrogate)	90754	321-60-8
Nitrobenzene-d_5 (method surrogate)	90755	4165-60-0
Terphenyl-d_{14} (method surrogate)	90756	1718-51-0

[1]CAS Registry Number® (CASRN) is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services.

Table 2. Alkylated polycyclic aromatic hydrocarbon homolog groups determined using this method and reported with estimated concentrations (schedule 5507).

[NWIS, National Water Information System]

Compound name	NWIS parameter
C_1-alkylated naphthalene	64122
C_2-alkylated naphthalene	64123
C_3-alkylated naphthalene	64124
C_4-alkylated naphthalene	64125
C_5-alkylated naphthalene	64126
C_1-alkylated phenanthrene/anthracene	64127
C_2-alkylated phenanthrene/anthracene	64128
C_3-alkylated phenanthrene/anthracene	64129
C_4-alkylated phenanthrene/anthracene	64130
C_5-alkylated phenanthrene/anthracene	64131
C_1-alkylated fluoranthene/pyrene	64132
C_2-alkylated fluoranthene/pyrene	64133
C_3-alkylated fluoranthene/pyrene	64134
C_4-alkylated fluoranthene/pyrene	64135
C_5-alkylated fluoranthene/pyrene	64136
C_1-alkylated benz[a]anthracene/chrysene	64137
C_2-alkylated benz[a]anthracene/chrysene	64138
C_3-alkylated benz[a]anthracene/chrysene	64139
C_4-alkylated benz[a]anthracene/chrysene	64140
C_5-alkylated benz[a]anthracene/chrysene	64141
C_1-alkylated benzopyrene/perylene	64142
C_2-alkylated benzopyrene/perylene	64143
C_3-alkylated benzopyrene/perylene	64144
C_4-alkylated benzopyrene/perylene	64145
C_5-alkylated benzopyrene/perylene	64146

This method, when combined with other methods of the USGS for the determination of organic substances in water described previously (Wershaw and others, 1987; Fishman, 1993; Zaugg and others, 2002), can be used to help evaluate environmental fate and transport of more than 200 semivolatile organic compounds.

This report describes method performance for the quantitative determination of 38 semivolatile compounds (most of which are PAHs). The semiquantitation of 25 alkylated PAH homolog groups associated with five parent PAHs also is described, but results must be obtained by means of a separate request to the NWQL. Method performance (mean bias and variability) was determined using Ottawa sand, a commercially available topsoil, and an environmental stream sediment, fortified at 1.5 and 15 micrograms per compound. Method detection limits (MDLs) were determined according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1997) using 25-g samples. Although no method performance data are presented for the 25 alkylated PAH homolog groups because of the lack of reference standards, reproducibility data using standard reference material are provided.

Finally, the reproducibility of the method was evaluated by using 10 environmental sediment samples. Results for this method also were compared to the existing Soxhlet method at the NWQL using 28 environmental sediment samples.

This new ASE method is more efficient and cost effective for extracting PAH compounds from solids than the NWQL Soxhlet method (Olson and others, 2004). It officially was approved and implemented at the NWQL in 2006.

Analytical Method

Organic Compounds and Parameter Codes: Polycyclic aromatic hydrocarbons, bottom sediment, soils, and solids mass per mass, pressurized solvent extraction, solid-phase extraction, gas chromatography/mass spectrometry, O-5506-06 (see tables 1 and 2)

1. Scope and Application

This new ASE method is suitable for the determination of 38 semivolatile organic compounds and polycyclic aromatic hydrocarbons (NWQL schedule 5506) and 25 alkylated PAH homolog groups (NWQL schedule 5507) in solids by GC/MS. The method extracts 25 g of bed sediment (stream and lakebeds), soil, or aqueous suspended sediment (minimum of 0.5-g material) to determine the method compounds in microgram-per-kilogram concentrations. The method is applicable to compounds that are (1) efficiently extracted from sediment samples using high-pressure water/isopropyl alcohol, (2) partitioned from the resulting water/isopropyl alcohol extract onto the divinylbenzene-vinylpyrrolidone copolymer organic phase, (3) volatile and thermally stable for gas chromatography (GC), (4) sufficiently stable to chemical and thermal degradation, and (5) are amenable to electron impact (EI) mass spectrometry (MS) analysis.

The names of the semivolatile and PAH compounds determined using this method, the National Water Information System (NWIS) parameter code, and Chemical Abstracts Service (CAS) number for each compound are listed in table 1. The alkylated PAH homolog groups that also can be determined using this method (NWQL schedule 5507) and their NWIS parameter codes are listed in table 2.

2. Summary of Method

Soil or sediment samples are collected in the field by using the sample-collection techniques outlined by Radtke (1997), Shelton and Capel (1994), and Mahler and Van Metre (2003). Core samples are collected using field techniques outlined by Van Metre and others (2004), and suspended sediments are collected using field techniques outlined by Mahler and Van Metre (2003). Samples are preserved by freezing at −20ºC with a 1-year sample-holding time limit (prior to sample extraction) from the date of sample collection (U.S. Environmental Protection Agency, 1998). This sample-holding time limit is provisional until a validated method can be used to determine the effectiveness of the sample-freezing procedure.

Surrogate compounds are added to the thawed sample prior to extraction using water/isopropyl alcohol on a pressurized solvent extraction system. The method compounds are isolated from the water/isopropyl alcohol extracts using disposable, polypropylene solid-phase extraction (SPE) cartridges that contain a divinylbenzene-vinylpyrrolidone copolymer phase. The SPE cartridges are partially dried for 5 minutes. The compounds of interest are eluted from the SPE cartridge with a mixture of dichloromethane (DCM) and diethyl ether (DEE) at an 80:20, volume-per-volume ratio. The DCM–DEE eluent is passed through a sodium sulfate/Florisil SPE cartridge to dry and further clean up the extract. The extract volume is reduced to 500 µL, and internal standard compounds are added prior to compound determination by capillary-column GC/MS.

The instrumental analysis consists of GC separation of the compounds followed by mass spectrometric (MS) identification and quantitation. The compounds are separated by GC on a fused-silica capillary column using temperature programming to optimize compound resolution. The compounds are identified by retention time on the GC column and by comparison of mass spectra to reference spectra obtained from authentic standards. The internal standard method is used to quantitate the compounds using a multipoint calibration curve.

3. Safety Precautions and Waste Disposal

3.1 Conduct all steps in the method that require the use of organic solvents, such as cartridge cleaning, bottle rinsing, cartridge elution, and extract concentration, in a fume hood. It is necessary to wear eye protection, gloves, and protective clothing in the laboratory area and when handling reagents, solvents, or any corrosive materials. Typical laboratory disposable nitrile gloves do not provide adequate protection from DCM, so be careful to avoid contact with DCM.

3.2 The liquid waste stream produced during sample preparation is about 95-percent water (pH 7 buffer), with the rest of the volume made up of organic solvents. These solvents include isopropyl alcohol, DEE, acetone, and DCM. Collect the wastestream in thick-walled carboys, and dispose according to local regulations for chlorinated wastestreams. Dispose of solvents used to clean or rinse glassware, equipment, and cartridges in the appropriate waste containers. The solid-waste stream produced during sample analysis is composed of used SPE cartridges, extracted sediment or soil, and assorted glassware (sample vials and pipettes). Dispose of the solid-waste stream according to NWQL policy (Maloney, 2005, section 3.6.6, “Sample Disposal”).

4. Interferences

Samples, collection equipment, ASE extraction cells, or SPE cartridges that are handled improperly might become contaminated [sample-collection protocols and cleaning procedures for field equipment (Radtke, 1997) must be followed (phosphate-free detergent, followed by copious amounts of tap water, and then deionized water) as well as thorough cleaning of laboratory equipment]. Compounds that compete with or displace the compounds of interest from the SPE cartridge materials (divinylbenzene-vinylpyrrolidone copolymer phase and Florisil) might cause interferences or low method recovery, or both. In addition, coextracted dissolved organic material, such as humic and fulvic acids, might reduce the SPE extraction efficiency and recoveries of the compounds of interest.

Phthalates and preservatives [butylated hydroxy toluene (BHT) and related compounds] in the SPE cartridge material and housing can potentially contribute to low-concentration contamination. For this reason, the analyses of laboratory reagent blanks are particularly important to provide information about the presence of laboratory contaminants (most of which are not method compounds). A field blank (reagent sand heated to 450°C for 4 hours) can be used to help determine if sample collection and equipment-cleaning procedures are sufficient to prevent contamination. Comparison of the sample with the laboratory blanks is especially important if compounds other than method compounds are to be identified in full-scan spectra. If interferences are identified in laboratory blanks (particularly method compounds), cleaning or replacement of parts might be necessary to remove interference(s) as much as possible.

Compounds that have gas-chromatographic retention times and characteristic ions with mass-to-charge ratios identical to, or similar to, the compounds of interest might interfere. Again, because of the complex nature of sediment and soil samples, this background interference might occur frequently.

5. Apparatus and Equipment

The equipment required, along with specific models and sources that were used to develop this method, are listed as follows.

5.1 *Cleaning and elution module* — For cleaning and preparation of SPE cartridges, Supelco, Inc., Visiprep Solid-Phase Extraction Vacuum Manifold or equivalent.

5.2 *Pressurized extraction system* — Dionex ASE™ 200 Accelerated Solvent Extractor capable of maintaining a pressure of 13,800 kPa (2,000 lb/in^2), and 200°C or equivalent.

5.3 *Vacuum tubing* — 1.27-cm (0.5 in.) outside diameter (OD) by about 3 m (118 in.) length, for drawing sample extracts by vacuum through SPE cartridges.

5.4 *Extraction cells* — Dionex ASE 200 stainless steel 22-mL extraction cells and end caps with PEEK (PolyEtherEtherKetone).

5.5 *Carboy* — Nalgene™, high-density polyethylene, thick-walled, capable of sustaining 200 kPa (29 in. of mercury) mercury vacuum, 10-L volume, Van Waters & Rogers Scientific, Inc. (VWR), VWR part no. 36494-090 or equivalent.

5.6 *Bottle-top solvent dispensers* — Adjustable from 2 to 5 mL, 5 to 25 mL, and 10 to 100 mL; Brinkman Dispensette, VWR or equivalent.

5.7 *40-mL receivers (concentrator tubes)* — Receivers that fit inside the SPE manifold (13 cm in length and 2.5 cm wide), tapered for solvent exchange, Allen Scientific Glassblowers, Inc. or equivalent.

5.8 *Solvent reservoirs for the ASE* — Amber glass, 2,000 mL, Dionex.

5.9 *Vacuum pump* — Any adjustable vacuum pump with sufficient capacity to maintain a vacuum of 200 kPa (29 in. of mercury).

5.10 *Analytical balances* — Balance for accurately weighing samples, 1,000 ± 0.1 g. Balance for standard preparation accurately weighs 10 ± 0.01 mg.

5.11 *Nitrogen evaporative concentrator* — Organomation N-Evap Model 124 or equivalent.

5.12 *Micropipettes* — 50-, 100-, and 200-µL fixed-volume and variable-volume micropipettes with disposable glass bores; VWR Scientific or equivalent.

5.13 *Glass syringes and stepper syringe dispensers* — 10- to 500-µL volumes, Hamilton part no. 83701 or equivalent.

5.14 *Adapters and valves* — Teflon, connects SPE cartridge barrel to male Luer fitting.

5.15 *Positive pressure nitrogen manifold* — 12-port, Supelco.

5.16 *Freezer* — Upright, capable of storing 100 or more 1,000-mL widemouthed jars at −20°C.

5.17 ***Gas Chromatography/Mass Spectrometry Analysis***

5.17.1 *Gas chromatograph/mass spectrometer*— Agilent Technologies 5973B MSD coupled to an Agilent Technologies 6890 GC and equipped with an autosampler, a split/splitless injector, and a computer controller (ChemStation instrument control and Target data review software) or equivalent. The GC system must be suitable for use with capillary-column GC analysis (GC conditions, section 8.1.1). Full-scan mass-spectral data are acquired using this system (MS conditions, section 8.2.3).

5.17.2 *Syringe* — 10 µL; Hamilton Co. Model 80377 for GC autosampler.

6. Reagents and Consumable Materials

6.1 Consumable Materials

6.1.1 *Helium carrier gas* (99.999 percent) — Gas chromatography carrier gas.

6.1.2 *Glass fiber thimble* — Whatman glass fiber thimble, item number 2814199 or equivalent.

6.1.3 *Nitrogen gas* — For extract concentration, 99.999 percent pure.

6.1.4 *Collection vials* — Dionex 60 mL, clear or amber collection vials or equivalent.

6.1.5 *Florisil SPE cartridges* — 6-mL barrel, packed with 1 g of Florisil, Argonaut Technologies, catalog number 712-0100-C or equivalent.

6.1.6 *Column reservoir* — Teflon 150 mL, empty column, custom.

6.1.7 *Isolation SPE cartridges* — 20-mL barrel, packed with 1g of divinylbenzene-vinylpyrrolidone copolymer; Oasis HLB material, Waters Inc., catalog number 186000117 or equivalent.

6.1.8 *Glass sample collection bottles* — Amber, 118 to 472 mL (4 to16 ounces), wide mouth, heated to 450°C for 4 hours, fitted with Teflon-lined screw caps or equivalent.

6.1.9 *Solvents* — Dichloromethane (DCM), pentane, acetone, isopropyl alcohol, diethyl ether (DEE), ethyl acetate; Burdick and Jackson, pesticide grade or equivalent.

6.1.10 *Organic free water* — Prepared by Solution 2000 purification system or equivalent.

6.1.11 *Potassium phosphate buffer* — pH 7.0 (dilute 10 g dipotassium hydrogen phosphate and 7 g potassium dihydrogen phosphate in 1 L reagent water).

6.1.12 *Dichloromethane: diethyl ether mixture* — 80:20 (volume-per-volume ratio).

6.1.13 *Water: isopropyl alcohol mixtures* — 50:50 volume-per-volume, and 20:80 volume-per-volume ratio (v/v).

6.1.14 *Sodium sulfate* — Aldrich Chemical Co. reagent grade or equivalent, heated to 450°C for at least 4 hours.

6.1.15 *Reagent sand* — Ottawa reagent sand or equivalent, Fisher Scientific, Inc., for samples, set spikes, and reagent blanks, heated to 450°C for 4 hours.

6.1.16 *Glass fiber filter thimbles* — 79-mm by 19-mm inside diameter by 1.5-mm thickness, heated to 450°C for 4 hours, Whatman, Inc., part no. 2814199.

6.1.17 *Disposable glass capillaries* — To fit the 50- and 100-µL fixed-volume micropipettes, heated to 450°C for 4 hours.

6.1.18 *PAH surrogate solution* — Containing 2-fluorobiphenyl, nitrobenzene-d_5, and terphenyl-d_{14} obtained as a mixed solution at 1,000 µg/mL per component from Supelco, Inc. Dilute purchased intermediate concentration solutions to a final mixed solution concentration of 40 ng/µL in methanol. Other appropriate surrogate compounds and levels can be added or substituted after demonstrating acceptable method performance.

6.1.19 *PAH spike solution* — Contains the individual semivolatile compounds and PAH compounds listed in table 1. Four solutions were obtained from Absolute Standards, Inc., each containing a subset of the semivolatile compounds. Individual compounds in each solution are at concentrations of 2,000 ng/µL. Dilute an aliquot of each solution into a single final spike solution. The final selected concentration of each component is 150.0 ng/µL in ethyl acetate.

6.1.20 *Standard reference material (SRM)* — Any sediment or soil reference material available to test the method for recovery of some or all of the selected compounds may be an appropriate quality assurance material. SRM 1944 (a natural marine sediment) from the National Institute of Standards and Technology (NIST) certified for specific PAH compounds with additional uncertified values was used for this study. No single SRM currently (2006) available contains all of the compounds determined using this method.

6.1.21 *Perdeuterated PAH internal standard (dPAHIS) solution* — Contains the following: 1,4-dichlorobenzene-d_4, naphthalene-d_8, phenanthrene-d_{10}, perylene-d_{12}, acenaphthene-d_{10}, and chrysene-d_{12}, all at 100 ng/µL in ethyl acetate.

6.2 Gas Chromatograph/Mass Spectrometer

6.2.1 *Capillary GC column* — Fused-silica, 25 m long by 0.20-mm inside diameter, internally coated with a 5-percent diphenyl and 95-percent dimethyl polysiloxane stationary phase with a 0.33-µm film thickness; J&W Scientific columns from Agilent Technologies, Ultra 2™ or equivalent.

6.2.2 *GC injection-port glass liner* — Use any instrument-specific splitless or direct injection-port liner that provides acceptable peak shape and detector response.

6.2.3 *GC/MS PAH calibration solution* — Prepare working solutions of the entire suite of individual PAH compounds listed in table 1 at 0.1, 0.2, 0.5, 1.0, 2.5, 5.0, 8.0, 10.0, and 20.0 ng/µL per component in ethyl acetate using mixed stock solutions, including PAH surrogate solution (section 6.1.18). Obtain stock solutions from Absolute Standards, Inc., Supelco, Inc. or equivalent. Aliquots of the dPAHIS solution (section 6.1.21) are added to each of the calibration solutions to produce individual dPAHIS compound concentrations of 10 ng/µL.

6.2.4 *Alkylated PAH homolog retention time source material* — Almost any crude oil sample can be used to assign GC retention times for alkylated PAH homolog groups and create reference mass spectra. The original material used was a sediment sample from the Powell Stream near Knoxville, Tennessee. It was submitted to the NWQL for the National Water-Quality Assessment Program (Station 03532000; sampled on December 13, 1995). Optionally, use Alberta Sweet Mix Blend (ASMB). ASMB crude is the standard oil used for dispersant-treating tests in the Emergencies Science Division of Environment Canada (Wang and others, 1994).

6.2.5 *GC/MS quality control/quality assurance solutions* — Concentrations of selected PAHs in these solutions are measured at periodic intervals within the analytical sequence to monitor instrument performance.

6.2.6 *Continuing calibration verification (CCV) solution* — A CCV solution, having individual compound concentrations of 2.5 ng/µL, is analyzed between every 10 environmental and laboratory quality control (QC) samples, verifying that the initial quantitation calibration is maintained.

6.2.7 *Instrument detection limit (IDL) solution* — An IDL solution, having individual compound concentrations of 0.2 ng/µL, is analyzed (1) at the beginning of the GC/MS sequence, and (2) at the end of the analytical sequence. This analysis is used to verify instrument performance near the

lowest concentrations of the calibration curve during the entire analytical sequence.

6.2.8 *Mass spectrometer calibration* — A solution of decafluorotriphenylphosphine (DFTPP) is analyzed before the first CCV analysis. This analysis verifies the initial mass spectrometer axis calibration and the relative abundance of ions formed over the mass range of the analysis. Prepare this solution from commercially available neat standards, Ultra Scientific or equivalent.

6.2.9 *Third-party check (TPC)* — A solution of all compounds or selected compounds. The TPC is analyzed after the initial calibration sequence to independently verify the instrument calibration. This solution is prepared from a source other than that used for preparing calibration standards. Currently (2006), a 0.4 ng/µL standard (stock solution from Supelco, Inc.) is used.

7. Sample Preparation Procedure

Samples are grouped into sets of up to 10 environmental samples (9 samples if an SRM is included), a laboratory spike, a laboratory blank, and possibly an SRM.

7.1 Sample Preparation and Quality Control

Retrieve samples that can be stored up to 1 year in a freezer, and allow them to thaw completely in a refrigerator prior to extraction.

NOTE: Do not allow samples to remain thawed prior to extraction in a refrigerator for more than 48 hours.

Thoroughly homogenize each sample with a clean spatula or scoopula. If total carbon or organic carbon has been requested, remove about a 20-g wet-weight aliquot of sample and place in an appropriate container (Wershaw and others, 1987). Retrieve all paperwork and sample bottles from their storage areas. Check that all paperwork has corresponding sediment sample, and vice versa.

7.1.1 The ASE 22-mL stainless-steel extraction cells are used for this procedure. Obtain 13 cells for up to nine environmental samples, spike, blank, SRM, and an empty cell for instrument cleaning. Fill the cleaning cell with sand because the extract will not need to be analyzed.

7.1.2 Use a clean razor blade to cut a pre-baked, glass fiber extraction thimble (79-mm by 19-mm inside diameter by 1.5-mm thickness) lengthwise and slightly overlap the edges to fit inside a 22-mL extraction cell. Cut off the excess thimble (about 10 mm). Place thimbles in all but the instrument cleaning cell.

7.1.3 Record the cell plus thimble weight as the pre-extraction weight.

7.1.4 Fill the laboratory reagent blank and laboratory reagent spike cells with sand. Add about 5 to 10 mL of sand to the bottom of the SRM cell. Place 1 to 2 g (dry weight) of SRM 1944 into an extraction cell with thimble and finish filling the cell with sand. Load wet sediment samples into cells while tapping gently to ensure cell is full.

NOTE: If the sample is rich in organic content (sooty or obviously petroleum based, or organic carbon content has previously been determined by analysis to be greater than about 5 percent), only add about 1 g of sample (dry weight) sandwiched between sand. This is the same procedure used for loading the cell containing the SRM.

7.1.5 Bring method PAH surrogate solution (section 6.1.18) and spike solutions to room temperature. Vortex each for 10 seconds to ensure homogeneity. Dispense 100 µL of the surrogate mixture into each sample, blank, and spike using a 100-µL stepper-syringe. Dispense 100 µL of the spike mixture into the spike sample with a separate micropipette.

7.1.6 Label two 60-mL collection vials for each sample by marking the laboratory ID "ID – 120" for the 120°C extract on one vial and "ID – 200" for the 200°C extract on the other vial.

7.1.7 Add 3 mL of pentane to the "ID – 200" vials.

7.1.8 Place the extraction cells in the following order on the ASE cell tray (upper tray): cleaning cell (filled with sand), spike, blank, up to nine environmental samples, and SRM.

7.1.9 Place the 60-mL extract collection vials (labeled as in section 7.1.6) on the ASE vial collection tray (lower tray). Place the vial for collecting the first ASE cleaning extract in the first tray position. Then place 12 appropriately labeled vials for collecting the 120°C ASE extracts in the next 12 tray positions. Then place 12 more appropriately labeled (in the same order) collection vials in tray positions 13 through 25 for collecting the 200°C extracts. Place an additional empty vial for collecting the ASE cleaning extract in the final position.

7.2 ASE Extraction

7.2.1 Load the Dionex AutoASE sequence (schedule) "pah_sediment.sched" for a full set of samples (cleaning cell, spike, blank, and up to 10 samples; see table 3). If the set contains less than 10 environmental samples, edit the schedule to remove extraction cells as needed.

The procedure uses two ASE extraction methods (sed120.met and sed200.met, see table 4) so that each sample is first extracted at 120ºC with isopropyl alcohol (IPA)/water (50:50, v/v) and at 200ºC with IPA/water (80:20, v/v). The method for the extraction at 200ºC is identical to the method for the 120ºC extraction listed in table 4 except the tempera-

ture is set at 200ºC and a different solvent bottle is used, which contains IPA/water (80:20, v/v).

NOTE: Ensure that two ASE solvent bottles contain sufficient IPA/water mixture to complete the extraction (allow about 1 L for a full set of 10 samples).

7.2.3 After extraction (allow about 1.5 hours for each sample), visually verify that there is between 40 to 50 mL in the two 60-mL collection vials for each sample, and check the computer-generated ASE sample log to determine if any potential problems (leaks, plugging, or mechanical failures) were reported that would require the sample extraction to be repeated if a sufficient amount of sample is available.

NOTE: It is generally necessary to empty the ASE 60-mL rinse collection vials at the end of the day if the extraction is scheduled to continue overnight.

7.2.4 After checking that sample extract volumes are acceptable, weigh the cell plus thimble plus dry sample. This weight minus the pre-extraction weight is the dry sample weight because the final ASE extraction is at 200°C and is followed by a 150-second purge using nitrogen gas.

NOTE: When the instrument is performing optimally, the sample is dry (as verified by comparing weights to a drying balance). However, if the thimble is damp or appears to contain moisture, it indicates that there was a problem during the extraction (leak or incomplete extraction), and the extraction must be repeated.

Table 3. An example of an accelerated solvent extraction (ASE) schedule for 13 cells.

[mL, milliliters; ID, identification; SRM, standard reference material]

Vial	Cell	Method file	Rinse (on/off)	Rinse bottle	Rinse volume (mL)	Sample ID
1	1	Sed120.met	On	B	5	Cleaning cell
2	2	Sed120.met	On	B	5	Set spike
3	3	Sed120.met	On	B	5	Set blank
4	4	Sed120.met	On	B	5	Sample 1
5	5	Sed120.met	On	B	5	Sample 2
6	6	Sed120.met	On	B	5	Sample 3
7	7	Sed120.met	On	B	5	Sample 4
8	8	Sed120.met	On	B	5	Sample 5
9	9	Sed120.met	On	B	5	Sample 6
10	10	Sed120.met	On	B	5	Sample 7
11	11	Sed120.met	On	B	5	Sample 8
12	12	Sed120.met	On	B	5	Sample 9
13	13	Sed120.met	On	B	5	Sample 10 (SRM)
14	2	Sed200.met	On	B	5	Set spike
15	3	Sed200.met	On	B	5	Set blank
16	4	Sed200.met	On	B	5	Sample 1
17	5	Sed200.met	On	B	5	Sample 2
18	6	Sed200.met	On	B	5	Sample 3
19	7	Sed200.met	On	B	5	Sample 4
20	8	Sed200.met	On	B	5	Sample 5
21	9	Sed200.met	On	B	5	Sample 6
22	10	Sed200.met	On	B	5	Sample 7
23	11	Sed200.met	On	B	5	Sample 8
24	12	Sed200.met	On	B	5	Sample 9
25	13	Sed200.met	On	B	5	Sample 10 (SRM)
26	1	Sed200.met	On	B	5	Cleaning cell

Table 4. An example of an accelerated solvent extraction (ASE) method for a 120°C extraction.

[lb/in^2, pounds per square inch; kPa, kilopascal; %, percent; IPA, isopropyl alcohol]

Extraction condition	Parameter set point
Pressure	2,000 lb/in^2 (13,800 kPa)
Temperature	120°C
Preheat time	0 minutes
Purge during preheat	Off
Heat time	6 minutes
Static time	10 minutes
Flush volume	50%
Purge time	150 seconds
Static cycles	3
Solvent A	IPA/water (50:50; volume per volume)
Solvent B	0%
Solvent C	0%
Solvent D	0%

7.2.5 Refrigerate the ASE extracts (up to 5 days) prior to SPE isolation and cleanup.

7.3 SPE Cartridge Cleaning

7.3.1 Place Teflon adapters on top of the 20-mL Oasis SPE cartridges obtained from a vacuum-sealed bag received from the manufacturer. Insert the tip of a 150-mL reservoir (polypropylene or Teflon) into a Teflon stopcock. Insert the reservoir with stopcock in the adapter above the Oasis SPE cartridge, and place the assembly on the SPE cleaning and elution module as shown in figure 1.

NOTE: Ensure waste carboy has sufficient empty volume to accommodate about 1 L.

7.3.2 Add 20 mL (the SPE barrel volume) of the elution solvent (DCM–DEE, 80:20 v/v) to rinse the Oasis SPE cartridges and reservoirs. Allow the solvent to drain by gravity until the phase is completely saturated. Then open the Luer-Lok flow-control valves on the vacuum manifold by turning them counterclockwise to allow the remaining solvent to be removed from the Oasis SPE cartridges by vacuum.

7.3.3 Rinse the cartridges with an additional 10 mL of DCM–DEE and allow 5 to 10 minutes for any residual solvent to be removed by vacuum (preferably just until visibly dry).

NOTE: Vacuum applied to the SPE cartridges must not exceed 10 minutes because laboratory air contains low concentrations of some of the method compounds that might introduce process contamination.

7.3.4 Attach Florisil SPE cartridges to the cleaning and elution module. Add 10 mL (the SPE barrel volume) of acetone to rinse the Florisil SPE cartridges. Allow the solvent to drain by gravity until the phase is completely saturated. Then, open the Luer-Lok flow-control valves on the vacuum manifold by turning them counterclockwise to allow the remaining solvent to be removed from the cartridges by vacuum. Rinse the cartridges with an additional 10 mL of acetone, and allow about 10 minutes for the vacuum to remove residual solvent (preferably just until visibly dry; see previous note).

7.4 SPE Extraction

Set up the SPE extraction module in preparation for extracting the ASE extracts according to figure 1.

7.4.1 Place lab ID labels matching the 60-mL collection vials on each corresponding cleaned reservoir and Oasis SPE cartridge assembly and ensure Teflon stopcocks are in the closed position (see fig. 1).

7.4.2 Add the 200°C ASE extract from the 60-mL collection vial to each corresponding reservoir. Add 50 mL of the phosphate buffer solution to the empty ASE collection vial. Cap and shake collection vial for 5 to 10 seconds. Add this rinse to each corresponding reservoir. Repeat the phosphate buffer rinse step one additional time, adding it to the appropriate reservoir. Open the Teflon stopcock between the Oasis SPE cartridge and the reservoir (fig. 1) to allow gravity to draw the ASE extract and buffer rinses through the Oasis SPE cartridges. A small vacuum might have to be applied to start flow through the SPE cartridge. Obtain the desired extraction flow-rate range (between 10 to 50 mL/min) by opening the vacuum manifold Luer-Lok flow-control valves. A small amount of vacuum might need to be applied once or twice during sample extraction.

7.4.3 Repeat this process (section 7.4.2) with the 120°C ASE extract.

NOTE: Reasonable extraction times range from 10 to 20 minutes for each of the 120°C and 200°C ASE extracts.

7.5 SPE Cartridge Drying

Disconnect the SPE cartridges from the reservoir assembly and dry them (but not completely dry) for 5 to 10 minutes on a positive pressure nitrogen manifold.

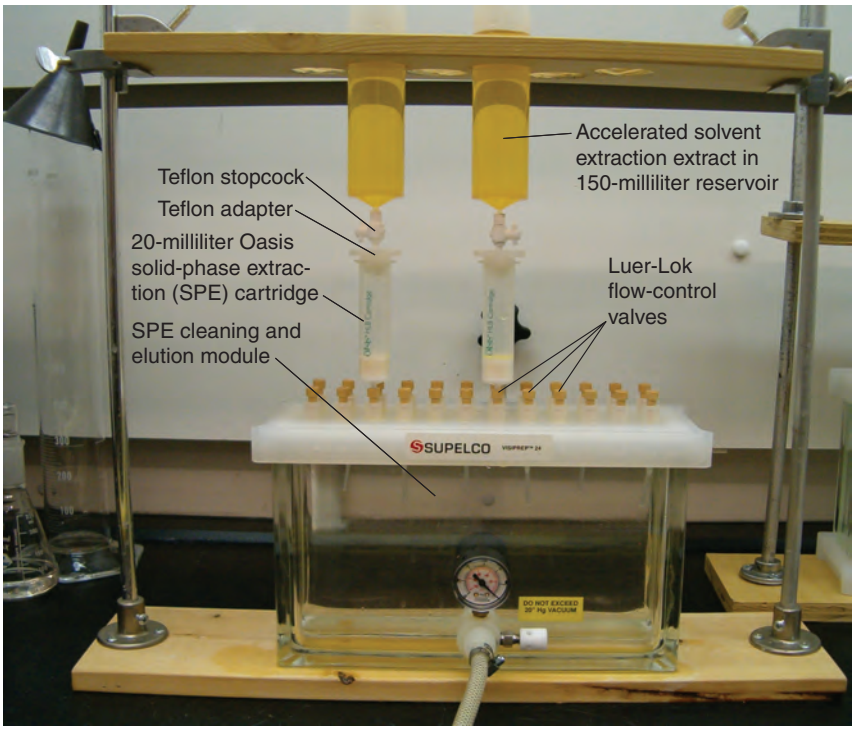

Figure 1. Solid-phase extraction assembly for accelerated solvent extracts for use in determining semivolatile organic compounds and polycyclic aromatic hydrocarbons.

NOTE: As the SPE phase dries, a lighter color can be observed at the wet/dry boundary layer. It is not necessary or desirable for the cartridge to dry completely. After the drying step, proceed immediately to the SPE elution step. The extract is not allowed to be held on the SPE cartridge for this method.

7.6 SPE Cartridge Elution

Set up the SPE extraction module in preparation for cartridge elution according to figure 2.

7.6.1 Place a 40-mL SPE receiver for each sample in the SPE cleaning and elution module.

7.6.2 Attach the corresponding 150-mL reservoirs (polypropylene or Teflon) to Oasis SPE cartridges with a Teflon adapter.

7.6.3 Add ~ 2.5 g baked sodium sulfate to the cleaned Florisil cartridge.

7.6.4 Attach the Florisil cartridge (with sodium sulfate) to the bottom of the dried Oasis SPE cartridge. Place this cartridge assembly on the SPE elution module directly above the 40-mL receiver (fig. 2).

7.6.5 Add 5 mL of the DCM–DEE elution mixture to the 60-mL ASE collection vial (not shown). Cap and shake collection vial for 5 to 10 seconds by rotating to ensure all the glass surfaces have been rinsed. Add this rinse to the corresponding reservoir.

7.6.6 Add 10 mL of DCM–DEE to the 150-mL solvent reservoir and elute the Oasis SPE cartridge by gravity into the 40-mL receiver. Add another 10 mL of the DCM–DEE and allow gravity to draw the elution solvent into the 40-mL receivers, making sure to thoroughly rinse the sides of the reservoir (fig. 2). Repeat this process one more time with 5 mL of DCM–DEE.

7.6.7 Using a large syringe or small amount of vacuum, force all residual DCM–DEE from the two SPE cartridges. The addition of 30 mL of DCM–DEE will result in the collection of about 25 mL of elution solvent. About 5 mL of the DCM–DEE will be retained on the SPE beds.

7.6.8 Transfer label from cartridge to receiver and cap receiver. Store capped receivers at 4°C or less, or proceed to the concentration step.

7.7 Concentration of Extract and Transfer to Vial

7.7.1 Using a nitrogen gas evaporator (N-evap), slowly evaporate the sample sxtracts to about 4 mL and add 20 µL of the dPAHIS internal standard solution (section 6.1.21).

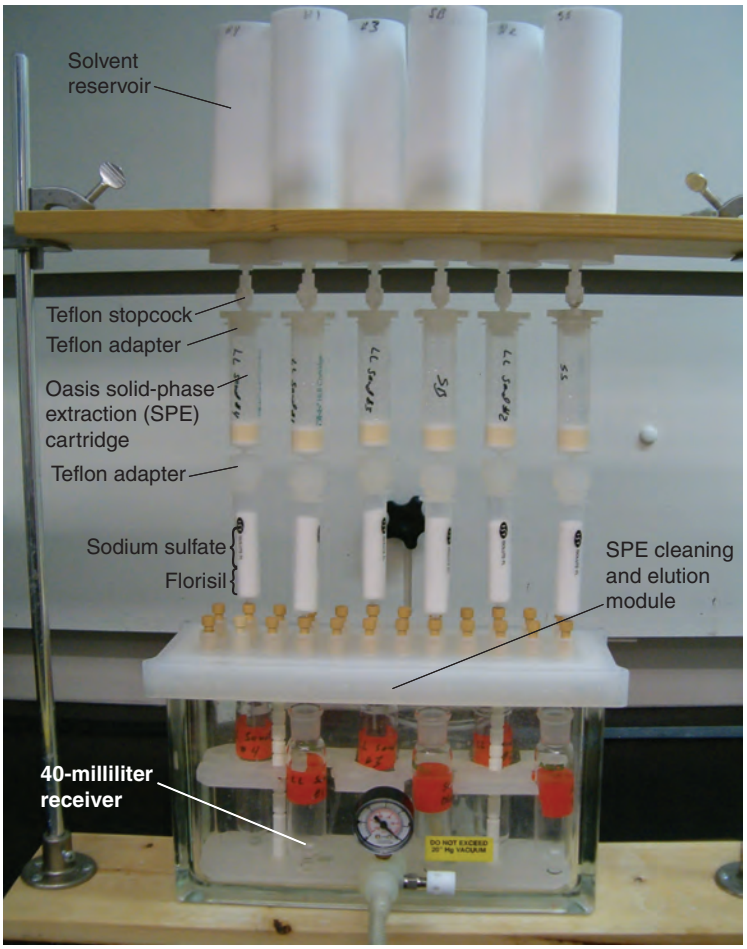

Figure 2. Solid-phase elution module assembly used in the analytical method for determining semivolatile organic compounds and polycyclic aromatic hydrocarbons.

7.7.2 Continue evaporation of the extract until the volume is reduced to 500 µL.

7.7.3 Vortex each receiver for 10 to 20 seconds, rinsing the extract as far up the sides of the receiver as possible.

7.7.4 Transfer the extract with a baked Pasteur pipette into a labeled, amber GC autosample vial. Cap vials with Teflon-lined screw caps and store at 4°C or less for up to 45 days until analysis by GC/MS.

8. Instrumental Analysis

Samples are analyzed by GC/MS using full-scan MS analysis. A capillary-column GC system is equipped with an autosampler and a split/splitless injection port operated in the splitless injection mode and is directly connected to a quadrupole mass spectrometer. A computer system is used to allow complete control of the autosampler, GC and MS operations, and to acquire, process, and store signals from the GC/MS. Complete details of GC/MS operation are beyond the scope of this report. Instead, the suggested GC/MS operating conditions and sample sequence used in this method are outlined in the following procedure. Users should consult the appropriate instrument manuals for additional details regarding general GC/MS system operation. Note that the GC/MS operating conditions are provided for guidance only. Different GC/MS systems will require different operating conditions to achieve acceptable instrument performance. Suggested GC/MS operating conditions to achieve acceptable instrument performance are indicated below.

8.1 Instrumental Conditions and Setup

8.1.1 *Suggested GC-operating conditions for PAHs.* Set initial oven temperature at 65°C (hold for 3 minutes), then ramp at 6°C/min to 320°C, and hold for 20 minutes to allow for sufficient column bake-out; injection port temperature, 285°C with electronic pressure control set for constant flow of helium gas of 0.7 mL/min, 1 µL, splitless injection.

8.1.2 *Determine compound retention times.* Following GC/MS setup, establish compound retention times with calibration standards. Peak identifications, retention times, mass-to-charge ratios, and abundances relative to the quantitation ion for PAHs, using the GC operating conditions described in section 8.1.1 with a J&W Scientific Ultra 2™ column from Agilent Technologies, are listed in table 5 for method compounds and homolog groups. The relative ion abundances are not provided for the alkylated PAH homolog groups because the ratios are different among isomers. The determination of retention times for the alkylated PAH homolog groups is described in section 8.1.3.

NOTE: Because of differences in GC columns, even from the same manufacturer, and operational characteristics between instruments, the elution profiles will vary. Therefore, it is critical to verify instrument-specific compound retention times. Use single-component standards to verify retention times and mass spectra of closely eluting or coeluting compounds. Verify retention times following any GC maintenance procedures applied to the capillary columns to improve chromatography.

Table 5. Retention times, relative retention times, gas chromatography/mass spectrometry quantitation ions, confirmation ions, and percent relative abundance of confirmation ions for individual method compounds and alkylated polycyclic aromatic hydrocarbon (PAH) homolog groups.

[Compounds are reported in chromatographic elution order; min, minute; compounds followed by **RR** are method internal standards and are followed by a designation (**RR-1**, **RR-2**…), which indicates their order as a retention reference; m/z, mass-to-charge ratio]

Compound (retention time order)	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion (m/z)	Confirmation ions (m/z)	Percent relative to quantitation ion abundance
1,4-Dichlorobenzene-d_4 **(RR-1)**	6.8	1.000	1	152	150, 115	150, 60
Nitrobenzene-d_5 (surrogate)	8.6	1.265	1	128	82, 98	280, 40
1,2,4-Trichlorobenzene	11.0	1.554	1	180	182, 185	95, 25
Naphthalene-d_8 **(RR-2)**	11.0	1.000	2	136	none	
Naphthalene	11.1	1.009	2	128	129, 102	10, 10
C_1-alkylated naphthalene[1]	14.0	1.272	2	141	142, 127	variable
2-Fluorobiphenyl (surrogate)	15.3	1.391	2	172	171, 85	30, 10
2-Ethylnaphthalene	15.9	1.445	2	141	156, 115	45, 25
2,6-Dimethylnaphthalene	16.1	1.464	2	141	156, 115	140, 25
C_2-alkylated naphthalene[1]	16.1	1.464	2	141	156, 115	variable
1,6-Dimethylnaphthalene	16.5	1.500	2	141	156, 115	125, 25
Acenapthylene	16.6	.937	3	152	151, 76	20, 30
1,2-Dimethylnaphthalene	17.2	1.564	2	151	156, 115	70, 25
Acenaphthene-d_{10} **(RR-3)**	17.7	1.000	3	162	164, 80	100, 40
Acenaphthene	17.8	1.006	3	153	154, 152	95, 50
2,3,6-Trimethylnaphthalene	19.1	1.079	3	170	155, 153	100, 25
C_3-alkylated naphthalene[1]	19.5	1.102	3	170	155, 153	variable
Diethyl phthalate	19.6	1.122	3	149	177, 176	25, 10
9H-Fluorene	19.8	1.186	3	166	165, 82	95, 15
1-Methyl-9H-fluorene	22.0	1.243	3	180	165, 89	130, 30
Hexachlorobenzene	22.2	1.244	3	284	286, 142	80, 40
Pentachloroanisole	22.4	1.254	3	265	267, 280	65, 90
Dibenzothiophene	23.0	1.284	3	184	139, 92[2]	15, 5
C_4-alkylated naphthalene[1]	23.0	1.286	3	184	169, 141	variable
Pentachloronitrobenzene	23.3	0.998	4	237	214, 142	70, 80
Phenanthrene-d_{10} **(RR-4)**	23.3	1.000	4	188	189, 94	15, 20

Table 5. Retention times, relative retention times, gas chromatography/mass spectrometry quantitation ions, confirmation ions, and percent relative abundance of confirmation ions for individual method compounds and alkylated polycyclic aromatic hydrocarbon (PAH) homolog groups.—Continued

[Compounds are reported in chromatographic elution order; min, minute; compounds followed by **RR** are method internal standards and are followed by a designation (**RR-1**, **RR-2**…), which indicates their order as a retention reference; m/z, mass-to-charge ratio]

Compound (retention time order)	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion (m/z)	Confirmation ions (m/z)	Percent relative to quantitation ion abundance
Phenanthrene	23.4	1.004	4	178	176, 89	20, 15
Anthracene	23.6	1.013	4	178	176, 89	20, 15
C_5-alkylated naphthalene[1]	23.9	1.026	4	198	[1]83	variable
Phenanthridine	24.2	1.034	4	179	178, 151	20, 15
9H-Carbazole	24.4	1.043	4	167	168, 139	15, 10
2-Methylanthracene	25.6	1.100	4	192	191, 96	45, 10
4,5-Methylenephenanthrene	25.7	1.103	4	190	189, 94	90, 10
C_1-alkylated phenanthrene/anthracene[1]	25.8	1.107	4	192	191, 95	variable
Anthraquinone	26.7	1.136	4	208	180, 152	100, 85
C_2-alkylated phenanthrene/anthracene[1]	28.0	1.202	4	206	191	variable
Fluoranthene	28.1	1.206	4	202	101, 203	20, 15
Pyrene	28.8	1.236	4	202	101, 203	20, 15
1-Methylphenanthrene	25.9	1.112	4	192	191, 94[2]	55, 5
C_3-alkylated phenanthrene/anthracene[1]	29.6	1.270	4	220	[2]05	variable
Terphenyl-d_{14} (surrogate)	29.9	1.238	4	244	122, 245	25, 20
C_4-alkylated phenanthrene/anthracene[1]	31.0	1.330	4	234	219	variable
C_1-alkylated fluoranthene/pyrene[1]	31.0	1.330	4	216	215, 108	variable
1-Methylpyrene	31.1	1.335	4	216	215, 108	70, 20
C_2-alkylated fluoranthene/pyrene[1]	32.0	1.373	4	230	215	variable
Benz[*a*]anthracene	33.4	.994	5	228	229, 226	20, 25
Chrysene-d_{12} **(RR-5)**	33.6	1.000	5	240	120, 241	25, 20
Chrysene	33.7	1.003	5	228	229, 114	20, 20
Bis(2-ethylhexyl) phthalate	34.5	1.029	5	149	167, 279	35, 10
C_3-alkylated fluoranthene/pyrene[1]	34.6	1.030	5	244	229	variable
C_1-alkylated benz[*a*]anthracene/ chrysene[1]	35.8	1.065	5	242	241, 227	variable
C_5-alkylated phenanthrene/anthracene[1]	36.4	1.083	5	248	233	variable
C_4-alkylated fluoranthene/pyrene[1]	36.9	.951	6	258	243	variable
C_2-alkylated benz[*a*]anthracene/ chrysene[1]	37.3	1.110	5	256	241	variable
Benzo[*b*]fluoranthene	37.5	.966	6	252	253, 126	20, 25
Benzo[*k*]fluoranthene	37.6	0.969	6	252	253, 126	20, 25
Benzo[*e*]pyrene	38.4	.990	6	252	250, 126	30, 20
Benzo[*a*]pyrene	38.6	.995	6	252	250, 126	25, 20
Perylene-d_{12} **(RR-6)**	38.8	1.000	6	264	260, 132	25, 30
Perylene	38.9	1.003	6	252	250, 126	25, 25
C_1-alkylated benzopyrene/perylene[1]	39.8	1.026	6	266	251	variable
C_5-alkylated fluoranthene/pyrene[1]	39.8	1.026	6	272	257	variable

Table 5. Retention times, relative retention times, gas chromatography/mass spectrometry quantitation ions, confirmation ions, and percent relative abundance of confirmation ions for individual method compounds and alkylated polycyclic aromatic hydrocarbon (PAH) homolog groups.—Continued

[Compounds are reported in chromatographic elution order; min, minute; compounds followed by **RR** are method internal standards and are followed by a designation (**RR-1**, **RR-2**…), which indicates their order as a retention reference; m/z, mass-to-charge ratio]

Compound (retention time order)	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion (m/z)	Confirmation ions (m/z)	Percent relative to quantitation ion abundance
C_3-alkylated benz[*a*]anthracene/ chrysene[1]	41.1	1.059	6	270	255	variable
C_2-alkylated benzopyrene/perylene[1]	42.0	1.082	6	280	265	variable
Indeno[1,2,3-*cd*]pyrene	42.0	1.082	6	276	138, 137	30, 20
C_4-alkylated benz[*a*]anthracene/ chrysene[1]	42.1	1.085	6	284	269	variable
Dibenz[*a,h*]anthracene	42.2	1.088	6	278	139, 279	30, 25
Benzo[*g,h,i*]perylene	42.7	1.101	6	276	138, 274	40, 20
C_3-alkylated benzopyrene/perylene[1]	43.2	1.113	6	294	279	variable
C_5-alkylated benz[*a*]anthracene/ chrysene[1]	44.8	1.155	6	298	283	variable
C_4-alkylated benzopyrene/perylene[1]	45.0	1.160	6	308	293	variable
C_5-alkylated benzopyrene/perylene[1]	45.4	1.170	6	322	307	variable

[1]Analysis of PAH homolog groups can be obtained by a separate request to the U.S. Geological Survey National Water Quality Laboratory.

[2] The ion abundance relative to the quantitation ion is less than 10 percent; and therefore the ion is used as a monitoring ion and not as a confirmation ion.

8.1.3 *Determine retention-time intervals for each alkylated PAH homolog group.* Because authentic standards are not available for most of the substituted PAHs, retention times for these groups are determined by using an alkylated PAH homolog standard reference material (section 6.2.4). The reference sample is analyzed at about 20 ng/µL. Extracted ion chromatograms are created using the quantitation and confirmation ions for each alkylated PAH homolog group. The retention times are determined for the first and last isomers for each alkylated PAH homolog group. Quantitation of the alkylated PAH homolog groups is explained in section 9.2.

8.1.4 Prior to each analytical sequence, assess GC/MS performance by examining peak shape, efficiency of separation for closely eluting compound pairs, and response-factor variation determined for the compounds. CCVs bracket every 10 samples and are the primary indicator of changes in instrument performance during an analytical sequence.

8.2 GC/MS Tuning and Calibration

8.2.1 Tune the GC/MS prior to analysis or after any instrument maintenance using automated or other tuning procedures as prescribed by the system manufacturer. Prior to any analysis, verify the GC/MS tune and mass axis calibration by injecting a solution of decafluorotriphenylphosphine (DFTPP). The relative mass fragment abundance and mass assignments need to be within the range of values specified by the U.S. Environmental Protection Agency (2004b) for method 8270c.

8.2.2 Calibration of the instrument adheres to all aspects set forth in the NWQL's Quality Management System (Maloney, 2005), as do all sections of this method that involve quality assurance (QA) and quality control (QC). Analyze appropriate calibration solutions (section 6.2.3, a 5-point calibration curve is required) and determine a best-fit calibration curve for each compound using the curve-fitting routines provided by the instrument manufacturer. Carefully inspect the curves to ensure a correlation coefficient (r^2) of 0.995 or greater and verify that the lowest calibration standard level meets the QA criteria outlined below. Calibration curve-fitting routines based on the relative response factor (RRF) are used to obtain a calibration curve for each compound. A linear calibration curve is suggested for most of the method compounds; however, other curve-fitting routines (quadratic curves and power curves) might be used for polar compounds. The same curve-fitting routine that demonstrates the "best fit" to the data for each compound must always be used in the method.

Check the calibration using the third-party check solution (section 6.2.9), which should result in ± 25 percent of expected concentrations. If these QA criteria cannot be met, the source of the problem must be identified and corrected before a new calibration curve is used. If necessary, perform instrument maintenance or prepare new calibration standards

or a new TPC solution. After calibration results are determined to be acceptable, assemble samples, set QC samples, mass spectrometer verification solutions, continuing calibration verification solutions, and instrument detection limit solutions into an analytical sequence, and analyze them under GC/MS conditions identical to those used for the calibration. A typical analytical sequence is listed in table 6. The quality (optical clarity) of the sample extracts and number of samples that need to be analyzed in the sequence might affect the CCV frequency. Use an automated sample injection system to inject 1 µL of the appropriate sample extract or standard solution into the GC/MS.

Table 6. Gas chromatography/mass spectrometry analytical sequence suggested for use with this method.

[PAH, polycyclic aromatic hydrocarbon]

Analytical sequence	Sample type
1	Decafluorotriphenylphosphine mass spectrometer calibration solution
2	Instrument blank (injection of pure solvent)
3	Instrument detection level (IDL) solution
4	Continuing calibration verification (CCV) solution
5	Set PAH spike
6	Set blank
7	Sample 1
8	Sample 2
9	Sample 3
10	Sample 4
11	Sample 5
12	Sample 6
13	Sample 7
14	Sample 8
15	CCV
16	Sample 9
17	Sample 10
18	Sample 11
19	Sample 12
20	Sample 13
21	Set quality-control reference material sample
22	CCV
23	IDL

8.2.3 The MS source temperature is kept at 200°C and the GC/MS transfer line at 290°C. Data acquisition conditions for full scan range from 45 to 450 amu, scanned at a rate of at least 2 scans per second (5–10 scans per peak), with the filament operated at 70 eV. Store all data electronically for subsequent qualitative identification, quantitation, and archiving.

8.3 Qualitative Identification

8.3.1 *Qualitative criteria and single-component identification.* The criteria outlined in this section apply for reporting compounds for all sample results in blanks, spikes, or environmental samples. Two criteria are evaluated when establishing a positive compound identification: expected relative retention time and comparative agreement of the mass spectrum.

The relative retention time (RRT) is the retention time of the compound normalized to the retention time of the assigned internal standard compound. The assigned internal standard is generally the perdeuterated polycyclic aromatic hydrocarbon in the dPAHIS mixture that elutes at a retention time nearest the compound of interest. The formula for determining RRT is

$$RRT = \frac{T_c}{T_{is}}, \quad (1)$$

where

T_c = retention time (referenced to the start of the analysis) for the compound of interest, and

T_{is} = retention time of the internal standard assigned to that compound.

Determine the RRT for each sample compound by analyzing standard solutions and internal standards under identical instrument conditions. The RRTs for compounds in samples and standards need to agree within 1 percent, and the expected RRT for samples must be within ± 0.1 minute. The RRT of a compound must be within the expected retention time window (± 0.1 minute), in the absence of coeluting interference that might cause retention time shifts, to meet the required qualitative criteria.

The second component for qualitative identification is comparison of reference standard mass spectra and sample spectra. The reference standard mass spectra are derived from authentic compound standards collected under identical GC/MS conditions as the sample spectra. The GC/MS operator must visually compare reference spectra, integrated ion ratios of the quantitation ion to two confirmation ions, and the elution of ion profiles to determine if the spectral match between standards and samples is reasonable. Peak area ratios of the quantification and qualifier ions must agree within ± 20 percent between standards and samples for concentrations greater than the minimum reporting level (MRL) in the absence of any obvious coeluting interference. Some of the method compounds have confirmation ions (table 5) that have abundances below 10 percent of the quantification ion. Confirmation of these compounds at concentration levels well below the MRL might be more difficult because the ion ratios can be more variable than the required ± 20 percent. The ion profiles for the quantification and qualification ions also must maximize within 2 scans (about 1 second) of each other in the absence of any obvious coeluting interference.

8.3.2 *Qualitative identification of the alkylalted PAH homolog groups.* Using the approach of Wang and others (1994) and the extracted ion chromatograms as a reference, critically examine peaks within a retention time window for spectral confirmation and typical alkylated PAH homolog group patterns. Because of the variability in ion ratios between isomers for the mulitcomponent groups, there are no rigid acceptance criteria. Sum the responses for all homolog peaks within the expected retention time window that match their extracted qualifier ion profiles (table 5), or expected ion profile patterns as shown for the C_4- and C_5-alkylated phenanthrene/anthracenes in Olson and others (2004, fig. 2). Note that a characteristic group of peaks is summed to yield a single concentration estimate. The spectra for peaks that make a substantial contribution to the total area need to be examined to ensure that they match with the reference mass spectrum. If not, their contribution to the total concentration is subtracted.

9. Calculation and Reporting of Results

The concentration of a compound is calculated after it has met qualitative criteria for retention time and mass spectral agreement (see section 8.3.1).

9.1 Determination of Single-component Compound Concentrations

The weight of sediment extracted in this method is limited by the extraction cell size (22-mL) and the amount of material that can be loaded into the cell. The dry weight of the sediment sample (in grams) is obtained after it is extracted at 200°C according to the following equation:

$$W_s = [(W_{cell} + W_{thimble}) + W_s] \text{ post-extraction} - (W_{cell} + W_{thimble}) \text{ pre-extraction}, \quad (2)$$

where

W_s = dry weight of sediment extracted, in grams;
W_{cell} = weight of ASE extraction cell, in grams;
$W_{thimble}$ = weight of glass fiber thimble, in grams.

Calculate the compound concentration in the sample, as follows:

$$\text{Concentration } (\mu g/kg) = (CFr) \times (Vf) / (W_s) \quad (3)$$

where

CFr = on-column concentration determined by calibration curve-fitting routines, in nanograms per microliter;
Vf = method pre-determined volume of extract (500 µL); and
W_s = dry weight of sediment extracted, in grams.

Calibration curve-fitting routines based on the relative response factor (RRF) are used to obtain a calibration curve for each compound. They are provided by the instrument manufacturer and summarized in Furlong and others (1996). If the calculated concentration of a compound in a sample exceeds the highest concentration point of the calibration curve, dilute the extract to bring the compound response within the range of the calibration curve and reanalyze the extract. If curve-fitting routines (linear, quadratic, and power curves) are used for calibration, verify that the sample compound response is not outside the working range of the calibration curve.

9.2 Calculation of Multicomponent Alkylated PAH Homolog Concentrations

Each alkylated PAH homolog group is composed of many discernable isomers, most without authentic reference standards. Manually integrate (all manual integrations are automatically identified for confirmation in secondary review) the isomer peak areas based on the appropriate quantitation ions (table 5) present in their expected retention time window range, subtracting any significant peaks that do not match the reference mass spectrum. Using the calibration curves for the compounds selected to represent each homolog group listed in table 7, calculate the concentration of each alkylated PAH homolog group listed in table 5. Reported concentrations are considered semiquantitative and reported as estimated ("E" remark code). If interferences are determined to be present within the integrated isomeric peaks (based upon comparison of mass spectra), then manually integrate that portion of the ion chromatogram corresponding to the interference and subtract its peak area from the total peak area.

9.3 Reporting Units

Report compound concentrations for field samples in micrograms per kilogram (µg/kg) dry sediment. Report surrogate data for each sample type as percent recovered and to three significant figures. Report data for the set spike and quality-control reference material samples as percent recovered. Compounds quantified in the set blank sample are reported in micrograms per kilogram of sand. Report compound concentrations for field samples to two significant figures.

9.4 Reporting Levels

Method detection limits (MDLs) using the procedures outlined by the U.S. Environmental Protection Agency (1997) have been calculated for this method and are discussed further in section 11. The MDL for each compound is used to determine the minimum reporting levels (MRLs). The MRLs have been established at two to five times the calculated MDL. Report qualitatively identified compound concentrations that are less than the MRL as estimated ("E" remark code) concentrations. The lowest quantitative threshold for reporting data has been set at 1 percent of the MRL. Compounds that are not detected are reported as being less than the MRL. Concentrations of alkylated PAH homolog groups that meet qualitative

Table 7. Compounds with relative response factors used for the quantitation of alkylated polycyclic aromatic hydrocarbon homologs.

[C_1–C_5, alkylated polycyclic aromatic hydrocarbon homolog series consisting of C_1, C_2, C_3, C_4, C_5 groups; RRFs, relative response factors]

Compound RRFs used for calculations	Homolog series
2,6-Dimethylnaphthalene	C_1-C_5 alkylated naphthalene
2-Methylanthracene	C_1-C_5 alkylated phenanthrene/anthracene
1-Methylpyrene	C_1-C_5 alkylated fluoranthene/pyrene
Benz[*a*]anthracene	C_1-C_5 alkylated benz[*a*]anthracene/chrysene
Benzo[*a*]pyrene	C_1-C_5 alkylated benzopyrene/perylene isomers

identification criteria are always reported as estimated with the "E" remark code.

10. Quality Assurance and Quality Control

The NWQL has prepared a laboratory Quality Management System document (Maloney, 2005) and quality-assurance and quality-control (QA/QC) guidance document (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998) for Analytical Services. These documents are followed in this method to establish and verify data quality and provide corrective actions for each QC sample type. The analyst uses laboratory quality-control data from reagent blank and spike samples, surrogate standards, and CCVs to determine if corrective actions are necessary. Standard reference material and instrumental checks provide external verification of method performance and are considered quality-assurance samples.

10.1 Laboratory Blank

The laboratory reagent blank (LRB) is an analyte- and matrix-free (Ottawa sand) sample with minimal compound interferences. The LRB is used to monitor the entire sample preparation and analytical procedure for possible laboratory contamination. Currently (2006) the blank is considered acceptable when a compound is undetected or detected at less than the MRL. However, the level of blank contamination will affect reporting data and the need for data qualifiers (Maloney, 2005). The concentrations of any compounds detected in the LRB sample are reported only if they first meet the qualitative identification criteria outlined in section 8.3.1 (specifically for all compound or ion retention times, ion ratios and mass spectra). The concentration of any compound detected in the LRB is not subtracted from the amount detected in environmental samples. Rather, if there are interferences that would prevent the analysis of a compound, the source of contamination is determined and eliminated before continuing (Maloney, 2005).

If method compounds are detected at any concentration level in greater than 10 percent of the historical laboratory blanks, they are considered to be chronic blank compounds and are treated as if they are present in all samples (Maloney, 2005). Based on initial blank (sand) results (table 8, section 11), method compounds are not anticipated to have chronic blank problems.

NOTE: Laboratory blanks will be evaluated annually (similar to the long-term method detection level) to reevaluate blank contamination for determining if reporting levels need to be updated (William Foreman, U.S. Geological Survey, written commun., 2005).

10.2 Laboratory Spike

The percent recovery from the laboratory reagent spike (LRS) is calculated from the spiking procedure described in sections 7.1.4 and 7.1.5. A 22-mL ASE cell filled with Ottawa sand (about 25 g) is spiked with 1.5 µg per compound, and the recoveries are calculated based on the amount spiked. The recovery is used to monitor method performance for the sample preparation set without considering the effects of sample matrix. The LRS results are compiled for long-term recovery performance used for creating control limits and charts. Control limits for the LRS are updated annually using 3 times F-pseudosigma of the LRS results from the previous year. If the recovery of a compound is not within control limits, the data can be transmitted three ways: estimated ("E" remark coded), a raised reporting level, or the data are reported as "deleted – ruined" (D – R). Before continuing, the source of the problem must be identified and corrected. If surrogate compound recoveries fall outside the QC criteria, corrective actions are taken (Maloney, 2005).

10.3 Surrogate Compounds

Surrogate standards are compounds similar in physical and chemical properties to the method compounds but are not expected to be present in the environment. They are added to each environmental and QA/QC sample and used to monitor preparatory steps, matrix effects, and overall method performance. Their recoveries are not used to correct compound concentrations in environmental samples. Typically, surrogate recoveries from at least 30 LRBs and LRSs are used to update QC criteria for each surrogate annually. Specific corrective actions are employed if surrogate(s) recoveries fall outside the QC criteria (Maloney, 2005).

10.4 Continuous Calibration Verification (CCV)

The CCV solutions are simply calibration solutions that are used to monitor the instrument's stability in comparison to the initial calibration curve. They bracket the environmental samples in the analytical sequence. The CCV control limits are established at ± 25 percent of the expected concentration for each compound. Instrument maintenance is generally required (cleaning the MS source, replacing the injection port liner, or clipping off about 1 loop of the GC column) to correct for CCV failures. After instrument maintenance, it is necessary to repeat the initial calibration. If a CCV fails the QC criteria, the affected samples are reanalyzed.

10.5 Decafluorotriphenylphosphine (DFTPP) Tuning

A DFTPP sample is analyzed at the beginning of each analytical sequence. It is used to assess mass spectrometer performance, such as sensitivity and resolution. The relative mass fragment abundance and mass assignments must be within the range of values specified by the U.S. Environmental Protection Agency (1997), and if these criteria cannot be met, cleaning the MS source is usually required, and furthermore, samples cannot be analyzed until the DFTPP tuning and fragmentation criteria are met.

10.6 Instrument Detection Limit (IDL)

The IDL solution is an aliquot of a low concentration calibration solution (0.2 ng/µL) representing compound concentrations near, but greater than, their respective MDLs. They bracket the samples in the analytical sequence, and the control limits are established at ± 25 percent of the expected concentration for each compound. If an IDL fails the QC criteria, the affected samples require reanalysis.

10.7 Third-party Check Solution

The third-party check solution is made independently from the other standard solutions. Typically it contains all the analytes in the method or at least one from every compound class at a concentration near the midpoint of the calibration curve. It is analyzed after establishing a new calibration curve, and calculated compound concentrations need to be within ±25 percent of the expected value. Maintaining the instrument will usually bring the third-party check solution back into compliance before samples can be analyzed.

10.8 Internal Standard Compounds

Internal standard compounds are added to automatically correct quantitative results for slight differences in extract volume (if the volume is not exactly 0.5 mL), as well as compensate for differences in the injected sample volume. They are also used to monitor and compensate for unexpected GC compound retention time shifts by providing RRT markers.

10.9 Standard Reference Material (SRM)

Standard reference materials (SRMs) received from an independent third party provide a matrix representative of environmental samples, and thus, an independent assessment of method performance. These reference materials typically are certified for a limited number of the compounds of interest. The SRM sample is prepared and analyzed with each analytical set. SRM samples provide information about the method long-term recovery performance; however, there are no process control criteria based on the SRM.

10.10 Matrix Spikes

The NWQL strongly suggests that field projects include matrix spikes in the QC sample design as a measure of method performance specific to their study area. An amount equivalent to 1.5 µg per analyte is spiked at the laboratory into the customer requested matrix samples, and the spike recovery range (based on criteria from the initial method validation study) is expected to be 60 to 120 percent. However, some sediment matrices might not yield the anticipated recoveries because of inherent difficulties in producing a uniform, thoroughly mixed spike sample, or because equilibration times needed to incorporate the compounds of interest differ widely in diverse sediment matrices (Northcott and Jones, 2000). Analysis of duplicate samples also is encouraged for evaluating reproducibility of results at environmental concentrations.

11. Results and Discussion of Method Validation

11.1 Mean Bias and Precision

Reagent-sand samples; stream-sediment samples collected from Cherry Creek near Garland Park, Denver, Colorado; and soil samples from a commercially available topsoil mixture were used to test method performance. Subsamples of each matrix were fortified at 1.5 and 15 µg for each method compound. In addition, samples of the three sample matrices were extracted and analyzed unfortified to determine the ambient concentrations of any method compounds (table 8).

Each fortified sample set was extracted and analyzed on different days, so comparisons of different matrices and concentrations include day-to-day variation. Mean bias and precision data from the analyses of the three matrices spiked at the higher amount (15 µg) are listed in table 9. Final recoveries were adjusted as footnoted by subtracting the mean concentrations measured in the unfortified samples. The natural compound contributions of the stream sediment to the 15-µg spike varied from 1.1 percent for benz[*a*]anthracene to 5.9 percent for bis(2-ethylhexyl) phthalate. The only compound contribution for the topsoil, bis(2-ethylhexyl) phthalate, contributed 4.1 percent to the 15-µg spike. Laboratory reagent spikes and laboratory reagent blanks were processed with each set of samples. The recovery for 1,2,4-trichlorobenzene for the 15-µg spike samples was less than 60 percent (table 9), probably because the compound is subject to volatility loses during sample preparation and solvent reduction steps; thus, the concentration of 1,2,4-trichlorobenzene will always be reported as estimated with the "E" remark code.

The mean bias and precision data for the three matrices spiked at 1.5 µg are listed in table 10.

Table 8. Semivolatile and polycyclic aromatic hydrocarbon compounds detected in unfortified reagent-sand, stream-sediment, and topsoil samples.

[µg/kg, micrograms per kilogram; < MRL, less than minimum reporting level; n, number of samples]

Compound (retention time order)	Average concentration (µg/kg)			Compound (retention time order)	Average concentration (µg/kg)		
	Sand n = 14	Stream sediment n = 3	Topsoil n = 3		Sand n = 14	Stream sediment n = 3	Topsoil n = 3
1,2,4-Trichlorobenzene	< MRL	< MRL	< MRL	9H-Carbazole	< MRL	< MRL	< MRL
Naphthalene	< MRL	< MRL	< MRL	2-Methylanthracene	< MRL	< MRL	< MRL
2-Ethylnaphthalene	< MRL	< MRL	< MRL	4,5-Methylenephenanthrene	< MRL	< MRL	< MRL
2,6-Dimethylnaphthalene	< MRL	< MRL	< MRL	1-Methylphenanthrene	< MRL	< MRL	< MRL
1,6-Dimethylnaphthalene	< MRL	< MRL	< MRL	Anthraquinone	< MRL	27.8	< MRL
Acenaphthylene	< MRL	< MRL	< MRL	Fluoranthene	< MRL	88.3	< MRL
1,2-Dimethylnaphthalene	< MRL	< MRL	< MRL	Pyrene	< MRL	85.6	< MRL
Acenaphthene	< MRL	< MRL	< MRL	1-Methylpyrene	< MRL	< MRL	< MRL
2,3,6-Trimethylnaphthale	< MRL	< MRL	< MRL	Benz[*a*]anthracene	< MRL	15.8	< MRL
9H-Fluorene	< MRL	< MRL	< MRL	Chrysene	< MRL	19.8	< MRL
Diethyl phthalate	< MRL	< MRL	< MRL	Bis(2-ethylhexyl) phthalate	< MRL	88.5	620.0
1-Methyl-9H-fluorene	< MRL	< MRL	< MRL	Benzo[*b*]fluoranthene	< MRL	35.0	< MRL
Hexachlorobenzene	< MRL	< MRL	< MRL	Benzo[*k*]fluoranthene	< MRL	24.1	< MRL
Pentachloroanisole	< MRL	< MRL	< MRL	Benzo[*e*]pyrene	< MRL	< MRL	< MRL
Dibenzothiophene	< MRL	< MRL	< MRL	Benzo[*a*]pyrene	< MRL	28.4	< MRL
Pentachloronitrobenzene	< MRL	< MRL	< MRL	Perylene	< MRL	< MRL	< MRL
Phenanthrene	< MRL	58.1	< MRL	Indeno[1,2,3-*c,d*]pyrene	< MRL	< MRL	< MRL
Anthracene	< MRL	39.6	< MRL	Dibenz[*a,h*]anthracene	< MRL	< MRL	< MRL
Phenanthridine	< MRL	< MRL	< MRL	Benzo[*g,h,i*]perylene	< MRL	40.6	< MRL

Table 9. Polycyclic aromatic hydocarbon and semivolatile compound mean bias and precision of spike recovery data for nine replicates with compounds spiked at 15 micrograms per sample in reagent-sand, stream-sediment, and topsoil samples.

[µg , micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; sed, sediment]

Compound name (retention time order)	Mean recovery (percent)			RSD (percent)		
	Sand	Stream sed	Topsoil	Sand	Stream sed	Topsoil
1,2,4-Trichlorobenzene[1]	56.6	52.0	52.5	7.0	7.6	7.0
Naphthalene	67.1	59.3	65.2	9.2	6.8	4.9
2-Ethylnaphthalene	77.5	78.4	82.2	10.1	6.6	4.4
2,6-Dimethylnaphthalene	79.2	80.2	82.4	10.5	6.3	4.4
1,6-Dimethylnaphthalene	79.4	81.3	82.2	10.0	6.0	4.4
Acenaphthylene	68.0	68.5	79.2	5.3	4.4	4.3
1,2-Dimethylnaphthalene	81.8	82.9	84.0	11.1	5.7	4.2
Acenaphthene	74.7	78.0	74.8	5.7	5.0	5.9
2,3,6-Trimethylnaphthalene	89.5	93.8	94.4	14.3	5.9	5.2
9H-Fluorene	81.1	88.4	87.4	5.4	4.0	7.0
Diethyl phthalate	76.6	66.0	59.2	12.5	13.0	9.7
1-Methyl-9H-fluorene	84.2	94.9	92.9	5.8	4.2	7.3
Hexachlorobenzene	77.0	86.9	80.2	5.9	5.4	6.1
Pentachloroanisole	80.2	89.9	86.1	5.0	3.8	6.4
Dibenzothiophene	87.4	98.7	95.2	5.5	4.1	7.8
Pentachloronitrobenzene	84.8	92.1	108.4	16.5	6.0	7.7
Phenanthrene	89.3	97.6*	94.7	4.5	6.5	5.2
Anthracene	88.2	94.4*	96.1	6.4	6.9	5.7
Phenanthridine	92.2	95.0	95.7	5.8	6.1	5.9
9H-Carbazole	95.6	100.6	100.8	5.9	7.8	5.3
2-Methylanthracene	86.0	93.7	99.1	6.8	7.3	5.7
4,5-Methylenephenanthrene	90.0	96.0	93.3	5.7	8.2	5.2
1-Methylphenanthrene	89.7	95.7	92.7	5.4	7.8	4.9
Anthraquinone	99.4	106.2*	109.4	5.8	9.4	5.7
Fluoranthene	94.3	107.2*	106.0	5.8	15.0	6.0
Pyrene	94.9	106.8*	105.7	6.5	13.9	5.6
1-Methylpyrene	92.2	102.1	109.0	9.4	9.5	7.1
Benz[*a*]anthracene	87.0	98.3*	97.7	6.3	7.2	6.8
Chrysene	86.8	97.4*	91.1	4.5	7.5	7.8
Bis(2-ethylhexyl) phthalate	82.4	69.4*	62.8*	16.2	11.4	24.6
Benzo[*b*]fluoranthene	85.6	101.2	97.7*	15.7	6.8	4.2
Benzo[*k*]fluoranthene	81.7	92.7	85.8*	12.8	5.5	4.3
Benzo[*e*]pyrene	78.6	94.2	92.4	8.5	4.5	12.1
Benzo[*a*]pyrene	83.0	92.8	90.2*	5.8	7.7	4.4
Perylene	74.1	86.3	85.2	5.0	4.9	5.1
Indeno[1,2,3-*c,d*]pyrene	86.0	98.4	119.0	12.3	5.3	4.9
Dibenz[*a,h*]anthracene	83.6	96.0	106.2	11.5	6.0	4.1
Benzo[*g,h,i*]perylene	80.3	96.3	99.3*	11.8	4.0	4.4

Table 9. Polycyclic aromatic hydocarbon and semivolatile compound mean bias and precision of spike recovery data for nine replicates with compounds spiked at 15 micrograms per sample in reagent-sand, stream-sediment, and topsoil samples.—Continued

[µg , micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; sed, sediment]

Compound name (retention time order)	Mean recovery (percent)			RSD (percent)		
	Sand	Stream sed	Topsoil	Sand	Stream sed	Topsoil
Surrogate compounds						
Nitrobenzene-d_5	83.1	53.7	63.8	22.1	11.6	8.2
2-Fluorobiphenyl	85.6	64.5	72.2	19.3	6.3	4.2
Terphenyl-d_{14}	99.6	93.8	99.3	13.9	8.8	4.9

[1]Concentration will be qualified in reports as estimated because recovery is less than 60 percent or variability is greater than 25 percent RSD.

[*]Percent recovery corrected for background concentration from the average of three unspiked samples.

Table 10. Polycyclic aromatic hydrocarbons and semivolatile compound mean bias and precision of spike recovery data for nine replicates with compounds spiked at 1.5 micrograms per sample in reagent-sand, stream-sediment, and topsoil samples.

[µg , micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; sed, sediment; MDL, method detection limit]

Compound name (retention time order)	Mean recovery (percent)			RSD (percent)		
	Sand	Stream sed	Topsoil	Sand	Stream sed	Topsoil
1,2,4-Trichlorobenzene[1]	49.6	49.5	50.8	13.2	6.8	12.5
Naphthalene	67.0	65.6	59.2	6.6	3.2	12.0
2-Ethylnaphthalene	83.6	83.2	71.2	5.3	4.3	7.9
2,6-Dimethylnaphthalene	86.5	85.9	73.4	5.7	4.8	8.1
1,6-Dimethylnaphthalene	86.0	86.5	73.2	4.8	3.8	7.9
Acenaphthylene	83.7	83.3	69.3	6.1	4.5	8.0
1,2-Dimethylnaphthalene	91.0	90.5	73.5	5.9	5.2	8.3
Acenaphthene	89.6	89.6	63.7	5.7	4.9	8.2
2,3,6-Trimethylnaphthalene	92.3	90.5	[7]5.9	6.7	4.3	11.2
9H-Fluorene	94.4	93.9	71.1	6.0	5.0	9.5
Diethyl phthalate	86.0	83.2	71.3	17.6	7.5	9.7
1-Methyl-9H-fluorene	100.4	98.5	75.6	9.9	6.1	11.2
Hexachlorobenzene	96.6	95.1	54.3	8.5	5.3	25.6
Pentachloroanisole	96.5	95.3	64.2	9.3	5.1	16.7
Dibenzothiophene	105.0	104.3	78.0	8.8	6.9	10.9
Pentachloronitrobenzene	91.4	91.8	82.6	8.1	4.9	12.0
Phenanthrene	102.2	102.6[*]	82.1	7.3	5.8	10.4
Anthracene	103.3	103.6[*]	85.6	6.6	5.8	10.7
Phenanthridine	99.1	101.2	82.9	10.1	6.9	10.4
9H-Carbazole	102.4	101.8	84.4	7.8	6.4	11.2
2-Methylanthracene	102.6	102.8	80.2	7.3	5.7	13.5
4,5-Methylenephenanthrene	105.9	106.2	81.9	6.8	5.7	10.8
1-Methylphenanthrene	110.7	110.7	81.8	7.1	6.4	11.7
Anthraquinone	117.1	117.6[*]	94.4	6.9	7.4	10.7
Fluoranthene	110.8	111.1[*]	89.2	6.8	6.1	11.0
Pyrene	112.7	113.2[*]	89.7	6.8	6.2	11.5

Table 10. Polycyclic aromatic hydrocarbons and semivolatile compound mean bias and precision of spike recovery data for nine replicates with compounds spiked at 1.5 micrograms per sample in reagent-sand, stream-sediment, and topsoil samples.—Continued

[µg , micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; sed, sediment; MDL, method detection limit]

Compound name (retention time order)	Mean recovery (percent)			RSD (percent)		
	Sand	Stream sed	Topsoil	Sand	Stream sed	Topsoil
1-Methylpyrene	113.1	113.5	83.5	6.7	6.4	13.0
Benz[*a*]anthracene	102.2	102.5*	75.7	7.6	6.2	19.7
Chrysene	101.8	102.2*	73.4	7.6	6.1	19.1
Bis(2-ethylhexyl) phthalate	127.6	124.1*	38.8*	12.6	7.5	21.2
Benzo[*b*]*fluoranthene*	95.5	95.4	67.7*	8.0	6.6	18.5
Benzo[*k*]fluoranthene	95.8	96.0	62.9*	7.0	5.0	19.9
Benzo[*e*]pyrene	98.9	98.9	67.7	7.0	5.3	14.0
Benzo[*a*]pyrene	98.2	98.2	77.6*	8.2	6.0	12.7
Perylene	87.4	86.4	68.7	6.4	4.6	10.5
Indeno[1,2,3-*c,d*]pyrene	102.4	102.6	69.5	7.3	6.1	19.3
Dibenz[*a,h*]anthracene	97.4	98.6	62.1	8.5	6.5	21.1
Benzo[*g,h,i*]perylene	98.6	98.3	70.5*	7.9	7.2	18.0
Surrogate compounds						
Nitrobenzene-d_5	62.7	61.8	66.3	12.2	6.5	27.4
2-Fluorobiphenyl	69.2	68.4	77.1	6.3	3.5	22.2
Terphenyl-d_{14}	109.1	109.7	139.9	6.7	5.3	20.9

[1]Concentration is estimated because recovery is less than 60 percent or variability is greater than 25 percent RSD.

*Percent recovery corrected for background concentration from the average of three unspiked samples.

The recoveries of PAH and semivolatile compounds from a 22-mL ASE cell filled with Ottawa sand (about 25 g) fortified at 1.5 µg per compound (table 10) averaged 88 percent ± 9.4 percent relative standard deviation.

Even though sediment matrices provide some retention of spiked compounds, they often add to the variability of measured results because of background matrix effects. This variability might be expected to be greater at the lower concentration spike level (table 10) than at the higher level (table 9) for the compounds that required recovery correction for ambient concentrations in the unspiked sample (the relevant compounds have been footnoted in tables 9 and 10); however, this trend was not always observed when comparing the standard deviations listed in tables 9 and 10.

Table 11 lists compounds that were investigated in the development of this method but were excluded because of low recovery, or are not expected to partition into the sediment based on Log Kow, or are available in more suitable NWQL methods.

In addition to determining the mean bias and precision data for the three matrices spiked at 1.5 µg (table 10), the initial method detection limits (MDLs) also were calculated for compounds spiked into Ottawa reagent-sand samples according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1997) described in section 11.2.

11.2 Method Detection Limits

The NWQL uses the long-term method detection level procedure (Childress and others, 1999) to determine compound-reporting conventions for water analytical methods. Because of the varied nature of sediment samples, the long-term method detection level (LT–MDL) procedure has not been implemented for sediment analyses.

Method detection limits (MDLs) were established using procedures outlined by the U.S. Environmental Protection Agency (1997). For this method, the MDL was determined from the nine replicate reagent spike (Ottawa sand) samples fortified at 1.5 µg per compound (table 10). For the set of nine samples, the sample standard deviation was computed and the MDL calculated from the following formula:

$$MDL = S \times t_{(n-1,\ 1-\alpha=0.99)}, \quad (4)$$

where

S = standard deviation of replicate analyses, in microgram per kilogram, at the lowest spike concentration;

n = number of replicate analyses; and

$t_{(n-1,\ 1-\alpha=0.99)}$ = Student's t-value for the 99-percent confidence level with n–1 degrees of freedom.

The calculated MDL for each compound is listed in table 12 using the 1.5-µg per compound spike in reagent-sand results from table 10 and assuming a 25-g sample size (60 µg/kg). The initial minimum reporting levels (MRLs) for compounds have been assigned based on a combination of MDL data, observed matrix interferences, and the impact of varied matrices on instrument performance.

The calculated initial MDLs averaged 14 µg/kg. The MRLs have been established at 50 µg/kg, or about two to five times greater than the calculated initial MDLs for most compounds (table 12). This precaution reduces the risk of reporting that a compound is less than the MRL (undetected), when it is actually in the sample near the MDL concentration (Childress and others, 1999). The MRLs for the alkylated PAH homolog groups also have been established at 50 µg/kg on the basis of the MRLs for the compounds selected to represent each group (table 7). The concentrations for qualitatively identified compounds detected less than the MRL are reported as estimated, regardless of the established MRL, because this method is classified as an "information-rich" method, as are other mass spectrometric methods (Childress and others, 1999).

A few compounds were spiked at a higher concentration than the suggested amount (U.S. Environmental Protection Agency, 1997) of two to five times the calculated MDL concentrations, and, therefore, the MDL has been defined as an "estimated MDL" in those cases, as footnoted in table 12.

11.3 Performance Data Using SRM 1944

SRM 1944 is natural marine sediment that contains specific PAH concentrations certified by the National Institute of Standards and Technology (NIST). Many alkylated PAH homolog groups are present but are not certified. Nine SRM 1944 samples were extracted and analyzed by this ASE

Table 11. Mean bias and precision of spike recovery data for nine replicates with compounds spiked at 1.5 and 15 micrograms per sample in reagent-sand, stream-sediment, and topsoil samples for compounds that are not included in this method.

[µg , micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation]

Compound name (retention time order)	Log Kow[1]	Spike amount (µg)	Mean recovery (percent)			RSD (percent)		
			Sand	Stream sediment	Topsoil	Sand	Stream sediment	Topsoil
Phenol	1.5	1.5	47.6	47.3*	79.0*	6.2	2.7	36.3
		15.0	28.2	26.4*	28.0*	7.2	5.9	4.9
p-Cresol	2.1	1.5	70.3	70.3*	63.3*	9.2	5.5	16.6
		15.0	49.9	44.9*	40.1*	10.2	11.0	3.7
Isophorone	2.6	1.5	38.1	37.7	15.8	20.4	7.5	20.3
		15.0	18.4	11.3	11.0	5.8	3.6	0.8
2,4-Dichlorophenol	3.1	1.5	87.8	90.9	67.7	13.6	9.9	11.8
		15.0	70.8	69.6	76.9	12.4	9.1	10.3
Quinoline	2.1	1.5	56.9	55.3	23.1	16.8	9.3	20.2
		15.0	28.5	17.2	16.1	10.1	4.8	2.9
Isoquinoline	2.1	1.5	63.0	62.3	25.1	13.6	8.5	18.1
		15.0	31.7	18.8	17.9	12.1	5.9	2.3
2,4,6-Trichlorophenol	3.5	1.5	94.7	95.7	95.2	8.1	7.0	10.9
		15.0	82.6	88.1	125.6	12.8	5.9	6.5
Dimethyl phthalate	1.6	1.5	35.1	32.1	80.8	44.8	8.8	35.7
		15.0	31.2	15.1	14.6	16.4	4.9	3.0
Pentachlorophenol	4.8	1.5	11.7	11.5	42.3*	9.0	0.9	26.1
		15.0	9.0	18.7	34.7*	6.1	5.2	47.8
Di-*n*-octyl phthalate	8.1	1.5	14.9	14.6	30.6	13.8	1.2	22.8
		15.0	30.4	10.4	4.9	26.5	1.6	2.0

[1]Log Kow calculated using the U.S. Environmental Protection Agency's exposure assessment tools and models (EPI-suite software, WSKOWWIN™ version 1.40; U.S. Environmental Protection Agency, 2004a).

*Percent recovery corrected for background concentration in the unspiked sample.

Table 12. Initial method detection limits calculated from the precision data reported in table 10 for the nine replicate reagent-sand samples spiked at 60 micrograms per kilogram per compound.

[µg/kg, micrograms per kilogram; %, percent; MDL, method detection limit; MRL, minimum reporting level]

Compound name (retention time order)	Spike amount (µg/kg)	Mean recovery (percent)	Initial MDL (µg/kg)	Initial MRL (µg/kg)
Naphthalene[1]	60	67.0	7.7	50
2-Ethylnaphthalene[1]	60	83.6	7.7	50
2,6-Dimethylnaphthalene[1]	60	86.5	8.5	50
1,6-Dimethylnaphthalene[1]	60	86.0	7.2	50
Acenaphthylene[1]	60	83.7	8.9	50
1,2-Dimethylnaphthalene[1]	60	91.0	9.2	50
Acenaphthene[1]	60	89.6	8.9	50
2,3,6-Trimethylnaphthalene[1]	60	92.3	10.8	50
9H-Fluorene[1]	60	94.4	9.8	50
Diethyl phthalate	60	86.0	26.4	50
1-Methyl-9H-fluorene	60	100.4	17.3	50
Hexachlorobenzene	60	96.6	14.3	50
Pentachloroanisole	60	96.5	15.5	50
Dibenzothiophene	60	105.0	16.0	50
Pentachloronitrobenzene	60	91.4	12.9	50
Phenanthrene	60	102.2	12.9	50
Anthracene[1]	60	103.3	11.9	50
Phenanthridine	60	99.1	17.3	50
9H-Carbazole	60	102.4	13.9	50
2-Methylanthracene	60	102.6	13.0	50
4,5-Methylenephenanthrene[1]	60	105.9	12.5	50
1-Methylphenanthrene	60	110.7	13.7	50
Anthraquinone[1]	60	117.1	14.0	50
Fluoranthene[1]	60	110.8	13.0	50
Pyrene[1]	60	112.7	13.2	50
1-Methylpyrene[1]	60	113.1	13.1	50
Benz[*a*]anthracene	60	102.2	13.4	50
Chrysene	60	101.8	13.5	50
Bis(2-ethylhexyl) phthalate	60	127.6	27.9	50
Benzo[*b*]fluoranthene	60	95.5	13.3	50
Benzo[*k*]fluoranthene[1]	60	95.8	11.6	50
Benzo[*e*]pyrene[1]	60	98.9	12.0	50
Benzo[*a*]pyrene	60	98.2	13.9	50
Perylene[1]	60	87.4	9.8	50
Indeno[1,2,3-*c,d*]pyrene	60	102.4	12.9	50
Dibenz[*a,h*]anthracene	60	97.4	14.4	50
Benzo[*g,h,i*]perylene	60	98.6	13.5	50
1,2,4-Trichlorobenzene[2]	60	49.6	11.4	50

[1]The compound was fortified at a concentration that was higher than five times the calculated MDL. Therefore, the MDL has been defined as an estimated MDL.

[2]Concentration is permanently estimated with the "E" remark code because recovery is less than 60 percent or variability is greater than 25 percent relative standard deviation.

method during a 2-month period, and results were compared to NWQL Soxhlet extraction method 2502 (table 13). Method precision for the certified PAH compounds by the ASE method ranged from about 7 to15 percent.The NIST certified results for SRM 1944 were obtained by 36-hour Soxhlet extraction with DCM and GC/MS analysis, so NIST certified results might be expected to be more comparable to NWQL method 2502 than this ASE extraction method. Hawthorne, Grabanski, and others (2000) have suggested that water-based extraction solvents cause clay particles to swell much more than typical organic solvents. Consequently, PAH molecules that are highly sequestered in clay pores are more available to subcritical water. The recovery results (table 13) of low molecular weight PAH compounds (for example, naphthalene, phenanthrene, and anthracene) are greater by 10 to 20 percent for this ASE method than by Soxhlet extraction with DCM and probably reflect this effect. As the solubility of higher molecular weight PAH compounds decreases in the hot IPA/water mixture, ASE recoveries generally are comparable to Soxhlet extraction with DCM. Hawthorne, Trembley, and others (2000) also observed this same trend for subcritical water extraction of SRM 1944 at 250ºC. The relatively high recovery of dibenz[*a,h*]anthracene (132 percent, see table 13) most likely is the result of poorly resolved GC peaks contributing to the peak area, similar to the situation observed for poor GC peak resolution of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene in SRM 1944 ASE extracts.

Table 14 lists mean concentrations of alkylated PAH homolog groups that are present in SRM 1944 but which are not reported by NIST. The Soxhlet extraction results for the alkylated PAHs were obtained by NWQL custom method 8022, which is the same as NWQL method 2502 (36-hour Soxhlet extraction with DCM).

It is impossible to compare absolute recoveries for the homolog groups in SRM 1944, as was possible for the parent PAHs (table 13), because there are no NIST-certified values; however, Soxhlet and ASE results are similar for those homolog groups that were detected (table 14). All of the relative standard deviations (RSDs) are 12 percent or less, indicating consistent integration and reproducible extraction efficiency.

11.4 Replicate Environmental Sample Results Using ASE Extraction

Nine duplicates and one triplicate sample were extracted using ASE to evaluate the reproducibility of the method (table 15).

For statistical purposes, the average deviation can be used for comparing results of two or three samples (Anderson, 1987). The average deviation (percent) was calculated for the 10 replicate samples in table 15 according to the following equation:

$$AD = [1 / n (| R_1 - \bar{R} | + | R_2 - \bar{R} | + | R_3 - \bar{R} |)] * 100 / \bar{R} \quad (5)$$

where

AD = average deviation, in percent;
n = number of samples (2 for duplicates or 3 for triplicates);
R = result $_{1 \text{ to } 3;}$ and
$\bar{R}$ = mean value.

Average deviations to evaluate method reproducibility are listed in table 16. Although replicate data for only 10 samples is not sufficient to adequately evaluate the reproducibility of this method, the observed average deviation ranges for the method compounds (table 16) provide an initial assessment. The mean average percent deviation of PAH compounds for 41 duplicate core samples extracted by Soxhlet extraction (Van Metre and others, 2004) ranged from 8.2 percent for anthracene to 15.4 percent for chrysene. The 10 duplicate sample results for the PAH compounds determined by this ASE method demonstrated greater average deviation (about 50 percent) than for the Soxhlet method of extraction used for core samples, most likely because of greater variation in the carbon content and matrix type of these samples (table 15) than for the core samples.

11.5 Accelerated Solvent Extraction (ASE) and Soxhlet Sample Results

Extraction results for ASE and Soxhlet for 28 sediment samples (including the average values for the 10 replicate samples, section 11.4) consist of a wide variety of mixed sample types (sand, silt, clay, soil, and soil cores) and organic carbon content. These results are listed in table 17.

The correlations (table 18) between the two extraction methods were calculated for each detected compound (excluding a few high results from sample extracts that required significant dilutions as footnoted in table 17; however, the ASE concentrations were much higher than the Soxhlet concentrations for all points that were not included).

Table 13. Concentrations certified by the National Institute of Standards and Technology for Standard Reference Material 1944 determined by Soxhlet extraction and this method.

[NIST, National Institute of Standards and Technology; µg/kg, micrograms per kilogram; SOX, Soxhlet; ASE, accelerated solvent extraction; RSD, relative standard deviation; n, number = 7 by Soxhlet, number = 9 by ASE]

Compound name	NIST certified (µg/kg)	Mean SOX (µg/kg)	Mean ASE (µg/kg)	SOX recovery (percent)	ASE recovery (percent)	SOX RSD (percent) n=7	ASE RSD (percent) n=9
Anthracene	1,770	1,440	1,877	81.3	106.0	7.79	10.26
Benz[*a*]anthracene	4,720	3,870	3,660	81.9	77.5	6.78	7.77
Benzo[*b*]fluoranthene[1]	3,870	3,160	3,050	81.7	98.9	8.63	8.32
Benzo[*k*]fluoranthene[1]	2,300	2,920	3,050	127.0	98.9	7.30	8.32
Benzo[*ghi*]perylene	2,840	1,680	1,893	59.2	66.6	7.05	13.24
Benzo[*a*]pyrene	4,300	3,170	3,363	73.6	78.2	7.61	12.08
Benzo[*e*]pyrene	3280	2,480	2,410	75.6	73.5	6.67	9.81
Chrysene	4,860	4,470	5,370	92.1	110.5	7.22	8.95
Dibenz[*a,h*]anthracene	424	347	561	81.8	132.2	7.38	8.13
Fluoranthene	8,920	6,670	8,970	74.8	100.5	6.07	10.69
Indeno[1,2,3-*cd*]pyrene	2,780	2,820	2,300	102.0	82.7	6.77	14.82
Naphthalene	1,650	820	1,980	49.3	120.0	10.5	15.70
Perylene	1,170	740	742	63.3	63.4	7.13	9.97
Phenanthrene	5,270	3,970	5,723	75.3	108.6	6.36	8.76
Pyrene	9,700	6,580	9,397	67.8	96.8	5.53	9.32

[1]Because of poor chromatographic peak shape, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were nearly unresolved when the ASE extracts were analyzed, so ASE concentrations were averaged for these two compounds.

Table 14. Concentrations of alkylated homolog groups detected in Standard Reference Material 1944 determined by Soxhlet extraction and this method, but not reported by the National Institute of Standards and Technology.

[µg/kg, micrograms per kilogram; SOX, Soxhlet; ASE, accelerated solvent extraction; RSD, relative standard deviation; NR, not reported; n, number = 7 by Soxhlet, number = 9 by ASE]

Compound name	Mean SOX (µg/kg)	Mean ASE (µg/kg)	SOX RSD (percent) n=7	ASE RSD (percent) n=9
C_1-alkylated naphthalene	1,090	1,847	12	10
C_2-alkylated naphthalene	2,630	3,990	9	9
C_3-alkylated naphthalene	6,180	7,053	8	3
C_4-alkylated naphthalene	NR	NR		
C_5-alkylated naphthalene	NR	NR		
C_1-alkylated phenanthrene/anthracene	5,630	6,840	12	4
C_2-alkylated phenanthrene/anthracene	6,110	6,677	6	7
C_3-alkylated phenanthrene/anthracene	3,330	4,623	8	12
C_4-alkylated phenanthrene/anthracene	NR	NR		
C_5-alkylated phenanthrene/anthracene	NR	NR		
C_1-alkylated fluoranthene/pyrene	7,930	9,277	7	9
C_2-alkylated fluoranthene/pyrene	5,430	6,210	10	9
C_3-alkylated fluoranthene/pyrene	NR	NR		
C_4-alkylated fluoranthene/pyrene	NR	NR		
C_5-alkylated fluoranthene/pyrene	NR	NR		
C_1-alkylated benz[*a*]anthracene/chrysene	4,570	3,897	8	6
C_2-alkylated benz[*a*]anthracene/chrysene	1,980	NR	8	
C_3-alkylated benz[*a*]anthracene/chrysene	NR	NR		
C_4-alkylated benz[*a*]anthracene/chrysene	NR	NR		
C_5-alkylated benz[*a*]anthracene/chrysene	NR	NR		
C_1-alkylated benzopyrene/perylene	4,860	3,637	10	10
C_2-alkylated benzopyrene/perylene	NR	NR		
C_3-alkylated benzopyrene/perylene	NR	NR		
C_4-alkylated benzopyrene/perylene	NR	NR		
C_5-alkylated benzopyrene/perylene	NR	NR		

Table 15. Replicate environmental sample results, in micrograms per kilogram, using accelerated solvent extraction.

[Lab ID, laboratory identification number; %, percent; OC, organic carbon; ND, not determined; RT, retention time; R_1, result one; R_2, result two; AD, average deviation, in percent; nd, not detected]

Compound	Lab ID:	20022910084			20022950052			20031220119			20020450012		
	Matrix / % OC:	Clay / 3.2			Clay / 3.1			Core / ND			Clay / ND		
	(RT order)	R_1	R_2	AD[1]	R_1	R_2	AD[1]	R_1	R_2	AD[1]	R_1	R_2	AD[1]
Naphthalene		13	12	4	20	12	25	24	18	14			
2-Ethylnaphthalene								7	5	17			
2,6-Dimethylnaphthalene		35	27	13	62	35	28	204	110	30	72	44	24
1,6-Dimethylnaphthalene		11	8	16	17	10	26	46	20	39	24	15	23
Acenaphthylene		4	2	33				25	10	43	5	nd	ND
1,2-Dimethylnaphthalene								20	10	33			
Acenaphthene								28	10	47			
9H-Fluorene					12	nd	ND	23	15	21	25	23	4
Diethyl phthalate		16	nd	ND									
1-Methyl-9H-fluorene													
Dibenzothiophene					7	6	8						
Phenanthrene		24	18	14	39	31	11	99	66	20	44	36	10
Anthracene		8	6	14	14	9	22	42	22	31	7	9	13
Phenanthridine													
9H-Carbazole													
2-Methylanthracene								24	15	23			
4,5-Methylenephenanthrene					10	7	18	42	32	14	8	8	0
1-Methylphenanthrene								36	26	16	5	3	25
Anthraquinone					20	nd	ND						
Fluoranthene		37	19	32	57	38	20	241	150	23	47	33	18
Pyrene		33	15	38	50	29	27	193	120	23	35	25	17
1-Methylpyrene								26	15	27			
Benz[*a*]anthracene		11	7	22	14	9	22	96	99	2	15	13	7
Chrysene		25	12	35	26	19	16	124	145	8	27	24	6
Bis(2-ethylhexyl) phthalate		195	100	32	117	84	16						
Benzo[*b*]fluoranthene		14	6	40	18	10	29	123	115	3	28	23	10
Benzo[*k*]fluoranthene		15	6	43	17	9	31	118	98	9	31	18	27
Benzo[*e*]pyrene								102	136	14	11	8	16
Benzo[*a*]pyrene					15	8	30	110	155	17	10	10	0
Perylene								715	600	9	659	600	5
Indeno[1,2,3-*c,d*]pyrene								126	184	19	27	20	15
Dibenz[*a,h*]anthracene											4	nd	ND
Benzo[*g,h,i*]perylene								109	135	11	20	18	5

Table 15. Replicate environmental sample results, in micrograms per kilogram, using accelerated solvent extraction.—Continued

[Lab ID, laboratory identification number; %, percent; OC, organic carbon; ND, not determined; RT, retention time; R_1, result one; R_2, result two; AD, average deviation, in percent; nd, not detected]

Compound	Lab ID:	20013060058			20013060057			20011930041			20031780065		
	Matrix / % OC:	Clay / 5.4			Clay / 6.4			Clay / 0.3			Soil / ND		
	(RT order)	R_1	R_2	AD[1]	R_1	R_2	AD[1]	R_1	R_2	AD[1]	R_1	R_2	AD[1]
Naphthalene		22	25	6	43	32	15	9	9	0			
2-Ethylnaphthalene													
2,6-Dimethylnaphthalene		116	192	25	216	140	21	9	7	10	10	15	20
1,6-Dimethylnaphthalene		38	64	25	66	25	45						
Acenaphthylene		28	40	18	45	35	13	46	32	18			
1,2-Dimethylnaphthalene													
Acenaphthene					46	28	24	27	24	6	45	72	23
9H-Fluorene		33	42	12	48	45	3	50	35	18			
Diethyl phthalate													
1-Methyl-9H-fluorene		12	12	0				8	4	33			
Dibenzothiophene		18	29	23	38	34	6	39	27	18			
Phenanthrene		251	400	23	658	500	14	745	630	8	17	12	17
Anthracene		69	100	18	139	100	16	159	110	18			
Phenanthridine								16	20	11			
9H-Carbazole		90	140	22	197	170	7	108	110	1			
2-Methylanthracene		17	19	6	30	18	25	23	15	21			
4,5-Methylenephenanthrene		66	110	25	138	100	16	104	79	14			
1-Methylphenanthrene		22	42	31	54	37	19	42	34	11			
Anthraquinone		204	300	19	466	380	10	230	233	1			
Fluoranthene		1,060	1,800	26	2,290	1,600	18	1,770	1,400	12	33	12	47
Pyrene		783	1,300	25	1,700	1,200	17	1,260	1,000	12	28	11	44
1-Methylpyrene		25	49	32	55	35	22	34	27	11			
Benz[*a*]anthracene		276	450	24	615	400	21	450	435	2	10	18	29
Chrysene		618	970	22	1,380	850	24	700	670	2	17	10	26
Bis(2-ethylhexyl) phthalate		212	350	25	406	180	39	78	87	5			
Benzo[*b*]fluoranthene		600	1,100	29	1,360	980	16	655	664	1	11	8	16
Benzo[*k*]fluoranthene		532	900	26	895	740	9	475	600	12	12	7	26
Benzo[*e*]pyrene													
Benzo[*a*]pyrene		413	670	24	766	590	13	456	430	3	10	6	25
Perylene													
Indeno[1,2,3-*c,d*]pyrene		520	900	27	1,050	780	15	407	600	19			
Dibenz[*a,h*]anthracene		126	200	23	259	155	25	85	48	28			
Benzo[*g,h,i*]perylene		451	700	22	896	620	18	344	500	18			

Table 15. Replicate environmental sample results, in micrograms per kilogram, using accelerated solvent extraction.—Continued

[Lab ID, laboratory identification number; %, percent; OC, organic carbon; ND, not determined; RT, retention time; R_1, result one; R_2, result two; AD, average deviation, in percent; nd, not detected]

Compound	Lab ID:	20031780064				20022410090		
	Matrix / % OC:	Soil / ND				Silt / 13.3		
	(RT order)	R_1	R_2	AD[1]	R_1	R_1	R_2	AD[1]
Naphthalene					102	60	35	37
2-Ethylnaphthalene								
2,6-Dimethylnaphthalene		109	122	6	677	540	800	13
1,6-Dimethylnaphthalene								
Acenaphthylene								
1,2-Dimethylnaphthalene								
Acenaphthene								
9H-Fluorene								
Diethyl phthalate								
1-Methyl-9H-fluorene								
Dibenzothiophene								
Phenanthrene		14	30	36				
Anthracene								
Phenanthridine								
9H-Carbazole								
2-Methylanthracene								
4,5-Methylenephenanthrene								
1-Methylphenanthrene								
Anthraquinone								
Fluoranthene		20	50	43				
Pyrene		17	40	40				
1-Methylpyrene								
Benz[*a*]anthracene		18	18	0				
Chrysene		20	32	23				
Bis(2-ethylhexyl) phthalate					241	100	160	30
Benzo[*b*]fluoranthene		14	22	22				
Benzo[*k*]fluoranthene		15	24	23				
Benzo[*e*]pyrene								
Benzo[*a*]pyrene		19	24	12				
Perylene								
Indeno[1,2,3-*c,d*]pyrene		16	18	6				
Dibenz[*a,h*]anthracene		6	8	14				
Benzo[*g,h,i*]perylene		11	15	15				

[1]The average deviation (AD), in percent, was calculated using equation 5 (Anderson, 1987).

Table 16. Mean average deviation and range of average deviations for compounds detected in nine duplicate sediment samples and one triplicate sample extracted using accelerated solvent extraction.

[AD, average deviation; %, percent; ND, not determined]

Compound (retention time order)	Mean AD[1] (%)	Range AD[1] (%)	Compound (retention time order)	Mean AD[1] (%)	Range AD[1] (%)
Naphthalene	14	0 – 37	4,5-Methylenephenanthrene	14	0 – 25
2-Ethylnaphthalene	17	17 – 17	1-Methylphenanthrene	20	11 – 31
2,6-Dimethylnaphthalene	19	6 – 30	Anthraquinone	10	1 – 19
1,6-Dimethylnaphthalene	27	11 – 45	Fluoranthene	26	12 – 47
Acenaphthylene	25	13 – 43	Pyrene	27	12 – 44
1,2-Dimethylnaphthalene	33	33 – 33	1-Methylpyrene	23	11 – 32
Acenaphthene	25	6 – 47	Benz[*a*]anthracene	14	0 – 29
9H-Fluorene	12	3 – 21	Chrysene	18	2 – 35
Diethyl phthalate[2]	ND	ND	Bis(2-ethylhexyl) phthalate	24	5 – 39
1-Methyl-9H-fluorene	17	0 – 33	Benzo[*b*]fluoranthene	18	1 – 40
Dibenzothiophene	14	6 – 23	Benzo[*k*]fluoranthene	23	9 – 43
Phenanthrene	17	8 – 36	Benzo[*e*]pyrene	15	14 – 16
Anthracene	19	13 – 31	Benzo[*a*]pyrene	15	0 – 30
Phenanthridine	11	11 – 11	Perylene	7	5 – 9
9H-Carbazole	10	1 – 22	Indeno[1,2,3-*c,d*]pyrene	17	6 – 27
2-Methylanthracene	19	6 – 25	Dibenz[*a,h*]anthracene	22	14 – 28
			Benzo[*g,h,i*]perylene	15	5 – 22

[1]The average deviation (AD), in percent, was calculated using equation 5 (Anderson, 1987).

[2]Diethyl phthalate was only detected in one sample, so the average deviation could not be determined.

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20022910084		20022950052		20031220119		20020450012		20013060058	
	Matrix / % OC:	Clay / 3.2		Clay / 3.1		Core / ND		Clay / ND		Clay / 5.4	
	Method:	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE
Naphthalene		13	13	21	16	10	21	4	nd	20	24
2-Ethylnaphthalene						3	6				
2,6-Dimethylnaphthalene		35	31	80	49	150	157	126	58	158	154
1,6-Dimethylnaphthalene		15	10	19	14	18	33	22	20	18	51
Acenaphthylene		<80	3			10	18	3	2	30	34
1,2-Dimethylnaphthalene						7	15				
Acenaphthene						13	19				
9H-Fluorene						15	19	22	24	46	38
Diethyl phthalate		2.3	8	12	nd						
1-Methyl-9H-fluorene						5	nd	5	nd	7	12
Dibenzothiophene				17	6.5					35	24
Phenanthrene		22	21	34	35	123	83	45	40	460	326
Anthracene		15	7	24	12	34	32	7	8	110	85
Phenanthridine											
9H-Carbazole										87	115
2-Methylanthracene		24	nd			10	20	4	nd	28	18
4,5-Methylenephenanthrene				10	9	20	37	11	8	115	88
1-Methylphenanthrene				12	nd	10	31	7	4	30	32
Anthraquinone				nd	10					257	252
Fluoranthene		25	28	52	48	263	196	45	40	1,900	1,430
Pyrene		21	24	47	40	211	157	37	30	1,500	1,042
1-Methylpyrene						11	21			41	37
Benz[*a*]anthracene		10	9	21	12	116	98	15	14	561	363
Chrysene		11	19	27	23	131	135	19	26	1,030	794
Bis(2-ethylhexyl) phthalate		210	148	127	101					336	281
Benzo[*b*]fluoranthene		15	10	19	14	147	119	24	26	1,140	850
Benzo[*k*]fluoranthene		12	11	5	13	109	108	18	25	821	716
Benzo[*e*]pyrene						90	119	10	9		
Benzo[*a*]pyrene				27	12	118	133	17	10	754	542
Perylene						467	658	902	630		
Indeno[1,2,3-*c,d*]pyrene						132	155	22	24	704	710
Dibenz[*a,h*]anthracene						26	nd	3	2	140	163
Benzo[*g,h,i*]perylene						72	122	15	19	542	576

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.—Continued

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20013060057		20011930041		20031780065		20031780064		20022410090	
	Matrix / % OC:	Clay / 6.4		Clay / 0.3		Soil / ND		Soil / ND		Silt / 13.3	
	Method:	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE
Naphthalene		18	38	6	9					<500	66
2-Ethylnaphthalene											
2,6-Dimethylnaphthalene		133	178	12	8	123	13	67	116	123	672
1,6-Dimethylnaphthalene		19	46							90	215
Acenaphthylene		21	40	30	39						
1,2-Dimethylnaphthalene											
Acenaphthene		12	37	25	26	<50	59				
9H-Fluorene		49	47	44	43						
Diethyl phthalate											
1-Methyl-9H-fluorene		5	nd	<50	6						
Dibenzothiophene		32	36	29	33						
Phenanthrene		587	579	724	688	<50	15	<50	22		
Anthracene		99	120	111	135						
Phenanthridine				16	18						
9H-Carbazole		102	184	90	109						
2-Methylanthracene		25	24	12	19						
4,5-Methylenephenanthrene		120	119	86	92						
1-Methylphenanthrene		33	46	30	38						
Anthraquinone		280	423	230	232						
Fluoranthene		1,970	1,945	1,400	1,585	<50	23	55	35		
Pyrene		1,480	1,450	1,100	1,130	<50	20	<50	29		
1-Methylpyrene		40	45	21	31						
Benz[*a*]anthracene		504	508	444	443	<50	14	<50	18		
Chrysene		1,000	1,115	730	685	<50	14		26		
Bis(2-ethylhexyl) phthalate		301	293	118	83					321	167
Benzo[*b*]fluoranthene		1,050	1,170	684	660	<50	10	<50	18		
Benzo[*k*]fluoranthene		898	818	566	538	<50	10	<50	20		
Benzo[*e*]pyrene											
Benzo[*a*]pyrene		702	678	566	443	<50	8	<50	22		
Perylene											
Indeno[1,2,3-*c,d*]pyrene		578	915	482	504			<50	17		
Dibenz[*a,h*]anthracene		120	207	89	67			<50	7		
Benzo[*g,h,i*]perylene		473	758	353	422			<50	13		

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.—Continued

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20013060059		20022560060		20022560059		20012560108		20022410092	
	Matrix / % OC:	Clay / 3.0		Clay / 1.6		Clay / 0.9		Soil / 0.0		Silt / 24	
	Method:	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE
Naphthalene		28	87			10	8	<50	5	<1,300	53
2-Ethylnaphthalene											
2,6-Dimethylnaphthalene		142	120	242	249	32	35			1,290	907
1,6-Dimethylnaphthalene		23	42	28	49	11	13			323	373
Acenaphthylene		46	45								
1,2-Dimethylnaphthalene											
Acenaphthene		26	108								
9H-Fluorene		51	122								
Diethyl phthalate								6	7		
1-Methyl-9H-fluorene		11	nd								
Dibenzothiophene		36	59								
Phenanthrene		608	1,330	25	16	9	7				
Anthracene		144	263	21	15						
Phenanthridine											
9H-Carbazole		100	250								
2-Methylanthracene		29	51								
4,5-Methylenephenanthrene		111	193								
1-Methylphenanthrene		49	87								
Anthraquinone		266	433								
Fluoranthene		1,740	2,590	29	27	13	14	1	13		
Pyrene		1,320	1,890	23	26	9	12	<50	10		
1-Methylpyrene		49	63								
Benz[*a*]anthracene		590	835	17	20			<50	8		
Chrysene		958	1,420	8	23			<50	13		
Bis(2-ethylhexyl) phthalate		660	489	382	110	39	48	59	29	972	204
Benzo[*b*]fluoranthene		1,150	1,000	17	30			<50	15		
Benzo[*k*]fluoranthene		740	1,080	14	36			<50	14		
Benzo[*e*]pyrene											
Benzo[*a*]pyrene		720	804	29	34			<50	14		
Perylene											
Indeno[1,2,3-*c,d*]pyrene		640	948					<50	18		
Dibenz[*a,h*]anthracene		144	260								
Benzo[*g,h,i*]perylene		482	790					<50	18		

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.—Continued

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20031780069		20031780070		20020630040		20022970068		20012480191	
	Matrix / % OC:	Soil / ND		Soil / ND		Clay / ND		Clay / 3.4		Soil / ND	
	Method:	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE	SOX[1]	ASE[1]
Naphthalene						28	43	<100	21	263	1,560
2-Ethylnaphthalene						8	9			35	88
2,6-Dimethylnaphthalene		87	13			29	23	158	168	85	112
1,6-Dimethylnaphthalene						33	33	24	35	75	127
Acenaphthylene		<50	32							884	3,250
1,2-Dimethylnaphthalene						14	10			33	53
Acenaphthene										1,580	3,000
9H-Fluorene						6	6			2,130	4,480
Diethyl phthalate								14	18		
1-Methyl-9H-fluorene						6	6			244	387
Dibenzothiophene											
Phenanthrene						36	52	12	15	46,400	96,000
Anthracene						3	5			6,650	12,000
Phenanthridine											
9H-Carbazole											
2-Methylanthracene						3	3			1,040	1,690
4,5-Methylenephenanthrene						2	nd			6,020	11,000
1-Methylphenanthrene						14	19			2,210	5,300
Anthraquinone											
Fluoranthene						13	24	20	19	131,000	293,000
Pyrene						14	24	23	20	106,000	228,000
1-Methylpyrene						10	8			2,860	5,620
Benz[*a*]anthracene						9	17	<100	11	49,500	98,000
Chrysene						15	27	<100	18	81,300	180,000
Bis(2-ethylhexyl) phthalate				<300	52						
Benzo[*b*]fluoranthene						12	19	<100	68	76,200	175,000
Benzo[*k*]fluoranthene						7	16	<100	71	60,300	133,000
Benzo[*e*]pyrene						12	19			44,200	118,000
Benzo[*a*]pyrene						10	10	27	59	62,500	135,000
Perylene						52	47			15,000	35,000
Indeno[1,2,3-*c,d*]pyrene						8	15			75,600	148,000
Dibenz[*a,h*]anthracene										12,900	30,000
Benzo[*g,h,i*]perylene						16	28			48,200	120,000

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.—Continued

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20012480193		20030940075		20031220109		20031220117		20031220120	
	Matrix / % OC:	Soil / ND		Silt / ND		Core / ND		Core / ND		Core / ND	
	Method:	SOX[1]	ASE[1]	SOX	ASE	SOX	ASE	SOX	ASE	SOX	ASE
Naphthalene		83	254	159	197	8	26	14	46	5	20
2-Ethylnaphthalene		14	28	31	27			2	nd	2	nd
2,6-Dimethylnaphthalene		33	46	164	81	2	6	92	97	86	86
1,6-Dimethylnaphthalene		28	51	59	55	13	17	12	30	10	18
Acenaphthylene		292	670	245	287	12	28	14	30	11	21
1,2-Dimethylnaphthalene		11	nd	33	21	7	20	7	18	3	nd
Acenaphthene		538	588	747	504	21	23	12	28	14	25
9H-Fluorene		710	865	1,180	820	26	30	27	90	16	24
Diethyl phthalate											
1-Methyl-9H-fluorene		150	98	129	90	6	nd	6	15	4	nd
Dibenzothiophene											
Phenanthrene		15,800	19,600	12,400	10,200	240	240	312	741	200	222
Anthracene		2,490	3,250	1,200	980	62	63	70	190	47	56
Phenanthridine											
9H-Carbazole											
2-Methylanthracene		393	454	222	215	14	30	14	42	12	20
4,5-Methylenephenanthrene		2,150	2,990	1,380	1,250	42	61	44	115	35	56
1-Methylphenanthrene		821	1,180	612	514	16	19	17	51	16	31
Anthraquinone											
Fluoranthene		50,200	68,000	21,100	20,000	508	494	653	1,100	633	614
Pyrene		40,700	54,000	14,800	13,500	431	390	492	850	502	476
1-Methylpyrene		1,100	3,460	553	585	21	37	22	49	20	34
Benz[*a*]anthracene		19,700	24,000	6,220	6,000	240	185	265	402	267	226
Chrysene		3,100	41,000	10,600	12,000	254	242	290	478	296	292
Bis(2-ethylhexyl) phthalate											
Benzo[*b*]fluoranthene		29,000	38,000	9,170	10,300	254	219	290	394	354	326
Benzo[*k*]fluoranthene		23,800	28,000	7,300	7,700	226	183	259	374	279	308
Benzo[*e*]pyrene		17,500	26,500	6,540	7,100	162	158	187	296	190	197
Benzo[*a*]pyrene		25,000	30,600	7,130	7,400	230	185	259	352	281	234
Perylene		6,220	8,300	1,790	3,600	344	356	217	323	447	530
Indeno[1,2,3-*c,d*]pyrene		29,300	33,600	6,890	5,880	227	170	150	260	288	221
Dibenz[*a,h*]anthracene		5,020	5,860	1,140	1,540	54	65	67	130	58	49
Benzo[*g,h,i*]perylene		20,000	28,500	5,930	4,040	134	154	150	260	152	189

Table 17. Soxhlet and accelerated solvent extraction concentrations, in micrograms per kilogram, for 28 sediment samples.—Continued

[ID, identification number; %, percent; OC, organic carbon; SOX, Soxhlet; ASE, accelerated solvent extraction; RT, retention time; ND, not determined; nd, not detected; <, less than]

Compound (RT order)	Lab ID:	20031200121		20031220186		20020450009	
	Matrix / % OC:	Core / ND		Core / ND		Clay / ND	
	Method:	SOX	ASE	SOX	ASE	SOX	ASE
Naphthalene		7	14	8	430	2	3
2-Ethylnaphthalene		4	8	3	256		
2,6-Dimethylnaphthalene		89	65	174	409	49	31
1,6-Dimethylnaphthalene		17	20	20	210	11	6
Acenaphthylene		11	19	12	131		
1,2-Dimethylnaphthalene		7	13	6	152	4	nd
Acenaphthene				20	135		
9H-Fluorene		8	14	21	96	3	7
Diethyl phthalate							
1-Methyl-9H-fluorene		4	nd	6	37		
Dibenzothiophene							
Phenanthrene		68	71	220	199	12	15
Anthracene		23	36	56	69	2	3
Phenanthridine							
9H-Carbazole							
2-Methylanthracene		7	nd	14	23	3	nd
4,5-Methylenephenanthrene		14	30	36	58	4	4
1-Methylphenanthrene		6	nd	16	25	2	nd
Anthraquinone							
Fluoranthene		198	177	520	408	11	16
Pyrene		153	143	409	327	6	10
1-Methylpyrene		9	nd	19	35		
Benz[*a*]anthracene		81	66	225	168	4	4
Chrysene		104	100	227	217	6	10
Bis(2-ethylhexyl) phthalate							
Benzo[*b*]fluoranthene		112	94	275	196	9	8
Benzo[*k*]fluoranthene		91	95	175	185	4	6
Benzo[*e*]pyrene		84	83	159	138	3	5
Benzo[*a*]pyrene		97	85	209	176	5	4
Perylene		317	360	515	600	165	206
Indeno[1,2,3-*c,d*]pyrene		62	65	205	168	4	nd
Dibenz[*a,h*]anthracene				41	55		
Benzo[*g,h,i*]perylene		61	82	114	140	2	nd

[1]Sample extracts required significant dilutions.

Table 18. Correlation of Soxhlet and accelerated solvent extraction results for 28 sediment samples.

[Ave, average; µg/kg, micrograms per kilogram; SOX, Soxhlet; ASE, accelerated solvent extraction; r^2, correlation coefficient; *m*, slope; *b*, intercept; *N*, total number of detection pairs if detected by both the ASE and Soxhlet method; NPE, number of points excluded]

Compound	Ave SOX (µg/kg)	Ave ASE (µg/kg)	r^2	*m*	*b*	*N*	NPE*
Naphthalene	21	69	0.827	1.4304	19	20	2
2-Ethylnaphthalene	11	28	0.832	1.8494	-2	7	1
2,6-Dimethylnaphthalene	145	155	0.801	0.6956	54	26	0
1,6-Dimethylnaphthalene	40	67	0.862	1.1617	20	22	0
Acenaphthylene	37	52	0.912	1.0808	18	14	2
1,2-Dimethylnaphthalene	13	19	0.651	0.8834	6	9	1
Acenaphthene	273	379	0.949	1.6687	-48	11	0
2,3,6-Trimethylnaphthalene	32	36	0.997	1.2188	-6	5	0
9H-Fluorene	272	396	0.938	1.7704	-62	16	0
Diethyl phthalate	8	4	0.278	0.3835	5	4	0
1-Methyl-9H-fluorene	42	72	0.908	1.2694	-8	8	0
Dibenzothiophene	30	32	0.764	1.8957	-25	5	0
Phenanthrene	1,597	1,569	0.979	1.0824	-4	21	1
Anthracene	588	912	0.992	1.7408	-111	19	0
9H-Carbazole	95	164	0.827	7.5696	-552	4	0
2-Methylanthracene	109	186	0.991	1.5710	-20	14	0
4,5-Methylenephenanthrene	261	341	0.981	1.2546	-9	16	1
1-Methylphenanthrene	106	148	0.967	1.2239	1	15	1
Anthraquinone	258	335	0.835	4.2777	-770	4	0
Fluoranthene	3,698	4,297	0.993	1.3012	-321	23	1
Pyrene	3,164	3,287	0.994	1.2871	-295	23	1
1-Methylpyrene	68	86	0.999	1.0401	9	13	2
Benz[*a*]anthracene	1,627	1,519	0.998	1.2017	-101	18	1
Chrysene	2,600	2,667	0.999	1.3040	-135	19	1
Bis(2-ethylhexyl) phthalate	255	164	0.888	0.6716	3	11	1
Benzo[*b*]fluoranthene	2,429	2,434	0.999	1.3004	-190	19	1
Benzo[*k*]fluoranthene	1,962	1,833	0.999	1.1689	-60	19	1
Benzo[*e*]pyrene	2,267	3,148	0.995	1.4758	-198	11	1
Benzo[*a*]pyrene	2,010	1,991	0.966	0.8969	8	17	3
Perylene	1,040	1,419	0.986	1.3714	-7	12	1
Indeno[1,2,3-*c,d*]pyrene	2,646	2,569	0.998	1.1361	-104	15	1
Dibenzo[*a,h*]anthracene	575	647	0.999	1.1701	27	12	1
Benzo[*g,h,i*]perylene	1,900	2,124	0.988	1.3801	-232	15	1

*Data point(s) were excluded from the correlation calculation because of possible dilution errors that might have resulted in significantly higher ASE concentrations than Soxhlet concentrations.

The average compound concentrations, slopes, and intercepts have been listed (table 18) to help compare the two methods. The average compound concentration recoveries using ASE generally are somewhat higher than by Soxhlet. A few very high concentrations, which required large extract dilutions (and possibly subject to dilution errors), were excluded from statistical calculations for some compounds (as footnoted in table 18) because least squares linear regression curves were excessively weighted toward the high measurements, thereby causing distorted average concentrations, slopes, and intercepts. Incidentally, all of the high concentrations that were excluded from the calculations were much higher by ASE than by Soxhlet extraction. For the more polar compounds, the average extraction efficiency generally is greater using ASE, as might be expected based on increased solubility in the more polar isopropyl alcohol/water extraction solvent. A few compounds (diethyl phthalate, 9H-carbazole, and anthraquinone) were only detected four times each (table 17), and thus, lack the necessary data to make meaningful correlations.

As was demonstrated with SRM 1944 (table 13), extraction of lower molecular weight PAH compounds, such as naphthalene and phenanthrene, from a variety of sediments also was more efficient by ASE than by Soxhlet, possibly because of increased solvent penetration from increased swelling of clay particles (Hawthorne, Trembley, and others, 2000). As the solubility of the PAHs in the hot isopropyl alcohol/water solvent mixture decreases (about the molecular weight of fluoranthene or higher), the correlation between the two methods is much better. This general trend of improved correlation with greater PAH molecular weight is shown in figure 3 for naphthalene and benzo[*a*]pyrene.

Figure 4 shows a boxplot for the ASE extraction results of 28 environmental sediment samples collected from throughout the United States. The samples are a mixture of soil, stream sediment, and suspended sediment, with the majority from urban sampling sites. The data are reported using a log scale to accommodate the large concentration ranges for each compound. At least one method compound was found in every environmental sample analyzed. Thirty-four compounds (excluding alkylated PAH homolog groups) were detected in at least one sample with concentrations ranging from 20 to 100,000 µg/kg. The most frequently detected compound, 2,6-dimethylnaphthalene, was detected in 23 of the 28 (82.1 percent) environmental samples with a concentration range of 15 to 907 µg/kg. At least one of the PAH homolog compounds was detected in 26 of the 28 samples (92.9 percent) with C_2-alkylated naphthalenes being detected in 26 samples. Thirteen out of 25 of the homolog groups (52 percent) were detected with concentrations ranging from 20 to 10,000 µg/kg. The C_1-alkylated PAHs accounted for 71 of the 185 (38.4 percent) alkylated PAH detections, whereas the C_2-alkylated and C_3-alkylated groups accounted for 35.1 and 22.2 percent of the detections, respectively. There were no detections greater than the minimum reporting level for C_4- and C_5-alkylated homolog groups. The absence of detections

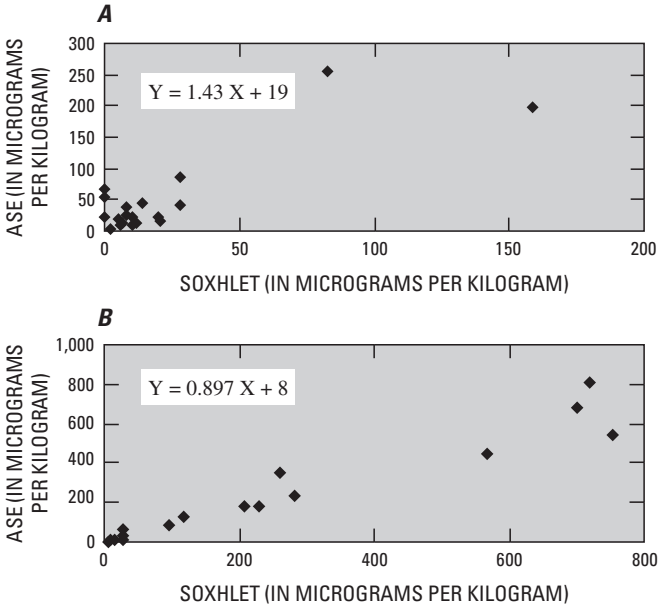

Figure 3. Least squares regression plots for concentrations of naphthalene (A) and benzo[*a*]pyrene (B) determined in 28 sediment samples by accelerated solvent extraction (ASE) and by Soxhlet extraction.

for the C_4- and C_5-alkylated homolog groups at or greater than the minimum reporting level also was observed for the NIST 1944 SRM. These results (concentration ranges and detection frequencies) demonstrate the usefulness of this method for determining the compound classes of interest in various sediment and soil types.

Summary and Conclusions

This report presents a method (U.S. Geological Survey National Water Quality Laboratory analytical method O-5506-06) for extracting environmental sediment samples with a commercially available Dionex ASE™ 200 instrument using accelerated solvent extraction (ASE). Water modified with isopropyl alcohol is used as the extraction solvent at elevated temperatures and pressure for the determination of 38 polycyclic aromatic hydrocarbons (PAHs) and semivolatile organic compounds with an additional option to report the semiquantitation of 25 alkylated PAH homolog groups, by gas chromatography/mass spectrometry. The concentrations of the alkylated PAH homolog groups are reported as estimated because of the lack of authentic standards.

This ASE method of sediment sample preparation has advantages over conventional Soxhlet extraction for sample automation, reduced extraction time, and reduced solvent volume. Sample preparation also is simplified over Soxhlet extraction with dichloromethane (DCM) because the ASE water/isopropyl alcohol extract is well suited for solid-phase extraction (SPE) extract cleanup, whereas DCM Soxhlet

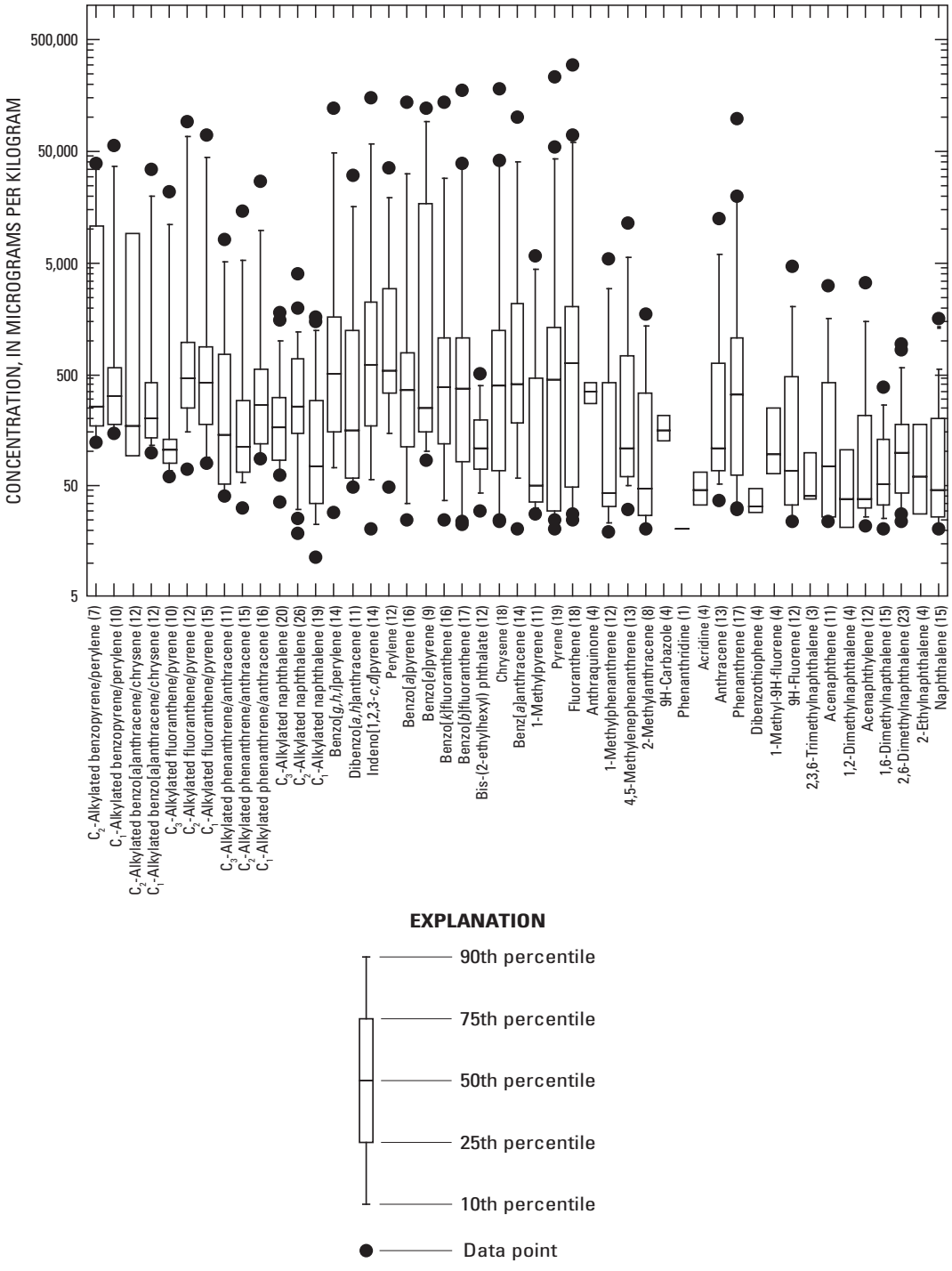

Figure 4. Results for analysis of 28 environmental soil and sediment samples. The concentration axis is in log scale to accommodate the large concentration ranges for the compounds of interest. The number of samples in which the compound was detected is listed after each compound name in parenthesis. Data points that are shown are outliers of the distribution.

extracts usually require a more complex gel permeation chromatography clean-up step.

The performance of the method (mean recovery and bias) was determined using Ottawa sand, a commercially available topsoil, and an environmental stream sediment, fortified at 1.5 and 15 micrograms per compound. The recoveries of PAH and semivolatile organic compounds from a 22-milliliter ASE cell filled with Ottawa sand (about 25 grams) fortified at 1.5 microgram per compound averaged 88 percent ± 9.4 percent relative standard deviation, and calculated initial method detection limits averaged 14 micrograms per kilogram (assuming a 25-gram sample size).

A National Institute of Standards and Technology certified natural marine sediment reference material (SRM 1944) was used to compare this ASE method with conventional 36-hour Soxhlet extraction using DCM. The recovery of low molecular weight PAH compounds (for example, naphthalene, phenanthrene, and anthracene) was greater by 10 to 20 percent using this ASE method compared to certified concentrations obtained by Soxhlet extraction. The recoveries for higher molecular weight PAH compounds were somewhat less than certified concentrations, but were identical to those obtained by the U.S. Geological Survey (USGS) Soxhlet extraction method. Method precision for the certified PAH compounds was between about 7 to 15 percent relative standard deviation in the reference material. Although absolute concentrations of alkylated PAH homolog groups in the reference material were not certified, their recoveries were similar to those obtained by the USGS Soxhlet extraction method, and precision was less than 12 percent relative standard deviation.

Replicate sample results for a diverse group of 28 environmental sediments also were used to compare ASE extraction with the existing USGS Soxhlet extraction. The same recovery trends for PAHs observed for SRM 1944 also were manifest in the sediment samples because compound correlations improved with increasing PAH molecular weight. The average compound concentration recoveries, slopes, and intercepts also were listed to help compare the two methods. The average extraction efficiency for the more polar compounds was greater using this ASE method, as might be expected based on increased solubility in the more polar isopropyl alcohol/water solvent.

The extraction of solids using this ASE method for the determination of PAHs and semivolatile compounds will augment other methods at the National Water Quality Laboratory to better understand their presence, fate, transport, and temporal and spatial distribution in the environment.

References Cited

Anderson, R.L., 1987, Practical statistics for analytical chemists: New York, VanNostrand Reinhold, 316 p.

Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T. J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p.

Curren, M.S.S., and King, J.W., 2001, Ethanol-modified subcritical water extraction combined with solid-phase microextraction for determining atrazine in beef kidney: Journal of Agricultural and Food Chemistry, v. 49, p. 2175–2180.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Furlong, E.T., Vaught, D.G., Merten, L.M., Foreman, W.T., and Gates, P.M., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of semivolatile organic compounds in bottom sediment by solvent extraction, gel permeation chromatographic fractionation, and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 95–719, 67 p.

Hawthorne, S.B., Grabanski, C.B., Martin, E., and Miller, D.J., 2000, Comparison of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction, and subcritical water extraction of environmental solids—Recovery, selectivity, and effects of sample matrix: Journal of Chromatography A, v. 892, p. 421–433.

Hawthorne, S.B., Trembley, S., Moniot, C.L., Grabanski, C.B., and Miller, D.J., 2000, Static subcritical water extraction with simultaneous solid-phase extraction for determining polycyclic aromatic hydrocarbons on environmental solids: Journal of Chromatography A, v. 886, p. 237–244.

Mahler, B.J., and Van Metre, P.C., 2003, A simplified approach for monitoring hydrophobic organic contaminants associated with suspended sediment—Methodology and applications: Archives of Environmental Contamination and Toxicology, v. 44, no. 3, p. 288–297.

Maloney, T.J., ed., 2005, Quality management system, U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 2005-1263, version 1.3, 9 November 2005, variously paginated. Accessed April 25, 2006, at *http://pubs.usgs.gov/of/2005/1263*

Nauss, K.M., 1995, Critical issues in assessing the carcinogenicity of diesel exhaust—A synthesis of current knowledge, *in* Diesel exhaust—A critical analysis of emissions, exposure, and health effects: Cambridge, Mass., Health Effects Institute, p. 11–61.

Northcott, G.L., and Jones, K.C., 2000, Developing a standard spiking procedure for the introduction of hydrophobic organic compounds into field-wet soil: Environmental Toxicology and Chemistry, v. 19, p. 2409–2417.

Olson M.C., Iverson, J.L., Furlong, E.T., and Schroeder, M.P., 2004, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of polycyclic aromatic hydrocarbon compounds in sediment by gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 03-4318, 45 p.

Radtke, D.B., 1997, Bottom-material samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A8, accessed December 14, 2004, at *http://pubs.water.usgs.gov/twri9A8/*

Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water Quality Assessment Program: U.S. Geological Survey Open-File Report 94-0458, 20 p.

Timme, P.J., 1995, National Water Quality Laboratory 1995 services catalog: U.S. Geological Survey Open-File Report 95–352, 92 p.

U.S. Environmental Protection Agency, 1997, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, p. 265–267.

U.S. Environmental Protection Agency, 1998, Evaluation of dredged material proposed for discharge in waters of the U.S.—Testing manual: EPA 823-B-98-004, February 1998, section 8.2.6 and table 8-2, accessed May, 17, 2005, at *http://www.epa.gov/waterscience/itm/*

U.S. Environmental Protection Agency, 2000, Method series 3545A, Pressurized fluid extraction, *in* Federal Register: Waste Management System; Testing and Monitoring Activities; draft update IVB of SW-846, accessed December 16, 2004, at *http://www.epa.gov/EPA-WASTE/2000/November/Day-27/f30111.htm*

U.S. Environmental Protection Agency, 2004a, EPI-suite website, accessed March 22, 2004, at *www.epa.gov/opptintr/exposure/docs/episuite.htm*

U.S. Environmental Protection Agency, 2004b, Method 8270c website, accessed October 27, 2004, at *www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf*

Van Metre, P.C., Wilson, J.T., Fuller, C.C., Callender, Edward, Mahler, B.J., 2004, Collection, analysis, and age-dating of sediment cores from 56 U.S. lakes and reservoirs sampled by the U.S. Geological Survey, 1992–2001: U.S. Geological Survey Scientific Investigations Report 2004–5184, 180 p.

Walker, S.E., Dickhut, R.M., Brause, C.C., Sylvia, S., Reddy, C.M., 2005, Molecular and isotopic identification of PAH sources in a highly industrialized urban estuary: Organic Geochemistry, v. 36, p. 619–632.

Wang, Zhendi, Fingas, Merv, and Li, Ken, 1994, Fractionation of a light crude oil and identification and quantitation of aliphatic, aromatic, and biomarker compounds by GC–FID and GC–MS, Parts I and II: Journal of Chromatographic Science, v. 32, p. 361–382.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, p. 79 and 80.

Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4186, 37 p.

Glossary

Continuing calibration verification (CCV) A standard solution that contains method compounds and is used to determine the bias of the present calibration curve for the method compounds. The CCV is an instrumental standard only and is not processed through preparative steps of the method.

Internal standard (IS) A compound not expected to be found in any environmental sample that is added to every sample extract in a known amount. The internal standard is used to measure the relative gas chromatographic/mass spectrometric (GC/MS) responses of other compounds and surrogates in each sample.

Long-term method detection level (LT–MDL) The minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero. The LT–MDL is calculated from replicate analyses of samples fortified with all the method compounds, and includes precision introduced by multiple instruments, multiple analysts, and multiple calibrations from 6 to 12 months (Childress and others, 1999).

Method detection limit (MDL) The minimum concentration of a substance that can be measured and reported with 99-percent confidence that the compound concentration is greater than zero (U.S. Environmental Protection Agency, 1997). The MDL is calculated from at least seven replicate analyses of samples fortified with all the method compounds. The MDL is used to establish initial method reporting levels, until the long-term method detection level can be calculated to include day-to-day precision.

Minimum reporting level (MRL) The lowest measured concentration of a compound that may be reliably reported by using a given analytical method (Timme, 1995).

Surrogate A compound not expected to be found in any environmental sample that is added to every sample in a known amount prior to sample processing. The surrogate is used to monitor method performance for each sample.

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