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

By Edward T. Furlong, Deborah G. Vaught, Leslie M. Merten, William T. Foreman, and Paul M. Gates

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND ADDITIONAL ABBREVIATIONS AND SYMBOLS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	3.38×10^{1}	ounce, fluid
meter (m)	3.3×10^{0}	foot
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
microliter (µL)	3.38×10^{-5}	ounce, fluid
micrometer (µm)	3.94×10^{-5}	inch
milliliter (mL)	3.38×10^{-2}	ounce, fluid
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
nanometer (nm)	3.94×10^{-8}	inch
picogram (pg)	3.53×10^{-14}	ounce, avoirdupois

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5(°C) + 32.$$

Abbreviated water-quality units used in this report:

°C	degree Celsius
°C/min	degree Celsius per minute
cm/s	centimeter per second
µg/kg	microgram per kilogram
mg/L	milligram per liter
mL/min	milliliter per minute
ng/µL	nanogram per microliter
pg/µL	picogram per microliter

Other abbreviations and symbols used in this report :

ACS	American Chemical Society
amu	atomic mass unit
CAS	Chemical Abstracts Service
CCV	continuing calibration verification solution
DFTPP	decafluorotriphenylphosphine
dPAH	perdeuterated polycyclic aromatic hydrocarbon
ECD	electron capture detector
eV	electron volts
FEP	fluorinated ethylene propylene
GC	gas chromatographic (or gas chromatograph)
GC/ECD	gas chromatography with electron capture detection
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HPLC	high-pressure liquid chromatography
ID	internal diameter
K-D	Kuderna-Danish
MDL	method detection limit
MS	mass spectrometric (or mass spectrometer)
NIST	National Institute of Standards and Technology
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
N-Evap	nitrogen gas evaporator
OC	organochlorine
OCIIS	organochlorine internal injection standard
PAH	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PTFE	polytetrafluoroethylene
QC	quality control
rpm	revolutions per minute
RRT	relative retention time
SOC	semivolatile organic compound
SOCIIS	semivolatile organic compound internal injection standard solution
SRM	Standard Reference Material
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
Wt.	weight
±	plus or minus
<	less than

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ABSTRACT

A method for the determination of 79 semivolatile organic compounds (SOCs) and 4 surrogate compounds in soils and bottom sediment is described. The SOCs are extracted from bottom sediment by solvent extraction, followed by partial isolation using high-performance gel permeation chromatography (GPC). The SOCs then are qualitatively identified and quantitative concentrations determined by capillary-column gas chromatography/mass spectrometry (GC/MS). This method is designed for simultaneous isolation of organochlorine (OC) pesticides, including toxaphene and polychlorinated biphenyls (PCBs). When OCs and PCBs are determined, an additional alumina-over-silica column chromatography step follows GPC cleanup, and quantitation is by dual capillary-column gas chromatography with electron-capture detection (GC/ECD).

Bottom-sediment samples are centrifuged to remove excess water and extracted overnight with dichloromethane. The extract is concentrated, centrifuged, and then filtered through a 0.2-micrometer polytetrafluoroethylene syringe filter. Two aliquots of the sample extract then are quantitatively injected onto two polystyrene-divinylbenzene GPC columns connected in series. The SOCs are eluted with dichloromethane, a fraction containing the SOCs is collected, and some coextracted interferences, including elemental sulfur, are separated and discarded. The SOC-containing GPC fraction then is analyzed by GC/MS. When desired, a second aliquot is further processed for OCs and PCBs by combined alumina-over-silica column chromatography. The two fractions produced in this cleanup then are analyzed by GC/ECD.

At a spike concentration of 800 micrograms per kilogram (µg/kg), recoveries ranged from 17.9 to 117.3 percent, with a mean recovery of 77.4 percent. At a spike concentration of 2,000 µg/kg, recoveries ranged from 1.3 to 106.4 percent, with a mean percent recovery of 61.4 percent. The corresponding variation in recoveries is reflected in both the standard deviations for individual SOCs and the standard deviation of recovery for all SOCs. These standard deviations average ±13.2 percent and ranged from 1.6 to 33.9 percent for individual SOCs spiked at

800 µg/kg. Standard deviations average ±5.2 percent and ranged from ±1.6 to ±33.9 percent for individual SOCs spiked at 2,000 µg/kg. This report fully describes and is limited to the determination of SOCs by GC/MS .

INTRODUCTION

Semivolatile organic compounds (SOCs) are operationally defined as solvent-extractable organic compounds that can be analyzed by gas chromatography. As a class, SOCs usually refer, but are not limited to, petroleum-derived compounds, polycyclic aromatic hydrocarbons (PAH), other industrially derived compounds, and polychlorinated organic compounds. Many SOCs are associated with solids in hydrologic environments. These solids include soils, bottom sediment, and suspended sediment, consisting of inorganic particles coated with heterogeneous organic matter. Both particle size and concentration of heterogeneous organic matter control the concentration of solids-associated SOCs. This method was devised to efficiently extract SOCs from a sediment or solids matrix and to partially isolate them from coextracted natural organic matter and elemental sulfur prior to instrumental analysis.

This method includes elements of U.S. Geological Survey (USGS) method O-5116-83 (semivolatile compounds, recoverable from bottom material) and O-3116-87 (base/neutral and acid extractable compounds, gas chromatography/mass spectrometry; Fishman, 1993, p. 27; Wershaw and others, 1987). It also uses elements of U.S. Environmental Protection Agency (USEPA) methods 3540B (Soxhlet Extraction), 3640A (Gel-Permeation Cleanup), 8080A (Organochlorine Pesticides and PCBs by Gas Chromatography), and 8270B (Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique); (U.S. Environmental Protection Agency, 1994).

There are several significant advantages of this method over previously used methods. The gel permeation step eliminates many co-extracted chemical interferences, reducing chemical noise contributions to the sample instrumental analysis and improving method detection limits. The gel permeation chromatography step itself has been miniaturized so that waste organic solvent volumes, associated disposal costs, and health risks are reduced. Compounds have been added to this method that have not been determined by previous USGS or USEPA methods, reflecting demand throughout the U.S. Geological Survey. One unique feature of this method is that it has been designed so that organochlorine (OC) insecticides and polychlorinated biphenyls (PCBs) can be determined from the same sediment sample extract. The determination of OC pesticides and PCBs is described in Foreman and others (1995).

The method described in this report supplements other USGS methods for determination of organic substances in bottom sediment described by Fishman (1993) and by Wershaw and others (1987). This method was initially implemented

in the National Water Quality Laboratory (NWQL) in January 1993. As a consequence of using the method under routine production, it was improved and enhanced, with final implementation in May 1993.

This report provides a detailed description of all aspects of the method from sampling protocol through calculation and reporting of results. Recovery data and method detection limits (MDLs) for 79 SOCs and 4 surrogate compounds are presented.

The development and implementation of a complex and comprehensive analytical chemical method, such as the method described in this report, requires extraordinary efforts from a large number of individuals. Substantial contributions were made to this report by Mary C. Olson, Jana L. Iverson, Larry S. Burt, and Dan A. Bottinelli. The report authors also acknowledge the following NWQL staff for their assistance in the design, development, testing, and implementation of this method: C.W. Roberts, Steve Werner, Janece Koleis, Robin Petrusak, Mark Sandstrom, and Tom Leiker of the Methods Research and Development Program; Craig Stapert, Jeff Deacon, and Brooke Connor of the Organic Chemistry Program; and Kim Pirkey and Surann Horodyski of the Quality Management Program. We would like to particularly acknowledge the assistance of Barbara Kemp in manuscript preparation.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Semivolatile organic compounds, bottom sediment, high-performance gel permeation chromatography, capillary-column gas chromatography/mass spectrometry, O-5130-95 (see table 1)

1. Scope and application

This method is suitable for the determination of semivolatile organic compounds (SOCs: a subset of the compounds identified by the USEPA as priority pollutants) in soils and sediment samples containing at least 50 µg/kg of each compound. This method is applicable to SOCs that are (1) efficiently extracted from the solid matrix by methanol or dichloromethane, (2) adequately separated from natural coextracted compounds by gel permeation chromatography (GPC), and (3) sufficiently volatile and thermally stable for gas chromatography/mass spectrometry (GC/MS). The SOCs determined using this method, the NWQL code, and Chemical Abstracts Service (CAS) number for each compound are listed in table 1.

Table 1. *Semivolatile organic compounds determined using this method*

[NWQL, National Water Quality Laboratory; CAS , Chemical Abstracts Service; GPC, gel permeation chromatography. Compounds designated with an asterisk (*) were inconsistently recovered in this method. Reported concentrations of these compounds are estimates]

Compound name	NWQL code	Parameter code	CAS number
Acenaphthene	5211	49429	83-32-9
Acenaphthylene	5212	49428	208-96-8
Acridine	5276	49430	260-94-6
C8-Alkylphenol	5256	49424	
Anthracene	5213	49434	120-12-7
Anthraquinone	5283	49437	84-65-1
Azobenzene	5272	49443	103-33-3
Benz[*a*]anthracene	5217	49436	218-00-9
Benzo[*c*]cinnoline	5280	49468	230-17-1
Benzo[*b*]fluoranthene	5218	49458	205-99-2
Benzo[*k*]fluoranthene	5220	49397	207-08-9
Benzo[*ghi*]perylene	5219	49408	191-24-2
Benzo[*a*]pyrene	5221	49389	50-32-8
2,2'-Biquinoline	5285	49391	119-91-5
bis(2-Chloroethoxy)methane	5214	49401	111-91-1
bis(2-Chloroethyl)ether	5215	49456	111-44-4
bis(2-Chloroisopropyl)ether*	5216	49457	108-60-1
bis(2-Ethylhexyl)phthalate	5223	49426	117-81-7
4-Bromophenyl-phenylether	5208	49454	101-55-3
Butylbenzylphthalate	5224	49427	85-68-7
9H-Carbazole	5278	49449	86-74-8
4-Chloro-3-methylphenol	5262	49422	59-50-7
2-Chloronaphthalene	5207	49407	91-58-7
2-Chlorophenol	5289	49467	95-57-8
4-Chlorophenyl-phenylether	5209	49455	7005-72-3
Chrysene	5225	49450	218-00-9
p-Cresol	5254	49451	106-44-5
Dibenz[*a,h*]anthracene	5232	49461	53-70-3
Dibenzothiophene	5275	49452	132-65-0
Di-*n*-butylphthalate	5235	49381	84-74-2
1,2-Dichlorobenzene	5234	49439	95-50-1
1,3-Dichlorobenzene	5222	49441	541-73-1
1,4-Dichlorobenzene	5233	49442	106-46-7
2,4-Dichlorophenol	5257	49417	120-83-2
Diethylphthalate	5237	49383	84-66-2

Table 1. *Semivolatile organic compounds determined using this method*--Continued

Compound name	NWQL code	Parameter code	CAS number
1,2-Dimethylnaphthalene	5267	49403	573-98-8
1,6-Dimethylnaphthalene	5266	49404	575-43-9
2,6-Dimethylnaphthalene	5265	49406	581-42-0
3,5-Dimethylphenol	5258	49421	108-68-9
Dimethylphthalate	5238	49384	131-11-3
4,6-Dinitro-2-methylphenol*	5271	49419	534-56-1
2,4-Dinitrophenol*	5268	49418	51-28-5
2,4-Dinitrotoluene	5203	49395	121-14-2
2,6-Dinitrotoluene	5205	49396	606-20-2
Di-*n*-octylphthalate	5239	49382	117-84-0
2-Ethylnaphthalene	5264	49948	939-27-5
Fluoranthene	5240	49466	206-44-0
9H-Fluorene	5210	49399	86-73-7
Hexachlorobenzene	5228	49343	118-74-1
Hexachlorobutadiene*	5229	49448	87-68-3
Hexachlorocyclopentadiene*	5230	49489	77-47-4
Hexachloroethane*	5231	49453	67-72-1
Indeno[1,2,3-*cd*]pyrene	5241	49390	193-39-5
Isophorone	5242	49400	78-79-1
Isoquinoline	5261	49394	119-65-3
2-Methylanthracene	5279	49435	613-12-7
1-Methyl-9H-fluorene	5273	49398	1730-37-6
1-Methylphenanthrene	5282	49410	832-69-9
1-Methylpyrene	5284	49388	2381-21-7
4,5-Methylenephenanthrene	5281	49411	203-64-5
Naphthalene	5246	49402	91-20-3
Nitrobenzene	5247	49444	98-95-3
2-Nitrophenol*	5255	49420	88-75-5
4-Nitrophenol*	5269	49423	100-02-7
N-Nitrosodi-*n*-propylamine	5245	49431	621-64-7
N-Nitrosodiphenylamine	5244	49433	156-10-5
Pentachloroanisole	5274	49460	1827-21-4
Pentachloronitrobenzene	5226	49446	82-68-8
Pentachlorophenol*	5227	49425	87-86-5
Phenanthrene	5248	49409	85-01-8

Table 1. *Semivolatile organic compounds determined using this method*--Continued

Compound name	NWQL code	Parameter code	CAS number
Phenanthridine	5277	49393	229-87-8
Phenol	5249	49413	108-95-2
Pyrene	5252	49387	129-00-0
Quinoline	5260	49392	91-22-5
2,3,5,6-Tetramethylphenol*	5263	49414	527-37-5
1,2,4-Trichlorobenzene	5201	49438	120-82-1
2,4,6-Trichlorophenol*	5204	49415	88-06-2
2,3,6-Trimethylnaphthalene	5270	49405	829-26-5
2,4,6-Trimethylphenol*	5259	49416	527-60-6
Benzo[*e*]pyrene-d_{12} (GPC surrogate)			
2-Fluorobiphenyl (method surrogate)	5288	49279	
Nitrobenzene-d_5 (method surrogate)	5287	49280	
Terphenyl-d_{14} (method surrogate)	5286	49278	
Laboratory set identifier	5290	99825	

2. Summary of method

An outline of the analytical method described in this report is shown in figure 1. The following is a brief summary.

2.1 Wet sediment samples are weighed, centrifuged to remove water, then mixed with preweighed amounts of anhydrous sodium sulfate to absorb residual moisture. The loose porous mixture formed is weighed into a glass thimble. Methanol (25 mL) is percolated through the sample to remove any water not bound by the sodium sulfate, and the sample then is extracted with 350 mL of dichloromethane for a minimum of 12 hours or overnight.

2.2 The combined wash and extract solvents are dried over sodium sulfate and reduced to 4 mL. Sulfur and some coextracted interferents are removed by the following GPC procedure. First, an aliquot of a GPC surrogate solution is added to each sample prior to isolation, to quantitatively assess GPC performance. Then a 1,400-µL aliquot of the sample extract is quantitatively injected onto a styrene-divinylbenzene GPC column and eluted with dichloromethane at a flow rate of 1 mL/min. Interferences elute from the column for about the first 13 minutes of the analysis and are not collected. The compounds then are collected in an approximately 8.6-mL fraction. Sulfur elutes immediately after this fraction and is not collected. When SOCs, OC pesticides, and PCBs are to be determined from a single extract, two separate aliquots are processed through the GPC from one extract. A 1,400-µL aliquot is processed for semivolatile compounds, and a 1,100-µL aliquot is processed for organochlorine compounds.

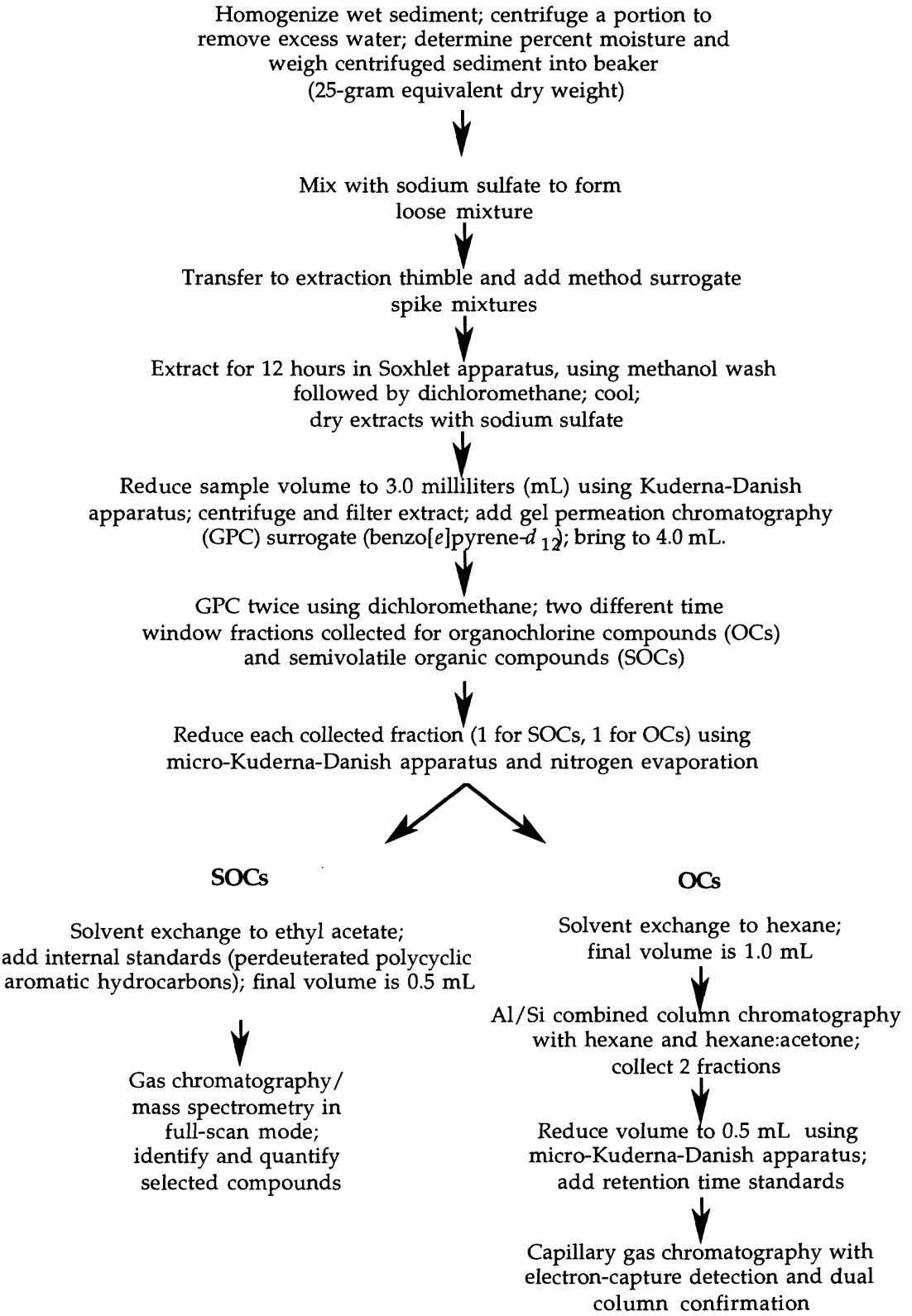


Figure 1. Flow path for this semivolatile organic compound method.

2.3 The fraction collected for semivolatile compounds from GPC is exchanged into ethyl acetate and reduced to 0.5 mL. A perdeuterated polycyclic aromatic hydrocarbon (dPAH) injection internal standard solution (50 µL) is added to each extract. The extract-containing vial then is sealed with a Teflon™ faced, silicone rubber septum. The final sample extract is held at -15°C until analysis.

2.4 The instrumental analysis consists of a gas chromatographic (GC) separation of the compounds followed by mass spectrometric (MS) identification and quantitation. These two components are integrated into a single instrument, commonly referred to as GC/MS. A 2-µL aliquot of sample extract is withdrawn by an autosampler and injected into the GC . The compounds are separated within the GC using a fused-silica capillary column with temperature programming to optimize compound separation. The compounds elute from the GC column into the MS source, where they are ionized by electron-impact ionization at 70 electron volts (eV). The ions pass through a quadrupole mass analyzer, where they are sorted by mass-to-charge ratio. The ion signal is detected and amplified by an electron multiplier. The amplified ion signal is collected for 1-second intervals and stored electronically as full-scan spectra. The SOCs are identified by comparison to a library of reference spectra. Quantitation is by the internal standard method using a multiple-point calibration curve.

3. Interferences

Organic compounds that are coextracted, collected in the GPC fraction, and have GC retention times and characteristic ions with masses identical to those of the selected SOCs of interest might interfere. In particular, hydrocarbons and hydrocarbon degradation products can significantly interfere in this analytical method.

4. Apparatus and equipment

The equipment required for this method follows. Specific models and sources that were used for the development of this method are also listed, as appropriate.

4.1 *Sample storage, dewatering, and percent moisture determination*

4.1.1 *Freezer*--upright, capable of storing 100 or more 1,000-mL wide-mouth jars at -15°C for up to 1 year.

4.1.2 *Centrifuge*--with four-place rotor, capable of 5,000 relative centrifugal force, International Equipment Co. Model EXD or equivalent.

4.1.3 *Centrifuge bottles*--250-mL Teflon (FEP) with sealing cap assemblies and centrifuge bottle adapter.

4.1.4 *Analytical balance*--top loading, capable of weighing 250 ±0.1 g.

4.1.5 *Moisture determination balance*--capable of moisture determination on a 1.8- to 2.2-g aliquot of sediment sample to ±0.1 percent moisture, Sartorius Corp. Thermo Control Balance Model YTC O1L or equivalent.

4.1.6 *Glass beakers*--borosilicate, 400-mL volume.

4.2 *Sediment extraction*

4.2.1 *Soxhlet apparatus*--85-mL extractor capacity, with 45/50 standard taper-top joint and 24/40 standard taper-bottom joint; fitted with a 500-mL round- or flat-bottom flask with a 24/40 standard taper joint and an Allihn extractor condenser with 45/50 bottom joint.

4.2.2 *Soxhlet extraction sample thimble*--borosilicate glass, 35 x 90 mm, Kontes, Inc. Model K-586500-0022EC or equivalent.

4.2.3 *Soxhlet extraction combined steam bath/condenser unit*--Organomation Associates, Inc. Model 13055 ROT-X-TRACT or equivalent.

4.2.4 *Fixed volume micropipet*--50, 100, and 200 µL sizes, Drummond micropipetor-microdispenser or equivalent.

4.2.5 *Separatory funnel*--1-L volume.

4.3 *Sediment extract concentration*

4.3.1 *Kuderna-Danish (K-D) evaporative concentrator*--500-mL flask, three-ball Snyder column, and a custom-designed 10-mL centrifuge receiver (see 4.3.2), all with 19/22 standard taper joints.

4.3.2 *Centrifuge receiver tube*--10 mL, made using the top of a 10-mL K-D receiver tube, with 19/22 standard female taper joint, fused to an 8-cm long by 1.6-cm outer diameter centrifuge tube volume graduated at 2, 3 and 5 mL; Allen Scientific Glassblowers, Inc. ASG-215-01 or equivalent.

4.3.3 *Kuderna-Danish combined steam bath/condenser unit*--Organomation Associates, Inc. Model 120 S-EVAP or equivalent.

4.3.4 *Nitrogen manifold sample concentrator*--Organomation Associates, Inc. Model 124 N-Evap or equivalent.

4.4 *Sediment extract filtration*

4.4.1 *Centrifuge*--International Equipment Co. Model HN-SII or equivalent.

4.4.2 *Syringe*--5-mL gas-tight or ground-glass syringe equipped with Luer-Lok™ fitting.

4.5 *Gel permeation chromatography*

4.5.1 *Gel permeation chromatography system*--an automated GPC system consisting of the following components from Waters Corporation or equivalent.

4.5.1.1 *High-performance liquid chromatography (HPLC) pump*--Model 501.

4.5.1.2 *Autosampler*--Model 717 with 2-mL injection loop capacity with tray storage region maintained at 20°C.

4.5.1.3 *Absorbance detector*--Model 441, with excitation wavelength set at 254 nm.

4.5.1.4 *Data module and integrator*--Model 746.

4.5.1.5 *Fraction collector*--no model number, fitted with in-house made tube holder capable of holding 36, 25-mL K-D receiver tubes.

4.5.1.6 *HPLC in-line precolumn filter unit*--Model WATO84560, with replaceable 0.2-µm filters.

4.5.1.7 *Column heater*--set at 27.0°C; Jones Chromatography Ltd. or equivalent.

4.5.1.8 *Nitrogen pressurization system*--consisting of a regulated grade 5 nitrogen source, PTFE tubing, a 23-gauge needle, and associated metal fittings and ferrules for connecting the needle to the nitrogen source via the tubing.

4.5.1.9 *Helium sparging system*--used for deoxygenating the dichloromethane solvent prior to GPC.

4.5.1.10 *HPLC pump priming syringe*--25 mL, Hamilton Gas-Tight 1,000 Series, Model 82520 or equivalent.

4.5.1.11 *Balance*--capable of weighing to 200 ± 0.0001 g; Mettler-Toledo Model AT 200 or equivalent.

4.5.1.12 *K-D receiver tube*--calibrated 25-mL volume, with 19/22 ground-glass stopper.

4.6 *GPC fraction concentration and solvent exchange*

4.6.1 *Water bath*--Precision Scientific Co. Model 82 or equivalent, fitted with a rack capable of holding at least eighteen 25-mL receiver tubes.

4.6.2 *Micro-Snyder column*--three-ball.

4.7 *Fraction concentration*

4.7.1 *Syringe*--10-µL volume; Hamilton Co. Model 80366 or equivalent; for addition of internal injection standard solution.

4.8 *Gas chromatography/mass spectrometry analysis*

4.8.1 *Gas chromatograph/mass spectrometer*--Hewlett-Packard 5989B MS Engine coupled to a Hewlett-Packard 5890 gas chromatograph, 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.

4.8.2 *Syringe*--10-µL volume; Hamilton Co. Model 80377 for GC autosampler or equivalent.

4.9 *Instrument calibration and spike standards solution preparation*

4.9.1 *Analytical balance*--capable of accurately weighing to 0.0001 g.

4.9.2 *Volumetric flasks*--varied volumes from 1- to 1,000-mL.

4.9.3 *Micropipets*--fixed- and variable-volume pipets from 25 to 250 µL.

4.9.4 *Syringes*--variable volumes from 10- to 500-µL.

5. Reagents and consumable materials

The reagents and consumable materials required for this method, listed as follows, are grouped by the specific preparation or analysis part of the method but are not repeated if used in more than one part of the method. Specific models and sources that were used for the development or implementation of this method also are listed, as appropriate.

5.1 *Sample storage, dewatering, and percent moisture determination*

5.1.1 *Sample containers*--wide-mouth, 1,000 mL, with PTFE-lined lids.

5.1.2 *Weighing boats*--disposable, aluminum, 5.1-cm diameter.

5.1.3 *Sodium sulfate*--anhydrous, granular, reagent grade, bake at 450°C for 8 hours and store in a ground-glass stoppered flask in a desiccator until used.

5.2 *Sediment extraction*

5.2.1 *Solvents*--dichloromethane and methanol, pesticide grade, or higher purity.

5.2.2 *Boiling chips*--preextract with dichloromethane and bake at 450°C for 8 hours.

5.2.3 *Disposable glass capillaries*--to fit the 10-, 25-, 50-, 100-, 200-, and 250-µL fixed-volume micropipets described in sections 4.2.4 and 4.9.3. Clean the glass capillaries by baking at 450°C for 8 hours.

5.2.4 *SOC surrogate solution*--contains nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-d_{14} obtained from Supelco, Inc. Dilute purchased intermediate concentration solutions to a final solution concentration of 40 ng/µL of each component in methanol. Add or substitute other appropriate surrogate compounds into this method after demonstrating acceptable method performance.

5.2.5 *Individual SOC spike solution*--contains the individual SOC compounds listed in table 1. Obtain three concentrated solutions, each containing a subset of the semivolatile compounds, from Supelco, Inc. A fourth solution was formulated in-house from individual standards. Subsequently this fourth solution was obtained from Protocol Analytical Laboratories. 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 concentration of each component is 50 ng/µL in dichloromethane.

5.2.6 *Standard reference materials (SRMs) or other quality-control (QC) reference materials*--Any SRM, round-robin, or other sediment or soil reference material available to test the method for recovery of some or all of the selected compounds may be an appropriate QC material. No single SRM currently available contains all of the compounds determined using this method. Suitable SRMs, containing subsets of compounds determined using this method, include:

5.2.6.1 *SRM 1941*--National Institute of Standards and Technology (NIST) Organics in Marine Sediment SRM.

NOTE 1: SRM 1941 is no longer available from NIST. It has been replaced with SRM 1941a, a verified renewal SRM, which should be suitable.

5.2.6.2 *Semivolatiles in soil QC material*--Environmental Resource Associates PriorityPollunT™ spiked soil, catalog number 720.

5.3 *Sediment extract concentration*

5.3.1 *Nitrogen gas*--for solvent evaporation, grade 5 or equivalent.

5.4 *Sample extract filtration*

5.4.1 *Filter*--0.2-µm pore size, 25-mm diameter disposable PTFE membrane syringe filter, Gelman Sciences Acrodisc™ CR or equivalent.

5.4.2 *Pasteur pipets*--disposable with rubber bulbs.

5.4.3 *GPC vial, 4-mL*--with open-top screw-cap and PTFE-faced silicone rubber septum. Supelco, Inc. part numbers 2-3219M, 2-3261M, and 3-3185M or equivalent.

5.4.4 *GPC-SOC surrogate solution*--contains benzo[*e*]pyrene-d_{12} at a concentration of 80 ng/µL in dichloromethane. Make solution from a neat standard, Cambridge Isotope Laboratories or equivalent.

5.5 *Gel permeation chromatography*

5.5.1 *Helium gas*--grade 5 or equivalent.

5.5.2 *Gel permeation chromatography columns*--two 30-cm-long by 7.5-mm ID columns packed with 5-µm diameter styrene-divinylbenzene resin particles having 50 Angstrom pore size; Polymer Laboratories, Ltd. PL Gel™ or equivalent. Connect the columns in series with a low dead-volume union.

5.5.3 *GPC-SOC fraction test solution*--contains di-*n*-octylphthalate, benzo[*ghi*]perylene and elemental sulfur, each at a maximum concentration of 250 pg/µL in dichloromethane. Note that an equivalent OC pesticide fraction test solution is used for determining the OC pesticide collection window when an aliquot of the sample extract is processed for OC pesticides. For specific details, refer to Foreman and others (1995).

5.6 *GPC fraction concentration and solvent exchange*

5.6.1 *Ethyl acetate*--pesticide-residue grade, or higher purity.

5.7 *Fraction concentration*

5.7.1 *Vial*--1.5- or 2-mL, amber glass, with aluminum crimp caps that have dual PTFE-faced silicone rubber septa.

5.7.2 *SOC internal injection standard (SOCIIS) solution*--contains the dPAH naphthalene-d_8, phenanthrene-d_{10}, fluoranthene-d_{10}, perylene-d_{12},

benzo[*ghi*]perylene-d_{12}, and chrysene-d_{12}, all at 50 ng/µL in ethyl acetate. This standard solution is made from individual neat standards, available from Cambridge Isotope Laboratories or equivalent.

5.8 *Gas chromatography/mass spectrometry analysis*

5.8.1 *Capillary GC column*--fused-silica, 30-m long by 0.32-mm ID, internally coated with a 5 percent diphenyl and 95 percent dimethyl polysiloxane stationary phase having a 0.25-µm film thickness; Restek Corp. Rt_x-5™ or equivalent.

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

5.8.3 *Silanizing reagent*--for deactivating GC injection-port liners; Supelco, Inc. Sylon CT or equivalent.

5.9 *Instrument calibration and quality-control solution preparation*

5.9.1 *GC/MS calibration standard solution*--Prepare working standards of the entire suite of individual SOC compounds listed in table 1 at 0.5, 1.0, 2.0, 5.0, 10, and 20 ng/µL in ethyl acetate using mixed stock solutions. Obtain stock solutions from Protocol Analytical Laboratories, Supelco, Inc. or equivalent. Aliquots of the SOCIIS solution (section 5.7.2), the SOC surrogate solution (section 5.2.4), and the GPC-SOC surrogate solution (section 5.4.4) are added to each of the calibration solutions to produce concentrations of 5 (SOCIIS solution), 3.2 (SOC surrogate solution), and 6.4 (GPC-SOC surrogate solution) ng/µL.

5.9.2 *GC/MS QC solutions*--Concentrations of selected SOCs in these solutions are measured at periodic intervals within the analytical sequence of the GC/MS to monitor instrument performance and to determine where in the sequence unacceptable results occur over 24 to 36 hours of analyses.

5.9.2.1 *Continuing calibration verification (CCV) solution*--A CCV solution, having individual compound concentrations of 5 ng/µL, is analyzed every 10 samples, verifying that the initial quantitation calibration is maintained.

5.9.2.2 *Mass spectrometer calibration*--a solution of decafluorotriphenylphosphine (DFTPP) that is injected following the CCV. This solution verifies the mass axis calibration and the relative abundances of ions formed over the mass range of the analysis. Prepare this solution from commercially available neat standards, Hewlett-Packard Corp. or equivalent.

6. Collection, shipment, and storage of sediment samples

6.1 *Sampling methods and sample-collection equipment*--Use sampling methods that will collect bottom-sediment samples that accurately represent organic contaminant compositions and concentrations at a given location and time. Use sample collection equipment that is free of plastic tubing, gaskets, and other parts that might leach interferences, sorb contaminants, or abrade and thus contaminate sediment samples. Detailed descriptions of samplers and sampling methods used to collect representative bottom-sediment samples are contained in Edwards and Glysson (1988). Samplers, equipment cleaning, sampling and postcollection processing procedures specific to the National Water-Quality Assessment (NAWQA) Program and applicable to other bottom-sediment sampling are contained in Shelton and Capel (1994).

6.2 *Cleaning procedures*--Wash all sample-collection equipment with phosphate-free detergent, rinse with distilled or tap water to remove all traces of detergent, and finally rinse with methanol (reagent grade or better, ultrapure preferred; contain methanol in a Teflon squeeze-bottle). Clean all sample-collection equipment before each sample is collected to prevent cross-contamination of the samples.

6.3 *Sample shipment*--Ship samples, contained in either 500- or 1,000-mL wide-mouth glass jars with PTFE-lined lids or other NWQL-approved containers, on ice via overnight carrier to the NWQL as soon as possible following collection.

6.4 *Sample storage*--Following login at the NWQL, samples are stored at -15°C in freezers until time of analysis. Sample holding times for this method have not been established, but are expected to be in excess of 6 months (Mudroch and MacKnight, 1991, p. 164).

7. Sample preparation procedure

Samples are grouped into sets that include 16 total samples, including QC samples, since two extraction units accommodate up to 16 samples. Typically, 11 to 12 field samples are included in a set, depending on the number of laboratory QC samples.

7.1 *Sample dewatering and percent moisture determination*

7.1.1 Retrieve samples from the freezer and allow to thaw.

7.1.2 Thoroughly homogenize each sample with spatula or scoopula.

7.1.3 Remove an approximately 20-g wet weight aliquot to an appropriate container for separate determination of total carbon and total inorganic carbon (Wershaw and others, 1987). Total organic carbon is obtained by difference.

7.1.4 Weigh approximately 150 g of homogenized sample into a tared 250-mL Teflon™ centrifuge bottle. Repeat with a second sample, identically weighing to ±0.1 g of the first sample for balanced centrifuge operation. Repeat for two more samples and centrifuge (4.1.2) the two pairs of four individual samples for 20 minutes at 2,000 rpm (fig. 2). Carefully decant the clear supernatant water; pipet the supernatant using a Pasteur pipet if the sediment pellet is too soft. If the supernatant is not clear, repeat centrifugation before decanting. Reweigh the centrifuge bottle.

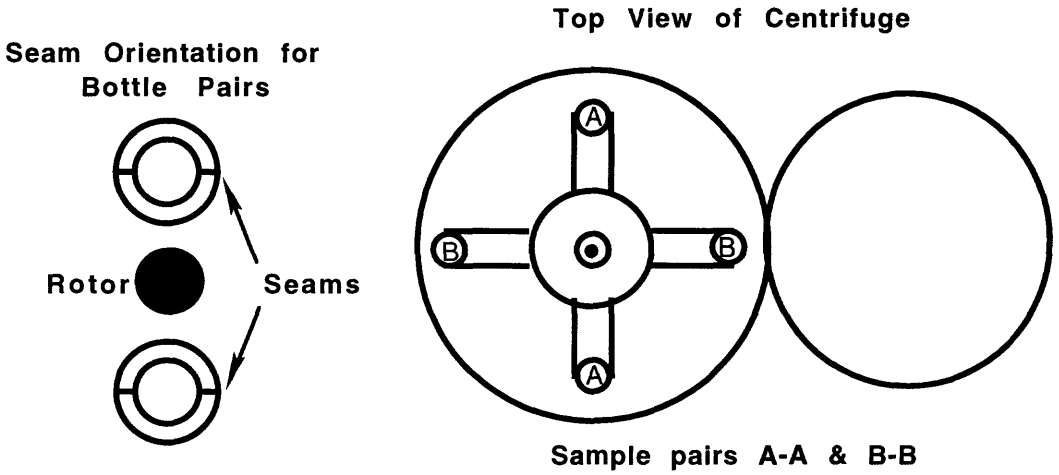


Figure 2. Orientation of centrifuge bottles.

7.1.5 Thoroughly rehomogenize the sediment sample in the centrifuge bottle. Remove a 1.8- to 2.2-g aliquot of sediment and determine the moisture content of the centrifuged sediment to ±0.1 percent using the moisture determination balance (4.1.5).

7.1.6 Based on determinations in section 7.1.5, calculate the weight of wet, centrifuged sediment needed to produce a 25-g equivalent dry weight sample (sample weight required for extraction equals 25 g/fraction dry weight). From this, calculate the total weight of water, in grams, present in this sample of wet, centrifuged sediment. Then determine the amount of anhydrous sodium sulfate required to adequately absorb the weight of water present in the sample. The amount of sodium sulfate required is equivalent to approximately four times the weight of water. If the sum of the weights of wet, centrifuged sediment and anhydrous sodium sulfate is less than 160 g, combine these two weights in a tared 400-mL beaker. If the combined calculated weights are greater than 160 g, reduce the target dry weight required by 20 percent to 20 g equivalent dry weight. Recalculate the required weights of wet sediment and anhydrous sodium sulfate and determine if the sum of these two weights is less than 160 g. If it is, combine these new recalculated weights in a tared 400-mL beaker. If not, repeat the equivalent dry-weight reduction and recalculation procedure until the combined calculated weight is less than 160 g. Record the combined weight to ±0.1 g. Mix thoroughly, and, if necessary, add additional sodium sulfate to ensure that the mixture is dry and loose, always remaining less than a net combined weight of 160 g of wet, centrifuged sediment and anhydrous sodium sulfate.

7.2 *Sediment extraction*

7.2.1 Add the sediment-sodium sulfate mixture to a Soxhlet extraction thimble. Repeat for all samples.

7.2.2 Prepare the following QC samples as required depending on types of analyses to be performed.

7.2.2.1 *Laboratory blank (set blank)*--Place 125 g of sodium sulfate into an extraction thimble. Optional blank matrix: Although not used for determinations described in this report, 25 g of clean Ottawa sand (baked at 600°C for 8 hours), mixed with approximately 100 g of sodium sulfate also can be used as a matrix.

7.2.2.2 *Set SOC spike sample*--Place 125 g sodium sulfate into an extraction thimble, place thimble into Soxhlet, and spike sodium sulfate with 100 µL of individual SOC spike solution (5.2.5) using a micropipet. Optional spike matrix: Although not used for determinations described in this report, 25 g of clean Ottawa sand (baked at 600°C for 8 hours), mixed with approximately 100 g of sodium sulfate also can be used as a matrix.

7.2.2.3 *SRM sample*--Place 4 to 25 g of appropriate SRM (see 5.2.6) into an extraction thimble; the amount extracted will depend on SRM availability, compound concentrations relative to the reporting level, and cost. Mix in 100 g of sodium sulfate to simulate step 7.1.6. (SRMs usually do not contain appreciable water.)

7.2.2.4 OPTION: *Set OC spike sample*--Included if OCs in field samples will also be determined by GC/ECD. Place 125 g sodium sulfate into an extraction thimble and spike with an appropriate amount of OC spike solution (refer to Foreman and others, 1995, p. 12) using a micropipet as in 7.2.2.2. Optional or additional spike sample types: Either along with, or in place of, the set OC spike sample, include a set PCB spike or set toxaphene spike sample as desired (Foreman and others, 1995, p. 12). Preparation of a spike sample containing more than one spike solution generally is not recommended because of the complexity of the PCB and toxaphene mixtures.

The previously described QC samples are extracted and processed through the remainder of the method exactly as the field samples.

7.2.3 Place the extraction thimble into a Soxhlet apparatus connected to a 500-mL flask containing 350 mL dichloromethane and 5 to 10 boiling chips.

7.2.4 Add 100 µL of SOC surrogate solution (5.2.4) on top of each sample contained in a thimble using a micropipet.

7.2.5 OPTION: Also add the appropriate volume of OC surrogate solution (refer to Foreman and others, 1995, p. 12) to the top of each sample if determining OCs by GC/ECD.

7.2.6 Carefully add 25 mL methanol to the top of the sample and allow 20 minutes for the solvent to percolate through sample to the thimble frit. This step helps remove any residual moisture not bound by the sodium sulfate.

NOTE 2: Do not use more than 25 mL of methanol during this step. The amount of methanol added must not exceed 7 percent of the total volume of dichloromethane plus methanol used during the extraction (see 7.3.2 note).

7.2.7 Attach the Soxhlet apparatus to the condenser and extract the sample at 70°C for at least 12 hours.

7.2.8 Following extraction, add about 50 g of sodium sulfate to the flask and swirl to remove residual water. Add additional sodium sulfate as needed to ensure water removal. Excessive amounts of water might require separation using a 1-L separatory funnel. Seal with a ground-glass stopper and store sodium sulfate-containing extract in a refrigerator for at least 4 hours.

7.3 *Sediment extract concentration*

7.3.1 Transfer the extract (but not the sodium sulfate) from the flask to a K-D concentrator (4.3.1) fitted with a 10-mL centrifuge receiver tube (4.3.2) containing boiling chips. Rinse the flask three times using 5- to 10-mL aliquots of dichloromethane and transfer these rinses to the K-D concentrator.

7.3.2 Concentrate the extract to about 4 to 6 mL at 70°C.

NOTE 3: The methanol used in the extraction step must be removed during this K-D concentration step, otherwise it will cause problems during the GPC cleanup (7.5). Methanol is completely removed only by the formation of an azeotrope having a 92.7 percent dichloromethane and 7.3 percent methanol composition that boils at 37.8°C (at 101.3 kPa). Therefore, the amount of methanol must not exceed 7 percent of the total extract volume of dichloromethane plus methanol in the Soxhlet extract (7.3.1); otherwise, the desired azeotrope composition will not occur during the K-D concentration (see 7.2.6 note).

7.3.3 Further reduce the extract to 3.0 mL using a gentle stream of nitrogen gas (4.3.4). Store extract in a refrigerator or freezer until step 7.4.

7.4 *Sediment extract filtration*

7.4.1 Place paired sets of extracts contained in uncapped centrifuge receiver tubes into a centrifuge (4.4.1) and centrifuge at 2,150 rpm for 10 minutes.

7.4.2 Tare a labeled, 4-mL GPC vial with cap and septum attached (5.4.3) to ±0.0001 g.

7.4.3 Attach a 0.2-µm PTFE filter to a 5-mL Luer-Lok syringe. Remove syringe plunger and place a tared GPC vial under filter-tip outlet.

7.4.4 Transfer the centrifuged extract to the syringe barrel using a Pasteur pipet, taking care not to dislodge the centrifuged solids.

7.4.5 Carefully insert the plunger into the syringe and pass the extract through the filter into the GPC vial. After expelling sample, push air through the filter to remove residual extract from the filter.

7.4.6 Rinse the centrifuge receiver tube with 500 µL dichloromethane, washing down the tube walls using the Pasteur pipet. Transfer the rinse (including disrupted centrifuged solids) to the syringe barrel using the Pasteur pipet. Filter this rinse into GPC vial as in 7.4.5.

7.4.7 Repeat step 7.4.6.

7.4.8 Add 50 µL of the GPC-SOC surrogate solution to the extract in the GPC vial if determining SOCs by GC/MS.

7.4.9 Bring extract volume up to 4 mL with dichloromethane and cap GPC vial. Store extract in a refrigerator or freezer until step 7.5.

7.5 *Gel permeation chromatography*

Complete details of GPC operation are beyond the scope of this report. Instead, the following procedure outlines the steps necessary for GPC instrument fraction calibration and subsequent cleanup of sample extracts. Consult the appropriate instrument manuals for additional details regarding general GPC system operation and NWQL standard operating procedure MS0024.0 (or subsequent revisions; available upon request) for detailed, method-specific GPC procedures.

7.5.1 The GPC data system should remain turned on continuously. Other system components, including the pump, autosampler, detector, fraction collector, and column heater, should be turned on at least 2 hours in advance of fraction calibration.

7.5.2 Degas the dichloromethane mobile phase with helium for 30 minutes prior to use.

7.5.3 Pump degassed dichloromethane through the GPC columns at the mobile phase flow rate of 1 mL/min for at least 2 hours prior to fraction calibration (7.5.8).

NOTE 4: Slowly ramp up the flow rate from 0.1 to 1 mL/min at 0.1-mL/min intervals over a 5-minute period to minimize pressure shock to the GPC columns.

7.5.4 Bring the GPC vial containing the sample to room temperature.

7.5.5 Just prior to vial pressurization (7.5.6) below, weigh the extract contained in the tared GPC vial with cap and septum to ±0.0001 g and record extract weight [Wt. Extract Before GPC = Wt. Extract and Vial Before GPC (7.5.5) minus the Vial Tare Wt. (7.4.2)]. Similarly, weigh GPC vials (with cap and septum) after injection. The fraction of the sample injected into the GPC system will be determined by weight difference before and after GPC injection.

7.5.6 For all samples, the GPC vial headspace is pressurized with nitrogen gas, just prior to beginning a GPC fractionation sequence. This pressurization assists the syringe in withdrawing the correct aliquot of extract or solution for injection into the GPC. Pierce the vial septum with the pressurization needle, and pressurize with 207 kPa nitrogen for about 1 minute. Make sure the end of the needle is not placed into the liquid. Rinse the needle with clean dichloromethane between vial pressurizations.

7.5.7 Establish GPC system cleanliness and baseline stability by injecting a 1,400-µL aliquot of fresh pesticide-grade dichloromethane (System Blank) and monitoring detector response at low attenuation (usually at attenuation 8). Fractions typically are not collected for GPC System Blank analyses.

7.5.8 *GPC fraction calibration* --Due to GPC column aging, the presence of residual methanol from sample extraction, and other factors, SOC elution times might vary between analyses of sample sets. Therefore, prior to beginning automated analysis, the fraction collection beginning and ending times are established for the SOCs (and subsequently for the OCs, if desired), to allow final configuration of the fraction collector.

7.5.8.1 Establish SOC fraction collection times by injecting 1,400 µL of the GPC-SOC fraction test solution (5.5.3) and monitoring the elution times of the peaks at low attenuation. Repeat injections of the GPC-SOC fraction test solution as necessary to ensure chromatographic reproducibility. Fractions are not collected for the GPC-SOC fraction calibration test analyses.

7.5.8.2 Figure 3 shows a typical GPC chromatogram resulting from analysis of the GPC-SOC fraction test solution. Set the "beginning time" on the fraction collector at the time when the detector baseline begins to rise for the di-*n*-octylphthalate peak. The beginning time is determined by processing the chromatogram resulting from the injection of the GPC-SOC fraction test solution at attenuation 8 and graphically determining when the baseline begins to rise, indicating the first peak.

7.5.8.3 Set the "end time" on the fraction collector for the GPC-SOC fraction at the valley between the benzo[*ghi*]perylene peak (the last SOC compound that elutes from the GPC, see fig. 3) and the sulfur peak.

NOTE 5: Different GPC fraction collection window start and end times are used when an aliquot of the sample extract is processed by GPC for OC pesticides and PCBs. Sulfur might carry over, resulting in a broad peak or a severe baseline rise in the GC/ECD chromatogram, in turn resulting in interferences with compound determinations. See Foreman and others (1995, p. 20) for further details.

7.5.9 Perform a GPC automated separation. Inject 1,400 µL of the sample extract and collect the GPC-SOC fraction in a 25-mL K-D receiver tube. Process each sample for 30 minutes. A suggested processing sequence, incorporating the sample types contained in a normal sample set at the NWQL (one set blank, set SOC spike, and SRM, 11 field samples, and one field sample duplicate), is shown in table 2. Repeated injections of the GPC-SOC fraction test solution and the System Blanks help ensure continued calibration and system cleanliness.

7.5.10 Reweigh the GPC sample vial with original cap and septum to ±0.0001 g as soon as possible after injection of the sample or following completion of automated separation. [Wt. of SOC Extract GPC'd = Wt. of SOC Extract and Vial Before GPC (7.5.5) minus Wt. of SOC Extract and Vial After GPC.]

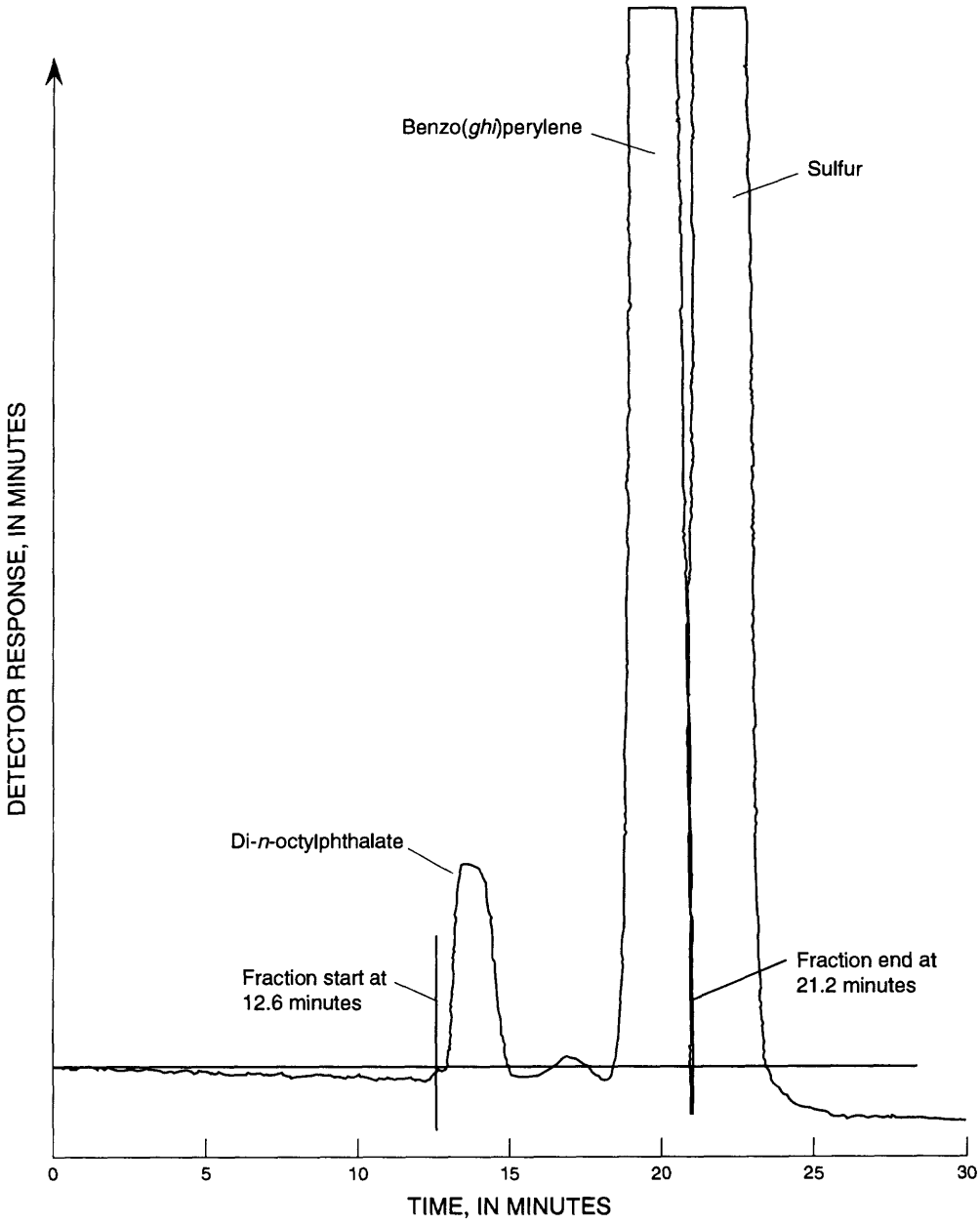


Figure 3. Gel permeation chromatogram of the semivolatile organic compound (SOC) fraction test solution at attenuation 8 showing the analytst-determined collection beginning and end times for the SOC fraction. Chromatographic conditions are listed in the text.

Table 2. *Suggested gel permeation chromatography processing sequence*

[SOC, semivolatile organic compound; GPC, gel permeation chromatography; SRM, Standard Reference Material]

Analysis sequence	Sample type
1	System blank
2	Set blank
3	Set SOC spike (or set spike options)
4	Sample 1
5	Sample 2
6	Sample 3
7	GPC-SOC fraction test solution (5.5.3)
8	System blank
9	Sample 4
10	Sample 5
11	Sample 6
12	Sample 7
13	Sample 8
14	GPC-SOC fraction test solution
15	System blank
16	Sample 9
17	Sample 10
18	Sample 11
19	Sample duplicate
20	SRM
21	GPC-SOC fraction test solution
22	System blank

7.5.11 Cap K-D receiver tube containing the GPC-SOC fraction with a ground-glass stopper and store in a refrigerator until the concentration step (7.6).

7.5.12 Replace the septum on the GPC sample vial and store the remaining non-GPC'd extract in a freezer until subsequent GPC injection for collection of an OC fraction (7.5.13) or reanalysis of an SOC fraction.

7.5.13 OPTION: If OC analysis is desired, repeat steps 7.5.1 through 7.5.12 but specifically for GPC-OC fraction collection. This requires initial fraction calibration (7.5.8) using the GPC-OC fraction test solution (see Foreman and others, 1995, p. 21). The extracts are then reprocessed using the sequence of table 2, replacing the set SOC spike and the GPC-SOC fraction test solution with the corresponding set OC spike and the GPC-OC fraction test solution. Use a

GPC injection volume of 1,100 µL (instead of 1,400 µL for SOCs) for all OC determinations. Details of GPC-OC steps are documented in NWQL standard operating procedure MS0024.0 (contact NWQL for copies of pertinent operating procedures).

7.6 *GPC-SOC fraction concentration and solvent exchange*

7.6.1 Add 4 mL of ethyl acetate and two to three small boiling chips to the extract and attach a three-ball micro-Snyder column to the top of the K-D receiver tube.

7.6.2 Slowly introduce the K-D receiver tube to a water bath (4.6.1) maintained at 80°C and reduce the solvent volume to about 4 mL or until solvent evaporation dramatically decreases. Remove the tube from the bath and cool.

7.6.3 Raise bath temperature to 85 to 87°C. Add two to three fresh boiling chips and 1 mL ethyl acetate to the K-D receiver tube, vortex, and replace into water bath for about 20 minutes. Do not reduce solvent volume to less than 1 mL.

7.6.4 Remove tube from water bath and reduce the extract to 0.5 mL using a gentle stream of nitrogen (4.3.4).

7.6.5 Transfer the fraction to a 1.8-mL amber autosampler vial using a Pasteur pipet. Add 50 µL of the SOC internal injection standard (SOCIIS) solution, cap the vial, and mix. Store in a freezer at -15°C until analysis by GC/MS.

8. Instrumental analysis

Samples are analyzed by GC/MS using a capillary column GC system equipped with an autosampler, a split/splitless injection port operated in the splitless mode, directly connected to a quadrupole mass spectrometer. A computer system is used to allow complete control of autosampler, GC and MS operations, and to acquire, process, and store the signal from the GC/MS. Complete details of GC/MS operation are beyond the scope of this report. Instead, the recommended 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 recommended GC/MS operating conditions are provided for guidance only. Different GC/MS systems will require different operating conditions to achieve acceptable instrument performance. Use any operating conditions that result in acceptable instrument performance.

8.1 *Instrumental conditions and setup*

8.1.1 Recommended GC operating conditions (Note: Use any operating conditions that provide acceptable levels of compound separation, identification, quantitation, precision, and recovery).

8.1.1.1 Injection port temperature: 285°C.

8.1.1.2 Splitless injection split time: 90 seconds. Split flow rate: 60 mL/min. Septum purge flow rate: 3 to 5 mL/min.

8.1.1.3 Sample injection volume: 2 µL.

8.1.1.4 Oven temperature program: Initial temperature 80°C (hold for 18 minutes). At 18 minutes, increase 4°C/min to 320°C, and hold for 10 minutes to allow for sufficient column bake-out.

8.1.1.5 Carrier gas: Helium at approximately 31 cm/s linear velocity measured at 150°C.

8.1.2 Determine compound retention times: Following GC/MS setup, establish compound retention times with calibration standards. Typical separations and peak shapes obtained for a solution of all SOCs using the GC/MS operating conditions of section 8.1 with an Rtx-5 GC column are shown in figure 4. Peak identifications, retention times, and mass-to-charge ratios of significant ions for all SOCs shown in figure 4 are listed in table 3.

CAUTION: Because of differences in GC columns, even from the same manufacturer, and operational characteristics between instruments, the elution profiles of the SOCs 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. Reverify retention times following any GC maintenance procedures applied to the guard or capillary columns to improve chromatography.

8.1.3 Prior to each analysis sequence, assess GC/MS performance by examining peak shape, by efficiency of separation for closely eluting compound pairs, and by response-factor variation determined for selected SOCs. Assess these criteria daily, relative to the performance obtained with a new capillary column, using freshly prepared continuing calibration verification (CCV) solutions. CCVs are the primary indicator of changes in instrument performance and are analyzed after every six samples.

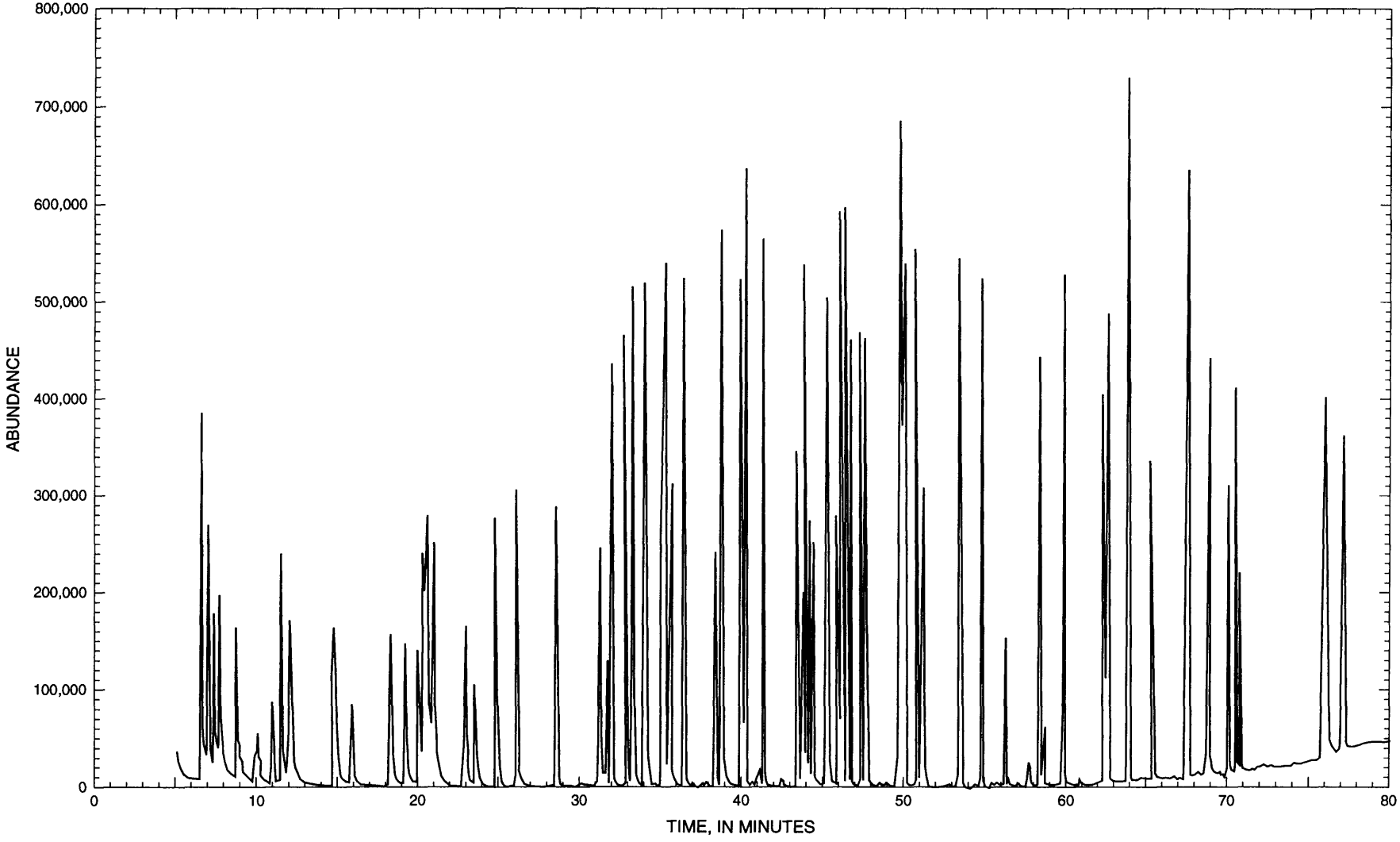


Figure 4. Total ion current gas chromatography/mass spectrometry chromatogram of semivolatile organic compounds determined in this study. Each compound is present at a concentration equivalent to 10 micrograms per kilogram (dry weight of sediment). Chromatographic conditions are listed in the text.

Table 3. *Retention times, relative retention times, and gas chromatography/mass spectrometry quantitation and confirmation ions for compounds determined using this method*

[Compounds reported in chromatographic elution order; min, minute; --, not used; compounds preceded by a * are method surrogates; compounds in boldface are internal standards and are followed by a designation (RR-1, RR-2,...) which indicates their order as a retention reference]

Compound	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion	Confirmation ion 1	Confirmation ion 2
bis(2-Chloroethyl)ether	7.649	0.338	1	93	95	63
Phenol	7.797	.345	1	94	66	65
2-Chlorophenol	8.148	.360	1	128	130	64
1,3-Dichlorobenzene	8.681	.384	1	146	148	111
1,4-Dichlorobenzene	8.997	.398	1	146	148	111
1,2-Dichlorobenzene	10.238	.453	1	146	148	111
bis(2-Chloroisopropyl)ether	11.401	.504	1	121	77	123
N-Nitrosodi-*n*-propylamine	12.650	.559	1	70	130	--
Hexachloroethane	12.790	.565	1	201	119	117
p-Cresol	13.471	.595	1	108	107	79
*Nitrobenzene-d_5	13.681	.605	1	128	82	98
Nitrobenzene	13.873	.613	1	123	77	51
Isophorone	17.015	.752	1	82	138	83
2-Nitrophenol	18.227	.806	1	139	65	109
C8-Alkylphenol	20.590	.910	1	122	121	107
bis(2-Chloroethoxy)methylether	21.079	.932	1	93	95	123
2,4-Dichlorophenol	22.153	.979	1	162	164	63
3,5-Dimethylphenol	22.284	.985	1	107	122	77
1,2,4-Trichlorobenzene	22.354	.988	1	180	182	145
Naphthalene-d_8 (RR-1)	22.624	1.000	--	136	--	--
Naphthalene	22.825	1.009	1	128	129	102
2,4,6-Trimethylphenol	24.632	1.089	1	121	136	91
Hexachlorobutadiene	25.200	1.114	1	225	227	260
Quinoline	26.370	1.166	1	129	102	128
Isoquinoline	27.627	1.221	1	129	102	128
4-Chloro-3-methylphenol	30.151	1.333	1	142	144	107
Hexachlorocyclopentadiene	31.813	1.406	1	237	239	235
2,4,6-Trichlorophenol	32.720	1.446	1	196	198	132
2,3,5,6-Tetramethylphenol	32.848	1.452	1	135	150	91
*2-Fluorobiphenyl	33.027	1.460	1	172	171	85

Table 3. *Retention times, relative retention times, and gas chromatography/mass spectrometry quantitation and confirmation ions for compounds determined using this method*--Continued

Compound	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion	Confirmation ion 1	Confirmation ion 2
2-Chloronaphthalene	33.412	1.477	1	162	164	127
2-Ethylnaphthalene	34.226	1.513	1	141	156	115
2,6-Dimethylnaphthalene	34.681	1.533	1	141	156	115
1,6-Dimethylnaphthalene	35.434	1.566	1	141	156	115
Acenaphthylene	36.441	1.611	1	152	151	76
Dimethylphthalate	36.581	1.617	1	163	77	194
1,2-Dimethylnaphthalene	36.678	1.621	1	141	156	115
2,6-Dinitrotoluene	36.914	.780	2	165	89	63
Acenaphthene	37.781	1.670	1	153	154	152
2,4-Dinitrotoluene	39.656	.838	2	165	89	63
4-Nitrophenol	39.685	.839	2	139	109	65
2,3,6-Trimethylnaphthalene	40.164	.849	2	170	155	153
9H-Fluorene	41.277	.873	2	166	165	83
Diethylphthalate	41.470	.877	2	149	177	176
4-Chlorophenyl-phenylether	41.532	.878	2	204	206	141
4,6-Dinitro-2-methylphenol	42.185	.892	2	198	121	105
N-Nitrosodiphenylamine	42.479	.898	2	169	168	167
2,4-Dinitrophenol	42.549	.899	2	184	154	63
Azobenzene	42.566	.900	2	182	105	77
4-Bromophenyl-phenylether	44.652	.944	2	248	250	141
1-Methyl-9H-fluorene	45.213	.956	2	180	165	89
Hexachlorobenzene	45.433	.960	2	284	286	142
Pentachloroanisole	45.661	.965	2	265	267	280
Dibenzothiophene	46.619	.986	2	184	139	92
Pentachlorophenol	47.058	.995	2	266	264	268
Pentachloronitrobenzene	47.190	.998	2	237	214	142
Phenanthrene-d_{10} (RR-2)	47.305	1.000	--	188	--	--
Phenanthrene	47.454	1.003	2	178	176	89
Anthracene	47.744	1.009	2	178	176	89
Acridine	48.078	1.016	2	179	178	89
Phenanthridine	48.746	1.030	2	179	178	151
9H-Carbazole	49.123	1.038	2	167	168	139
2-Methylanthracene	51.066	1.080	2	192	191	96
4,5-Methylenephenanthrene	51.260	1.084	2	190	189	95
Benzo[*c*]cinnoline	51.312	1.085	2	180	151	152

Table 3. *Retention times, relative retention times, and gas chromatography/mass spectrometry quantitation and confirmation ions for compounds determined using this method*--Continued

Compound	Retention time (min)	Relative retention time	Retention reference compound	Quantitation ion	Confirmation ion 1	Confirmation ion 2
1-Methylphenanthrene	51.479	1.088	2	192	191	95
Di-*n*-butylphthalate	51.954	1.098	2	149	150	205
Anthraquinone	52.702	.960	3	208	180	152
Fluoranthene-d_{10} (RR-3)	54.897	1.000	--	212	--	--
Fluoranthene	55.020	1.002	3	202	101	203
Pyrene	56.352	1.026	3	202	101	203
*Terphenyl-d_{14}	57.730	1.052	3	244	122	245
1-Methylpyrene	59.985	1.093	3	216	215	108
Butylbenzylphthalate	61.189	.956	4	149	91	206
Benz[*a*]anthracene	63.964	.999	4	228	229	226
Chrysene-d_{12} (RR-4)	64.035	1.000	--	240	--	--
Chrysene	64.195	1.002	4	228	229	114
bis(2-Ethylhexyl)phthalate	65.127	1.017	4	149	167	279
2,2 '-Biquinoline	66.932	1.045	4	256	255	128
Di-*n*-octylphthalate	68.749	.951	5	149	150	279
Benzo[*b*]fluoranthene	70.400	.973	5	252	253	126
Benzo[*k*]fluoranthene	70.444	.974	5	252	253	126
*Benzo[*e*]pyrene-d_{12}	71.624	.990	5	264	260	132
Benzo[*a*]pyrene	72.036	.996	5	252	250	126
Perylene-d_{12} (RR-5)	72.323	1.000	--	264	--	--
Indeno[1,2,3-*cd*]pyrene	77.609	1.073	5	276	138	137
Dibenz[*a,h*]anthracene	77.636	1.073	5	278	139	279
Benzo[*ghi*]perylene	78.713	1.088	5	276	138	274

8.1.4 Change instrument operating characteristics or service the GC/MS under any one of the following conditions:

1. When the instrumentally determined concentrations of greater than one-third of the CCV components fail to fall within ± 25 percent of the stated concentrations,

2. When mass assignments for compounds with known spectra are incorrect, or

3. When peak shape deterioration or separation efficiency fail to meet performance criteria.

Adjust instrument electron multiplier voltages for consistently low response. Maintenance operations include replacing the injection port liner and septum; if these replacements do not result in acceptable performance, remove short (0.3 m) lengths of the capillary column to restore GC/MS performance. If these steps do not improve GC/MS performance, then mass spectrometer source cleaning or other maintenance might be required. Operators exercise professional judgment to interpret results from CCV analyses, assess performance changes, and determine the appropriate course of instrument operation adjustment or maintenance.

NOTE 6: Tune and calibrate the GC/MS (as described in the next subsection) after any instrument maintenance. Use automated or other tuning procedures as prescribed by the GC/MS system manufacturer.

8.2 *GC/MS tuning and calibration*

8.2.1 The first component of GC/MS calibration is mass axis calibration. The mass spectrometer tuning procedure ensures that mass assignments for spectra are correct. Tuning is usually an automated, computer-controlled procedure that the analyst performs when mass calibration check standards do not meet established criteria or when GC/MS maintenance or repair have been performed. If automated procedures are available, tune the mass spectrometer using the procedures and software supplied by the instrument manufacturer. In addition to optimizing mass axis calibration, the automated tuning procedure contained in GC/MS systems also optimizes signal intensity, the ion resolution (separation between two ions separated by one mass unit), and ion peak shape.

8.2.2 The second component of GC/MS calibration is quantitation range calibration. Determine quantitation range calibration by measuring the instrument response and calculating response factors for all compounds across the range of compound concentrations used in this method. Calibration solution concentrations are 0.5, 1.0, 2.0, 5.0, 10 and 20 ng/μL. Plot the response for each concentration and use a linear fit to compare response in relation to concentration. If measured sample concentrations are higher than the highest standard used for the linear calibration line determination, then either dilute the sample or qualify the original data from the undiluted sample.

8.3 *GC/MS analysis*

8.3.1 Prior to any analysis, verify the GC/MS tune and mass axis calibration by injecting a solution of decafluorotriphenylphosphine (DFTPP). The relative mass fragment abundances and mass assignments must be within the range of values specified by the U.S. Environmental Protection Agency (1992, p. 567). If the instrument does not meet these specified criteria, corrective action, in the form of source cleaning, instrument maintenance, and recalibration, must be performed. Analyze calibration solutions and determine a calibration curve.

Produce a quantitative calibration curve as specified in section 8.2.2. Carefully inspect the curves to ensure linearity and verify that the lowest calibration standard is reliably quantified. After calibration results are determined to be acceptable, assemble samples, set QC samples, mass spectrometer verification solutions, and continuing calibration verification solutions into an analytical sequence, and analyze them under conditions identical to those used for the calibration. A typical analytical sequence is listed in table 4. Use an automated sample injection system to inject 2 µL of the appropriate sample extract or standard solution into the GC/MS. Data acquisition conditions are a mass range of 45 to 450 amu, scanned at a rate of 2.4 scans per second, with the filament operated at 70 eV. Store all data electronically for subsequent qualitative identification, quantitation, and archiving.

8.4 *Qualitative identification*

8.4.1 Two criteria are evaluated when establishing a positive compound identification: expected relative retention time and comparative fit of the mass spectrum.

8.4.2 The relative retention time (RRT) is the retention time of the compound normalized to the retention time of an internal standard. The internal standard used is one of several perdeuterated polycyclic aromatic hydrocarbons (dPAHs) added to the sample just prior to analysis. The particular dPAH used depends on where in the chromatogram the compound of interest elutes. The formula for determining RRT is

$$RRT = \frac{T_c}{T_{is}} \tag{1}$$

where T_c is the retention time (referenced to the start of the analytical run) of the compound of interest and T_{is} is the retention time of the internal standard used for that compound. Determine the RRT for each compound by analyzing standard solutions of SOCs and internal standards under identical instrumental conditions as used for samples. Compare RRTs; the match between samples and standards should agree within 1 percent. RRTs for SOCs determined in this method are listed in table 3.

8.4.3 The second component for qualitative identification is comparison of library and sample mass spectra. Library mass spectra are from authentic compound standards, collected under identical GC/MS conditions as the sample spectra. Library spectra are compared automatically by computer routines and also visually by the GC/MS operator. In addition, ratios of the integrated abundances of one quantitation to two confirmation ions are compared between standards and samples. Area ratios must agree within ±20 percent between standards and samples. After each SOC in a sample has been qualitatively identified, calculate the concentration of each.

Table 4. *Gas chromatography/mass spectrometry analysis sequence suggested for use in this method*

[SOC, semivolatile organic compound; SRM, Standard Reference Material]

Analytical sequence	Sample type
1	Continuing calibration verification (CCV) solution
2	Set blank
3	Set SOC spike
4	Sample 1
5	Sample 2
6	Sample 3
7	Decafluorotriphenylphosphine mass spectrometer calibration solution
8	Continuing calibration verification solution
9	Sample 4
10	Sample 5
11	Sample 6
12	Sample 7
13	Sample 8
14	Continuing calibration verification solution
15	Instrument blank (injection of pure solvent)
16	Sample 9
17	Sample 10
18	Sample 11
19	Sample duplicate
20	Set SRM
21	Continuing calibration verification solution
22	Instrument blank

9. Calculation of results

The calculation of a final concentration of an SOC in a sediment sample requires multiple calculations, as follows.

9.1 Calculate the relative response factors for each SOC from the calibration analyses conducted in 8.2.2 using a best-fit, linear regression model (rearranging the equation of the form $y=mx + b$):

$$RRF_c = \left[\frac{\left(\frac{area_c}{area_{is}} \right) - b}{\left(\frac{amt_c}{amt_{is}} \right)} \right] \quad (2)$$

where RRF_c = the relative response factor for the SOC of interest;
$area_c$ = the integrated peak area of the SOC of interest;
$area_{is}$ = the integrated peak area of the dPAH internal standard used for the SOC of interest;
amt_c = the mass of the SOC of interest, in nanograms;
amt_{is} = the mass in nanograms of the SOCIIS solution (see section 5.7.2) used for the SOC of interest; and
b = the y-intercept of the best-fit linear regression line.

9.2 Calculate the dry weight of sediment extracted, in grams (W_S):

$$W_s = W_w \times f_d \tag{3}$$

where W_w = wet weight of sediment, in grams (7.1.6); and
f_d = dry-weight fraction of sediment (7.1.6).

9.3 *Calculate sample SOC concentrations*

If the compound of interest has met the qualitative identification criteria listed in 8.4, calculate the compound concentration in the sample as follows:

$$C = \left(\frac{amt_{is} \times A_c}{RRF_c \times A_{is} \times W_S} \right) \times D_f \tag{4}$$

where C = the concentration of the compound of interest in the sample, in micrograms per kilogram;
amt_{is} = the mass of dPAH internal standard added to the sample, in nanograms;
A_c = the area of the quantitation ion for the compound of interest;
RRF_c = the relative response factor for the compound of interest, calculated above in 9.1;
A_{is} = the area of the quantitation ion for the dPAH internal standard;
W_S = the weight of sample extracted, in grams, calculated above in 9.2; and
D_f = dilution factor, which is calculated from equation 5.

$$D_f = \left[\frac{\text{final extract volume (µL)}}{\text{injection volume (µL)}} \times \frac{1}{F_{GPC}} \right] \tag{5}$$

where F_{GPC} = fraction of the total extract processed through the GPC, equal to (W_1/W_2),

where W_1 = weight of sample extract processed through the GPC, in grams; and

W_2 = weight of sample extract before GPC, in grams.

9.4 Calculate the percent recovery of the surrogate compounds in each sample using

$$R_a = \left[\frac{C_S}{(C_a \times V_a)/W_S} \right] \times 100 \quad (6)$$

where R_a = recovery of surrogate in sample, in percent;

C_S = concentration of surrogate in sample, in micrograms per kilogram, calculated using equations 4 and 5;

C_a = concentration of compound in the SOC surrogate solution added to the sample, in nanograms per microliter (5.2.4);

V_a = volume of SOC surrogate solution added to the sample, in microliters (7.2.4); and

W_S = dry weight of sample, in grams (calculated in 9.2).

9.5 Calculate the percent recovery of compounds in set SOC spike sample using

$$R_b = \left[\frac{C_S}{(C_b \times V_b)/W_S} \right] \times 100 \quad (7)$$

where R_b = recovery of spiked compound in the set SOC spike sample, in percent;

C_S = concentration of compound in set SOC spike sample, in micrograms per kilogram, calculated using equations 4 and 5;

C_b = concentration of compound in individual SOC spike solution added to sample, in nanograms per microliter (5.2.5);

V_b = volume of individual SOC spike solution added to the sample, in microliters (7.2.2.2); and

W_S = specified method dry weight, 25 g.

NOTE 7: Sediment is not used in either the set SOC spike or the laboratory blank. Use the same specified method dry weight, 25 g, for calculation of individual SOC concentrations in SOC spike (9.3) and for determination of percent recovery (equations 6 and 7).

9.6 Calculate the percent recovery of compounds in the SRM sample using

$$R_{SRM} = \frac{C_S}{C_{SRM}} \times 100 \quad (8)$$

where R_{SRM} = recovery of spiked compound in the SRM sample, in percent;
C_S = determined concentration of compound in the SRM sample, in micrograms per kilogram (calculated in 9.3); and
C_{SRM} = expected concentration of compound in the SRM sample, in nanograms per gram (5.2.6).

9.7 Calculate the percent moisture of the uncentrifuged sediment (7.1.5) using

$$\text{percent moisture in uncentrifuged sediment} = \frac{(W_a - W_b) + W_b(f_w)}{W_a} \times 100 \quad (9)$$

where W_a = weight of sample-water mixture prior to centrifugation, in grams (from 7.1.4);
W_b = weight of centrifuged sample-water mixture after decanting water, in grams (from 7.1.4); and
f_w = wet-weight fraction of centrifuged and decanted sediment, calculated by dividing the percent moisture content (7.1.5) by 100.

NOTE 8: The percent moisture of the uncentrifuged sediment is not required for calculation of the compound concentrations in micrograms per kilogram dry-weight sediment. Users can calculate the percent moisture value of the compound concentrations in micrograms per kilogram wet-weight sediment for comparison with historical data that are normalized to wet weight of sediment. The percent moisture of the uncentrifuged sediment calculated in equation 9 does not include any water decanted from the sediment sample prior to sample freezing for storage (6.4). Concentrations normalized to dry weight are more accurate than those normalized to wet weight because of the highly variable amounts of water used to process sediment samples on site.

10. Reporting of results

10.1 *Reporting units*--Report compound concentrations for field samples in micrograms per kilogram dry sediment (µg/kg). Report surrogate data for each sample type as percent recovered. Report data for the set spike and SRM samples as percent recovered. Compounds quantified in the set blank sample are reported in micrograms per kilogram, assuming a 25-g dry-sample weight. Report compound concentrations for field samples to two significant figures. Report surrogate data for each sample type to three significant figures.

10.2 *Reporting limits*--Estimates of method detection limits (MDLs) using the procedures outlined by the U.S. Environmental Protection Agency (1992) have been performed for this method and are discussed further in section 11.3. The individual MDL for each compound determined using this method is also the method reporting limit. Report qualitatively identified compound concentrations (those SOCs that are identified from relative retention time and MS spectral fit) that are less than the method reporting limit as estimated values. Compounds that are not detected are reported as being less than the method reporting limit.

11. Method performance

This method was put into routine use on January 7, 1993, prior to the completion of method validation at the NWQL. Through routine use, some deficiencies were identified in the GPC portion of the method. These problems apparently did not affect the recoveries of compounds during validation, but were noticeable in the set SOC reagent spikes. The GPC problem resulted from incomplete loading of the autosampler-withdrawn GPC aliquot onto the GPC columns. This problem was corrected by transferring the method to a new GPC system, one better designed for the sample aliquots used in this method. Additional minor discrepancies in analysis, resulting from converting the GC/MS method from the original instrument to a GC/MS setup for routine use, were also identified and corrected. As a result, those samples that might have been adversely affected by GPC performance were reextracted and reanalyzed. Samples that did not require reextraction were either reanalyzed or the original GC/MS data reintegrated using a revised spectral library to correct discrepancies. The status of each sample set is listed in table 5. Additional modifications were made to the adsorption chromatography step used to further isolate OCs and PCBs, improving performance and reliability. These modifications are extensively documented in Foreman and others (1995) and are not discussed in this report.

The extraction, isolation, and analysis procedures described in this report and the following method-performance discussion reflect all method improvements that were completely implemented as of May 19, 1993. These performance data include SOC matrix spike recoveries at two concentrations in one sediment type and at one concentration in a second sediment type; sample surrogate recoveries; and recoveries from two types of method quality-control samples—set SOC spike and set SRM samples that were processed along with field-sediment samples analyzed for the NAWQA Program.

Table 5. *Status of 1993 data sets and corrective actions taken to account for gel permeation chromatography changes and other method transfer discrepancies*

[GPC, gel permeation chromatography; GC/MS, gas chromatography/mass spectrometry; H-P, Hewlett-Packard]

Set identifier	Initial instrument used for GPC fractionation	Corrective action		
		Complete reextraction and reanalysis	Reanalysis of original extract	Reprocessing of original GC/MS data
007A	H-P		X	
012A	H-P		X	
020A	H-P		X	
022A	H-P		X	
032A	H-P		X	
048A	H-P		X	
054A	H-P	X		
061A	H-P	X		
068A	H-P	X		
074A	H-P	X		
081A	Waters		X	
109A	Waters			X
123A	Waters			X
123B	Waters		X	
130A	Waters		X	
130B	Waters		X	
131A	Waters		X	
133A	Waters		X	
133B	Waters			X
137A	Waters			X
137B	Waters		X	
137C	Waters		X	
139A	Waters		X	
139B	Waters			X
139C	Waters			X
145A	Waters			X
145B	Waters		X	
145C	Waters		X	
147A	Waters		X	
147B	Waters			X
152A	Waters		X	
152B	Waters		X	
158A	Waters			X
158B	Waters		X	
162A	Waters	X		
162B	Waters	X		
165A	Waters			X

11.1 *Recoveries from spiked sediment*

11.1.1 The performance of this method for the extraction, isolation, and analysis of SOCs was evaluated by adding aliquots of standard solutions to seven sediment samples and processing the spiked samples through the entire method. Three unspiked sediment samples were processed with each set of spiked samples to determine the concentrations of any SOCs present in the sediment prior to spiking. Reagent spikes and unspiked blank samples also were processed with each set.

11.1.2 Two sediment types were used for evaluating method performance. The first was a sediment sample dredged from Evergreen Lake, Evergreen, Colorado. The Evergreen Lake sediment was dredged as part of routine dam maintenance, and sediment was collected from a mound that had been dredged several weeks prior to collection. The sediment sample is relatively coarse with a substantial sand component. Calculated mean recoveries, in percent, for all SOCs determined using this method from seven Evergreen Lake sediment samples, each set spiked at 800 or 2,000 µg/kg, are listed in tables 6 and 7. These recoveries were corrected for matrix contributions by subtracting the mean concentrations of detectable compounds measured in the three unspiked samples.

11.1.3 At both concentration ranges, some spiked SOCs were not detected. These particular SOCs are qualitatively identified but are not quantified by this method; they are denoted by asterisks (*) in table 1. These SOCs were included in the original method, but were not reproducibly recovered during validation.

At a spike concentration of 800 µg/kg, recoveries ranged from 17.9 to 117.3 percent, with a mean recovery of 77.4 percent. At a spike concentration of 2,000 µg/kg, recoveries ranged from 6.8 to 69.5 percent, with a mean recovery of 54.5 percent. The corresponding variation in recoveries is high and is reflected in both the standard deviations for individual SOCs and the standard deviation of recovery for all SOCs. These high standard deviations reflect four aspects of this method, and average ±13.2 percent and range from 1.6 to 33.9 percent for individual SOCs spiked at 800 µg/kg, and average 5.2 percent and range from 2.0 to 36.9 percent for individual SOCs spiked at 2,000 µg/kg.

11.1.4 The first aspect of this method that contributes to the observed variations in recoveries is the relative complexity of the extraction, isolation, and analysis procedures. The process of removing the relatively hydrophobic SOCs from aquatic sediment and carrying out all the detailed procedures required to produce an isolate that is amenable to GC/MS analysis results in numerous manipulations. It is during these manipulations that volatilization, spillage, thermal or photolytic degradation can occur and potentially contribute to SOC losses.

Table 6. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 800 micrograms per kilogram*

[µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate means and standard deviations; < ERL, less than estimated reporting limit; GPC, gel permeation chromatography. Method compounds spiked at an equivalent sediment concentration of 800 µg/kg. Method surrogates spiked at a concentration of 160 µg/kg. Method GPC surrogate spiked at a concentration of 320 µg/kg]

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
Phenol	671	262	83.9	32.8	39.1	7
bis(2-Chloroethyl)ether	276	136	34.5	17.1	49.4	7
2-Chlorophenol	324	158	40.4	19.8	48.9	7
1,3-Dichlorobenzene	260	159	32.5	19.9	61.2	7
1,4-Dichlorobenzene	267	216	33.4	27.0	80.8	6
1,2-Dichlorobenzene	292	166	36.5	20.7	56.8	7
bis(2-Chloroisopropyl)ether	447	230	55.9	28.8	51.5	7
Hexachloroethane	153	87	19.1	10.9	57.0	7
N-Nitrosodi-*n*-propylamine	567	195	70.8	24.3	34.3	7
p-Cresol	684	234	85.5	29.3	34.3	7
Nitrobenzene	401	220	50.2	27.5	54.9	7
Isophorone	674	165	84.3	20.6	24.4	7
2-Nitrophenol	491	271	61.3	33.9	55.3	7
C8-Alkylphenol	451	74	56.4	9.2	16.4	7
bis(2-Chloroethoxy)methane	410	119	51.3	14.8	28.9	7
2,4-Dichlorophenol	515	133	64.4	16.6	25.8	7
3,5-Dimethylphenol	578	196	72.2	24.5	34.0	7
1,2,4-Trichlorobenzene	389	147	48.6	18.4	37.8	7
Naphthalene	403	186	50.3	23.3	46.2	7
2,4,6-Trimethylphenol	476	127	59.5	15.9	26.7	7
Hexachlorobutadiene	374	171	46.8	21.3	45.6	7
Quinoline	537	161	67.1	20.2	30.1	7
Isoquinoline	671	262	83.8	32.7	39.0	7
4-Chloro-3-methylphenol	623	175	77.8	21.9	28.1	7
Hexachlorocyclopentadiene	<ERL	<ERL	<ERL	<ERL	<ERL	0
2,4,6-Trichlorophenol	631	188	78.9	23.5	29.8	7
2,3,5,6-Tetramethylphenol	462	143	57.7	17.8	30.9	7
2-Chloronaphthalene	557	136	69.6	17.0	24.5	7
2-Ethylnaphthalene	544	128	68.0	16.0	23.5	7
2,6-Dimethylnaphthalene	576	121	72.0	15.2	21.1	7

Table 6. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 800 micrograms per kilogram*--Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
1,6-Dimethylnaphthalene	567	140	70.9	17.5	24.7	7
Acenaphthylene	639	122	79.9	15.3	19.2	7
1,2-Dimethylnaphthalene	620	116	77.5	14.4	18.6	7
Dimethylphthalate	736	114	92.0	14.3	15.5	7
2,6-Dinitrotoluene	673	108	84.1	13.5	16.0	7
Acenaphthene	648	105	81.0	13.1	16.2	7
2,4-Dinitrophenol	<ERL	<ERL	<ERL	<ERL	<ERL	0
2,4-Dinitrotoluene	702	105	87.8	13.2	15.0	7
4-Nitrophenol	784	163	97.9	20.4	20.9	7
2,3,6-Trimethylnaphthalene	670	83	83.7	10.4	12.4	7
9H-Fluorene	770	87	96.2	10.9	11.3	7
4-Chlorophenyl-phenylether	675	68	84.4	8.5	10.1	7
Diethylphthalate	708	66	88.5	8.2	9.3	7
4,6-Dinitro-2-methylphenol	798	250	99.8	31.2	31.3	6
N-Nitrosodiphenylamine	673	45	84.1	5.7	6.7	7
Azobenzene	658	52	82.3	6.5	7.9	7
4-Bromophenyl-phenylether	697	55	87.1	6.9	7.9	7
1-Methyl-9H-fluorene	740	45	92.5	5.6	6.1	7
Hexachlorobenzene	722	49	90.2	6.1	6.8	7
Pentachloroanisole	720	48	90.0	6.0	6.7	7
Dibenzothiophene	836	66	104.5	8.3	7.9	7
Pentachlorophenol	772	264	96.5	33.0	34.3	7
Pentachloronitrobenzene	705	55	88.1	6.9	7.9	7
Phenanthrene	824	45	103.0	5.6	5.5	7
Anthracene	731	38	91.4	4.7	5.1	7
Acridine	650	26	81.3	3.2	3.9	7
Phenanthridine	677	37	84.6	4.6	5.4	7
9H-Carbazole	724	47	90.5	5.9	6.5	7
2-Methylanthracene	938	41	117.3	5.1	4.4	7
Benzo[*c*]cinnoline	763	59	95.4	7.4	7.8	7
4,5-Methylenephenanthrene	883	41	110.3	5.1	4.6	7
1-Methylphenanthrene	833	38	104.1	4.8	4.6	7
Di-*n*-butylphthalate	751	20	93.9	2.4	2.6	7
Anthraquinone	758	32	94.7	4.0	4.2	7
Fluoranthene	862	21	107.7	2.7	2.5	7

Table 6. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 800 micrograms per kilogram*--Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
Pyrene	770	21	96.3	2.6	2.7	7
1-Methylpyrene	775	24	96.8	3.0	3.1	7
Butylbenzylphthalate	560	24	70.0	3.1	4.4	7
Benz[*a*]anthracene	813	13	101.6	1.6	1.6	7
Chrysene	779	21	97.4	2.6	2.7	7
bis(2-Ethylhexyl)phthalate	240	41	29.9	5.1	16.9	7
2,2'-Biquinoline	710	53	88.8	6.7	7.5	7
Di-*n*-octylphthalate	144	59	17.9	7.4	41.1	7
Benzo[*b*]fluoranthene	649	27	81.1	3.3	4.1	7
Benzo[*k*]fluoranthene	811	59	101.3	7.4	7.3	7
Benzo[*a*]pyrene	633	22	79.2	2.8	3.5	7
Indeno[1,2,3-*cd*]pyrene	546	44	68.3	5.5	8.1	7
Dibenz[*a,h*]anthracene	747	59	93.3	7.4	7.9	7
Benzo[*ghi*]perylene	875	69	109.4	8.6	7.9	7
Nitrobenzene-d_5 (method surrogate)	123	68	77.1	42.6	55.3	7
2-Fluorobiphenyl (method surrogate)	85	29	53.1	17.9	33.8	7
Terphenyl-d_{14} (method surrogate)	125	10	77.9	6.1	7.8	7
Benzo[*e*]pyrene-d_{12} (GPC surrogate)	318	29	99.3	9.1	9.1	7

11.1.5 The second aspect of this method that contributes to the observed recovery variations is the individual variations associated with the sample matrix. Even though the SOCs are spiked into a single sediment type, Evergreen Lake sediment, the coextracted interferences, and background SOC contributions can vary among spiked samples and result in variable recoveries.

11.1.6 GPC performance is the third aspect of this method that contributes to the observed variable recoveries. Although the GPC recovery does not control the recovery of SOC method surrogates, and by inference SOC compounds (discussed in 11.2), there is variation inherent in the GPC isolation step, which contributes to the observed variation of SOC recovery in spiked sediment samples.

Table 7. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 2,000 micrograms per kilogram*

[µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate means and standard deviations; < ERL, less than estimated reporting limit; GPC, gel permeation chromatography. Method compounds spiked at an equivalent sediment concentration of 2,000 µg/kg. Method surrogates spiked at a concentration of 160 µg/kg. Method GPC surrogate spiked at a concentration of 320 µg/kg]

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
Phenol	1,034	125	51.7	6.2	12.1	7
bis(2-Chloroethyl)ether	992	90	49.6	4.5	9.1	7
2-Chlorophenol	804	341	40.2	17.0	42.4	7
1,3-Dichlorobenzene	967	87	48.3	4.3	9.0	7
1,4-Dichlorobenzene	1,049	75	52.4	3.7	7.1	7
1,2-Dichlorobenzene	1,013	79	50.7	4.0	7.8	7
bis(2-Chloroisopropyl)ether	849	59	42.4	3.0	7.0	7
Hexachloroethane	814	169	40.7	8.4	20.7	7
N-Nitrosodi-*n*-propylamine	1,115	79	55.8	3.9	7.1	7
p-Cresol	1,003	56	50.1	2.8	5.6	7
Nitrobenzene	978	75	48.9	3.8	7.7	7
Isophorone	1,075	68	53.7	3.4	6.4	7
2-Nitrophenol	913	81	45.7	4.0	8.8	6
C8-Alkylphenol	999	110	50.0	5.5	11.0	7
bis(2-Chloroethoxy)methane	972	55	48.6	2.7	5.7	7
2,4-Dichlorophenol	813	292	40.6	14.6	35.9	6
3,5-Dimethylphenol	1,157	72	57.9	3.6	6.2	7
1,2,4-Trichlorobenzene	1,042	55	52.1	2.7	5.3	7
Naphthalene	1,074	52	53.7	2.6	4.8	7
2,4,6-Trimethylphenol	1,289	151	64.4	7.6	11.7	7
Hexachlorobutadiene	1,020	72	51.0	3.6	7.1	7
Quinoline	1,274	64	63.7	3.2	5.0	7
Isoquinoline	1,224	58	61.2	2.9	4.7	7
4-Chloro-3-methylphenol	723	295	36.1	14.8	40.8	7
Hexachlorocyclopentadiene	240	136	12.0	6.8	56.6	7
2,4,6-Trichlorophenol	657	738	32.8	36.9	112.4	4
2,3,5,6-Tetramethylphenol	1,202	126	60.1	6.3	10.5	7
2-Chloronaphthalene	1,155	45	57.7	2.2	3.9	7
2-Ethylnaphthalene	1,091	50	54.5	2.5	4.6	7
2,6-Dimethylnaphthalene	1,069	53	53.4	2.7	5.0	7

Table 7. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 2,000 micrograms per kilogram*--Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
1,6-Dimethylnaphthalene	1,159	53	57.9	2.6	4.6	7
Acenaphthylene	1,151	46	57.6	2.3	4.0	7
1,2-Dimethylnaphthalene	1,105	52	55.2	2.6	4.7	7
Dimethylphthalate	1,167	55	58.3	2.8	4.7	7
2,6-Dinitrotoluene	1,161	75	58.0	3.8	6.5	7
Acenaphthene	1,310	85	65.5	4.3	6.5	7
2,4-Dinitrophenol	<ERL	<ERL	<ERL	<ERL	<ERL	0
2,4-Dinitrotoluene	1,160	81	58.0	4.0	7.0	7
4-Nitrophenol	429	347	21.5	17.3	80.8	6
2,3,6-Trimethylnaphthalene	1,250	73	62.5	3.7	5.9	7
9H-Fluorene	1,354	71	67.7	3.6	5.3	7
4-Chlorophenyl-phenylether	1,226	74	61.3	3.7	6.0	7
Diethylphthalate	1,247	75	62.4	3.7	6.0	7
4,6-Dinitro-2-methylphenol	<ERL	<ERL	<ERL	<ERL	<ERL	0
N-Nitrosodiphenylamine	1,182	75	59.1	3.7	6.3	7
Azobenzene	1,224	68	61.2	3.4	5.6	7
4-Bromophenyl-phenylether	1,240	77	62.0	3.9	6.2	7
1-Methyl-9H-fluorene	1,295	80	64.7	4.0	6.2	7
Hexachlorobenzene	1,255	76	62.8	3.8	6.1	7
Pentachloroanisole	1,315	69	65.8	3.4	5.2	7
Dibenzothiophene	1,327	77	66.3	3.9	5.8	7
Pentachlorophenol	414	40	20.7	2.0	9.7	7
Pentachloronitrobenzene	1,301	89	65.1	4.4	6.8	7
Phenanthrene	1,391	79	69.5	3.9	5.7	7
Anthracene	1,390	80	69.5	4.0	5.7	7
Acridine	1,267	83	63.3	4.2	6.6	7
Phenanthridine	1,304	94	65.2	4.7	7.2	7
9H-Carbazole	1,319	114	66.0	5.7	8.6	7
2-Methylanthracene	1,252	70	62.6	3.5	5.6	7
Benzo[*c*]cinnoline	1,236	70	61.8	3.5	5.7	7

Table 7. *Recovery of semivolatile organic compounds from Evergreen Lake sediment samples spiked at 2,000 micrograms per kilogram*--Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
4,5-Methylenephenanthrene	1,343	85	67.2	4.2	6.3	7
1-Methylphenanthrene	1,301	57	65.0	2.8	4.4	7
Di-*n*-butylphthalate	1,102	93	55.1	4.7	8.5	7
Anthraquinone	1,286	71	64.3	3.5	5.5	7
Fluoranthene	1,339	66	67.0	3.3	4.9	7
Pyrene	1,198	50	59.9	2.5	4.2	7
1-Methylpyrene	1,301	64	65.0	3.2	4.9	7
Butylbenzylphthalate	908	113	45.4	5.6	12.4	7
Benz[*a*]anthracene	1,254	99	62.7	5.0	7.9	7
Chrysene	1,261	71	63.0	3.6	5.7	7
bis(2-Ethylhexyl)phthalate	136	58	6.8	2.9	43.0	7
2,2'-Biquinoline	1,199	70	60.0	3.5	5.8	7
Di-*n*-octylphthalate	<ERL	<ERL	<ERL	<ERL	<ERL	0
Benzo[*b*]fluoranthene	1,062	86	53.1	4.3	8.1	7
Benzo[*k*]fluoranthene	1,031	87	51.5	4.4	8.5	7
Benzo[*a*]pyrene	1,083	105	54.1	5.2	9.7	7
Indeno[1,2,3-*cd*]pyrene	1,076	84	53.8	4.2	7.8	7
Dibenz(*a,h*)anthracene	994	217	49.7	10.9	21.9	7
Benzo[*ghi*]perylene	1,311	352	65.5	17.6	26.8	7
Nitrobenzene-d_5 (method surrogate)	64	8	39.9	4.7	11.8	7
2-Fluorobiphenyl (method surrogate)	79	4	49.4	2.8	5.6	7
Terphenyl-d_{14} (method surrogate)	85	8	53.3	4.9	9.3	7
Benzo[*e*]pyrene-d_{12} (GPC surrogate)	180	18	56.3	5.8	10.3	7

11.1.7 GC/MS analysis is the fourth aspect of this method that contributes to the observed variable recoveries. There is inherent variation to the injection of sample extracts, chromatographic separation, ion formation, and integration of ion signal. This variability changes with each sample injected into the GC/MS system. Although this aspect and the other three sources of variability cannot be quantitatively separated to determine the relative importance of their contributions, all contribute to the total variability measured.

11.1.8 The second sediment type was a bottom sample collected from the lower Mississippi River in 1986. After collection, this sediment had been size-separated and consisted of particles less than 63 µm in diameter. This sediment was light brown, and was received as a dry sample from the donor. Unlike the

Evergreen Lake sample, this sediment was completely used in the method validation. The sample was spiked with SOCs at one concentration, 400 µg/kg. Calculated mean recoveries, in percent, for all SOCs determined using this method from seven Mississippi River sediment samples are listed in table 8. Calculated mean recoveries are corrected for matrix contributions by subtracting the mean concentrations of detectable SOCs measured in three unspiked samples.

11.1.9 At the 400-µg/kg spiking concentration level, recoveries ranged from 18.7 to 368.7 percent, with a mean of 65.8 percent. The extremely high recovery 368.7 percent is for pentachlorophenol, which does not perform well in either extraction or analysis. Assuming that the recovery of pentachlorophenol is in error, likely from coeluting interferences, then the range of reported recoveries is from 18.7 to 162.1 percent, with a mean of 61.2 percent. This range, while still large, is within expected limits of variation, especially when the relatively low spike concentration and the presence of SOCs of interest in the sample at significant concentration are considered.

11.2 *Blank contamination and surrogate and SRM recoveries from routine analysis*

11.2.1 As noted earlier, the method outlined in this report was put into routine production prior to complete evaluation of the method validation data. In support of the NAWQA Program, approximately 440 sediment samples were analyzed for SOCs. Blank extract results and reagent spike and SRM recoveries are available from the 40 sample sets used to process these samples. Method and GPC surrogate recoveries are shown in figures 5, 6, 7, and 8. The observed variations in the surrogate recoveries result from both method-related losses and losses inherent to individual sample matrix effects.

11.2.2 The three method surrogates nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-d_{14} are plotted against each other in figure 9. The significant (p=0.05) correlations among all three method surrogates suggest that the dominant control on method surrogates is individual sample variation. The correlation between 2-fluorobiphenyl, a more volatile surrogate, with terphenyl-d_{14} suggests that losses due to volatilization are not the primary controlling variable for sample surrogate recoveries. In addition, there are no significant correlations between the three method surrogates and the GPC surrogate benzo[*e*]pyrene (fig. 10). This lack of correlation makes it highly unlikely that the GPC step is controlling method recovery. Taken together, these results suggest that individual sample matrix effects control recoveries of method surrogates from individual samples.

Table 8. *Recovery of semivolatile organic compounds from Mississippi River sediment samples spiked at 400 micrograms per kilogram*

[µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate means and standard deviations; < ERL, less than estimated reporting limit; GPC, gel permeation chromatography. Method compounds spiked at an equivalent sediment concentration of 400 µg/kg. Method surrogates spiked at a concentration of 160 µg/kg. Method GPC surrogate spiked at a concentration of 320 µg/kg]

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
Phenol	<ERL	<ERL	<ERL	<ERL	<ERL	6
bis(2-Chloroethyl)ether	162	40	40.5	10.1	25.0	7
2-Chlorophenol	280	41	70.0	10.2	14.6	7
1,3-Dichlorobenzene	105	45	26.3	11.2	42.6	7
1,4-Dichlorobenzene	137	67	34.3	16.7	48.8	7
1,2-Dichlorobenzene	147	54	36.7	13.4	36.6	7
bis(2-Chloroisopropyl)ether	245	52	61.2	12.9	21.1	7
Hexachloroethane	<ERL	<ERL	<ERL	<ERL	<ERL	5
N-Nitrosodi-*n*-propylamine	432	96	108.1	23.9	22.1	7
p-Cresol	92	33	23.1	8.3	36.1	7
Nitrobenzene	221	44	55.2	11.1	20.0	7
Isophorone	280	35	70.0	8.7	12.4	7
2-Nitrophenol	257	43	64.3	10.9	16.9	7
C_8-Alkylphenol	300	24	74.9	6.1	8.1	7
bis(2-Chloroethoxy)methane	283	37	70.8	9.3	13.1	7
2,4-Dichlorophenol	172	77	42.9	19.2	44.7	7
3,5-Dimethylphenol	<ERL	<ERL	<ERL	<ERL	<ERL	3
1,2,4-Trichlorobenzene	193	41	48.2	10.3	21.3	7
Naphthalene	221	39	55.3	9.8	17.7	7
2,4,6-Trimethylphenol	114	17	28.4	4.1	14.6	7
Hexachlorobutadiene	210	58	52.5	14.5	27.6	7
Quinoline	183	22	45.7	5.4	11.9	7
Isoquinoline	189	164	47.2	41.0	87.0	6
4-Chloro-3-methylphenol	485	73	121.2	18.3	15.1	7
Hexachlorocyclopentadiene	<ERL	<ERL	<ERL	<ERL	<ERL	0
2,4,6-Trichlorophenol	449	47	112.3	11.7	10.4	7
2,3,5,6-Tetramethylphenol	101	16	25.2	3.9	15.5	7
2-Chloronaphthalene	291	31	72.8	7.7	10.5	7
2-Ethylnaphthalene	109	16	27.2	3.9	14.5	7
2,6-Dimethylnaphthalene	128	16	32.0	4.0	12.5	7

Table 8. *Recovery of semivolatile organic compounds from Mississippi River sediment samples spiked at 400 micrograms per kilogram*--Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
1,6-Dimethylnaphthalene	110	17	27.5	4.3	15.6	7
Acenaphthylene	306	30	76.5	7.6	10.0	7
1,2-Dimethylnaphthalene	131	14	32.9	3.4	10.3	7
Dimethylphthalate	431	55	107.7	13.8	12.8	7
2,6-Dinitrotoluene	441	26	110.1	6.5	5.9	7
Acenaphthene	316	32	78.9	8.0	10.2	7
2,4-Dinitrophenol	<ERL	<ERL	<ERL	<ERL	<ERL	7
2,4-Dinitrotoluene	400	38	99.9	9.5	9.5	7
4-Nitrophenol	306	156	76.4	39.1	51.1	7
2,3,6-Trimethylnaphthalene	122	12	30.4	3.0	9.9	7
9H-Fluorene	325	39	81.2	9.7	11.9	7
4-Chlorophenyl-phenylether	329	39	82.2	9.8	11.9	7
Diethylphthalate	349	51	87.4	12.8	14.6	7
4,6-Dinitro-2-methylphenol	399	69	99.7	17.3	17.4	7
N-Nitrosodiphenylamine	249	26	62.4	6.5	10.3	7
Azobenzene	312	32	78.1	8.0	10.3	7
4-Bromophenyl-phenylether	356	53	89.0	13.2	14.8	7
1-Methyl-9H-fluorene	118	16	29.4	4.1	14.0	7
Hexachlorobenzene	357	48	89.2	12.0	13.4	7
Pentachloroanisole	135	20	33.9	5.0	14.9	7
Dibenzothiophene	126	11	31.6	2.8	9.0	7
Pentachlorophenol	1,475	525	368.7	131.3	35.6	7
Pentachloronitrobenzene	163	17	40.7	4.4	10.7	7
Phenanthrene	311	37	77.7	9.2	11.9	7
Anthracene	302	36	75.4	8.9	11.8	7
Acridine	101	15	25.2	3.7	14.8	7
Phenanthridine	134	19	33.5	4.7	14.0	7
9H-Carbazole	314	35	78.4	8.7	11.1	7
2-Methylanthracene	90	10	22.5	2.6	11.6	7
Benzo[*c*]cinnoline	155	23	38.7	5.7	14.6	7

Table 8. *Recovery of semivolatile organic compounds from Mississippi River sediment samples spiked at 400 micrograms per kilogram*–Continued

Compound (in elution order)	Mean amount recovered (µg/kg)	Standard deviation of amount recovered (µg/kg)	Mean recovery (percent)	Standard deviation of mean recovery (percent)	Relative standard deviation (percent)	*n*
4,5-Methylenephenanthrene	123	12	30.9	3.0	9.8	7
1-Methylphenanthrene	131	24	32.8	6.1	18.6	7
Di-*n*-butylphthalate	278	57	69.4	14.2	20.4	7
Anthraquinone	199	20	49.8	5.0	10.1	7
Fluoranthene	335	43	83.8	10.7	12.8	7
Pyrene	290	36	72.5	9.0	12.4	7
1-Methylpyrene	114	10	28.4	2.6	9.0	7
Butylbenzylphthalate	268	32	67.0	7.9	11.8	7
Benz[*a*]anthracene	302	33	75.5	8.2	10.9	7
Chrysene	323	42	80.8	10.4	12.9	7
bis(2-Ethylhexyl)phthalate	98	31	24.5	7.8	31.8	7
2,2'-Biquinoline	135	14	33.9	3.5	10.3	7
Di-*n*-octylphthalate	75	15	18.7	3.7	19.6	7
Benzo[*b*]fluoranthene	300	42	75.1	10.5	14.0	7
Benzo[*k*]fluoranthene	294	39	73.6	9.7	13.1	7
Benzo[*a*]pyrene	297	38	74.3	9.6	12.9	7
Indeno[1,2,3-*cd*]pyrene	314	36	78.6	9.1	11.5	7
Dibenz[*a,h*]anthracene	373	50	93.4	12.5	13.4	7
Benzo[*ghi*]perylene	416	55	104.1	13.7	13.2	7
Nitrobenzene-d_5 (method surrogate)	88.4	16.2	55.3	10.1	18.3	6
2-Fluorobiphenyl (method surrogate)	141	11	88.4	6.7	7.6	7
Terphenyl-d_{14} (method surrogate)	125	15	78.0	9.4	12.1	7
Benzo[*e*]pyrene-d_{12} (GPC surrogate)	81	15	25.5	4.6	18.0	7

11.2.3 The types and significance of laboratory contamination contributing to SOC recoveries are illustrated by the detections identified in set blanks listed in table 9. The SOC classes and concentrations determined in set blanks are typical of those found in analytical laboratories, particularly the phthalate esters.

11.2.4 As part of routine quality control, a separate sample of Standard Reference Material was analyzed as a part of each sample set. Three SRMs were used in routine method operation. Two of these SRMs were produced by the National Institute of Standards and Technology (NIST) and consist of natural sediment that has been certified for specific SOC concentrations, with additional uncertified values also reported. The NIST SRM 1939 is

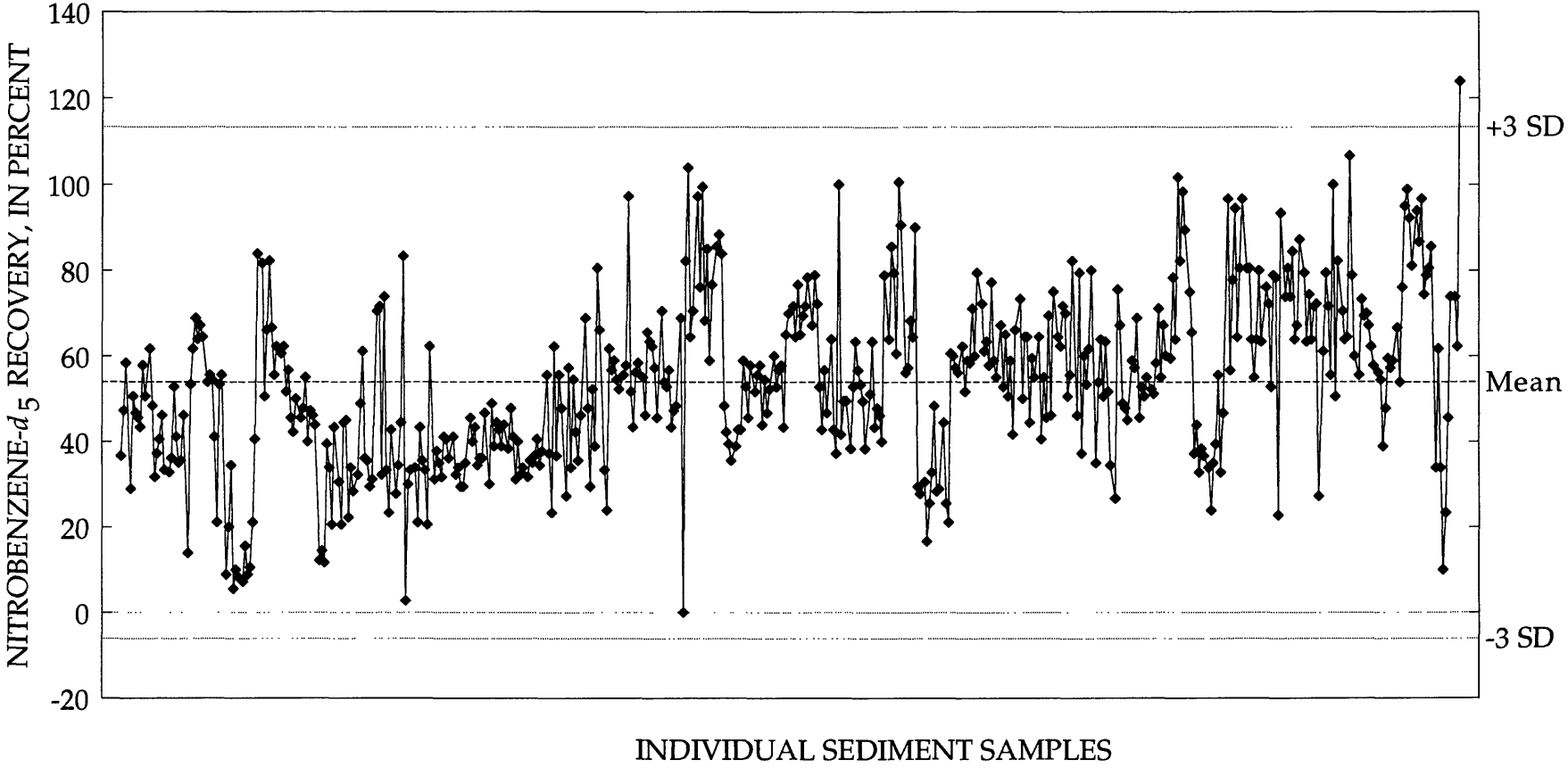


Figure 5. Control chart of nitrobenzene-d_5 recoveries from sediment samples.

[Mean= mean recovery, in percent; -3 SD= lower (three standard deviations) control limit; +3 SD = upper (three standard deviations) control limit]

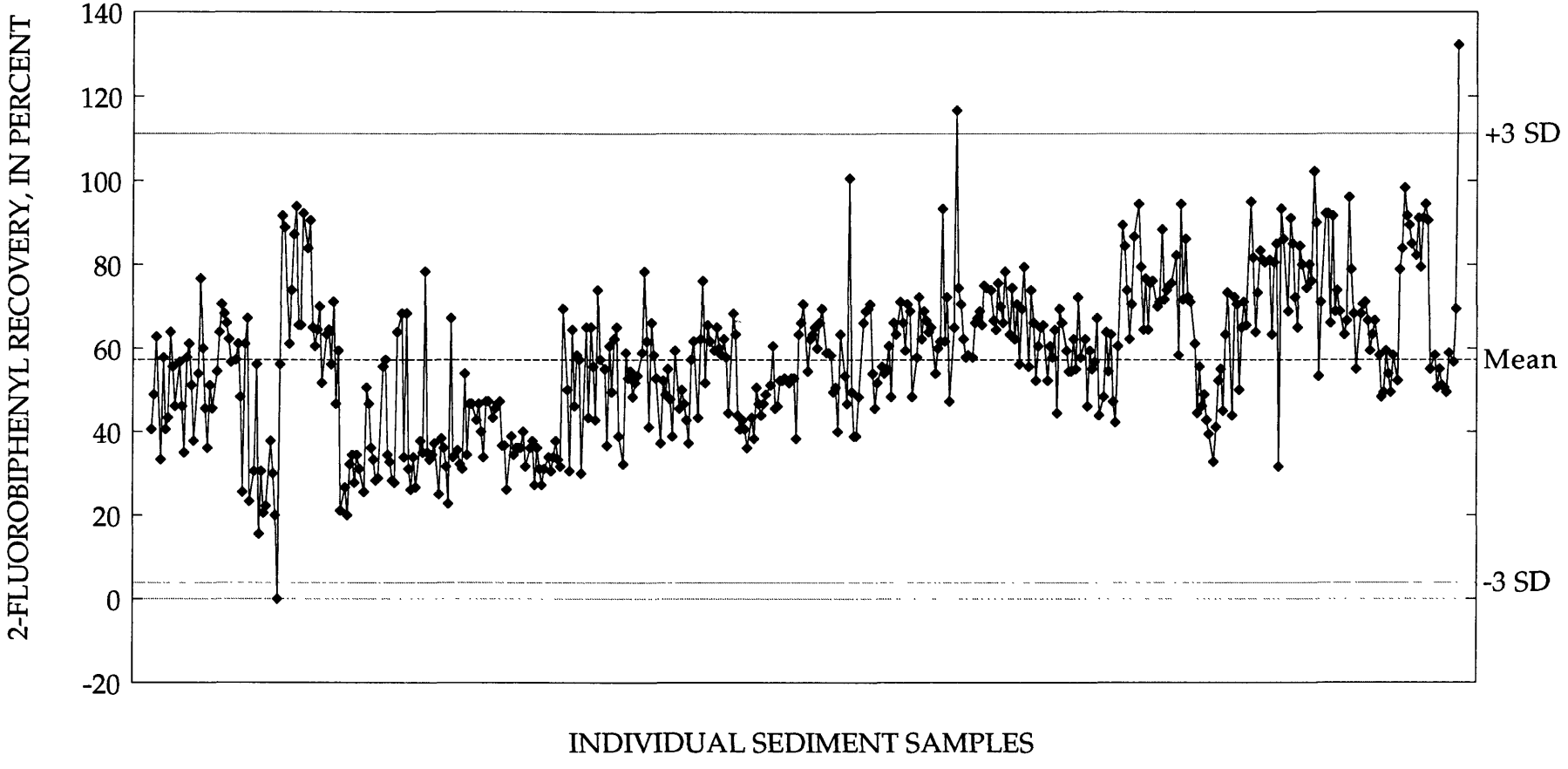


Figure 6. Control chart of 2-fluorobiphenyl recoveries from sediment samples.

[Mean= mean recovery, in percent; -3 SD= lower (three standard deviations) control limit;
+3 SD = upper (three standard deviations) control limit]

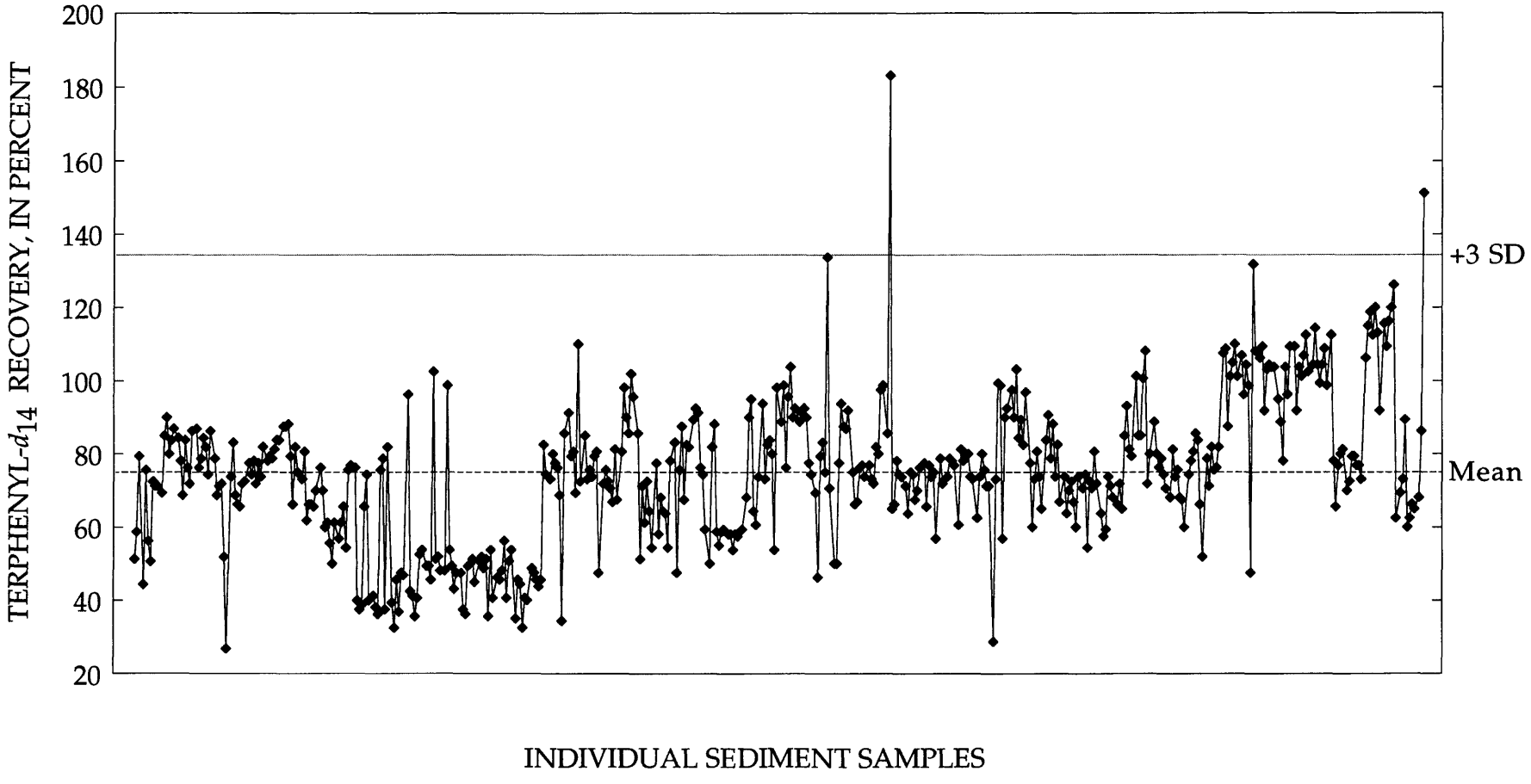


Figure 7. Control chart of terphenyl-d_{14} recoveries from sediment samples.

[Mean = mean recovery, in percent; +3 SD = upper (three standard deviations) control limit]

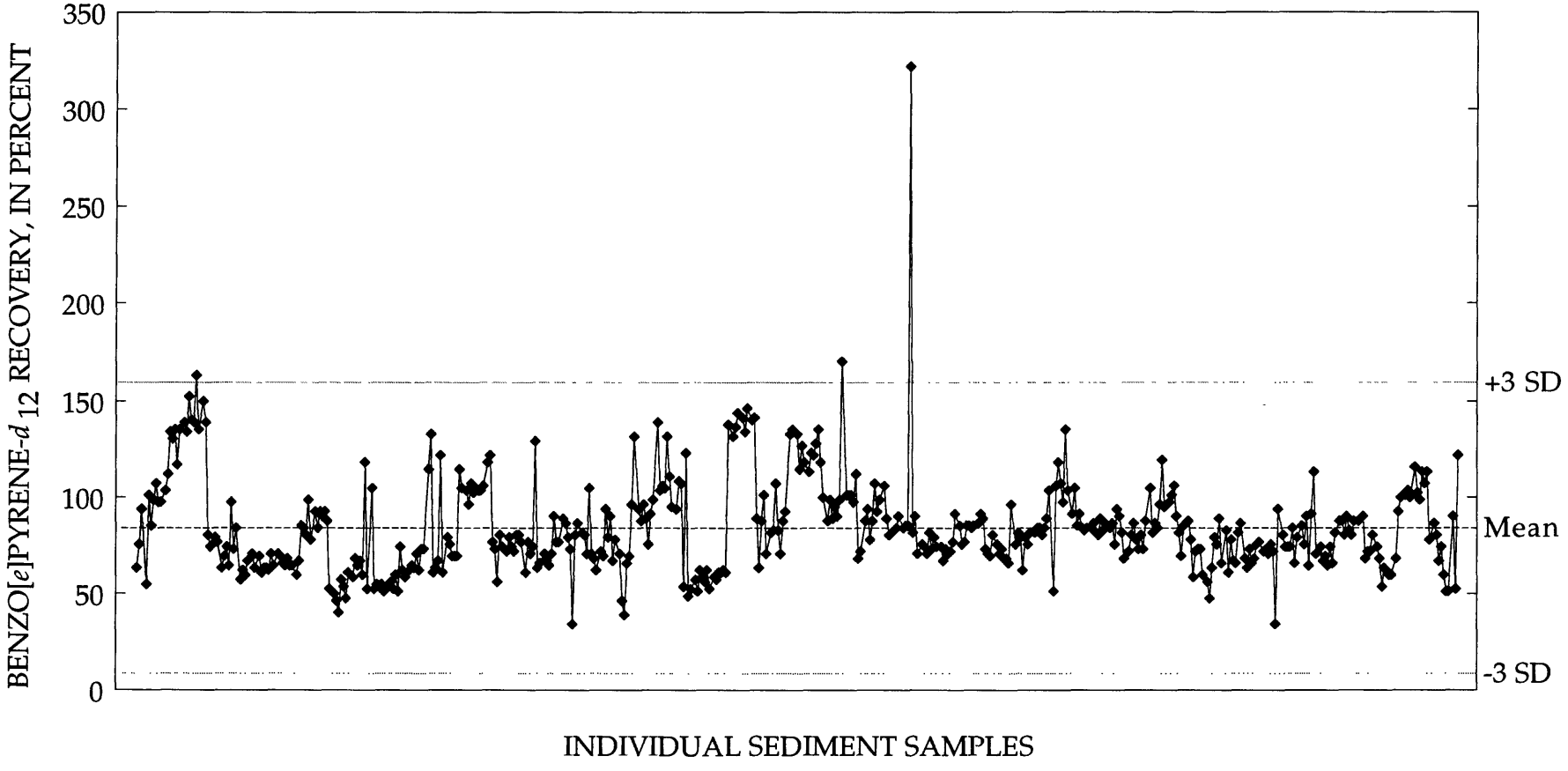
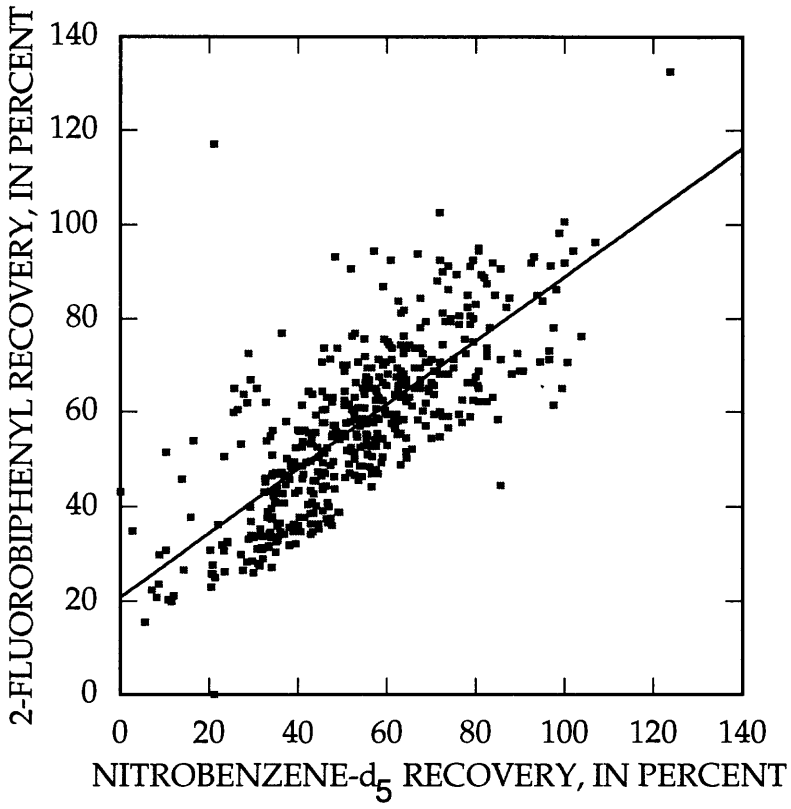


Figure 8. Control chart of benzo[*e*]pyrene-d_{12} recoveries from sediment samples.

[Mean= mean recovery, in percent; -3 SD= lower (three standard deviations) control limit;
+3 SD = upper (three standard deviations) control limit]



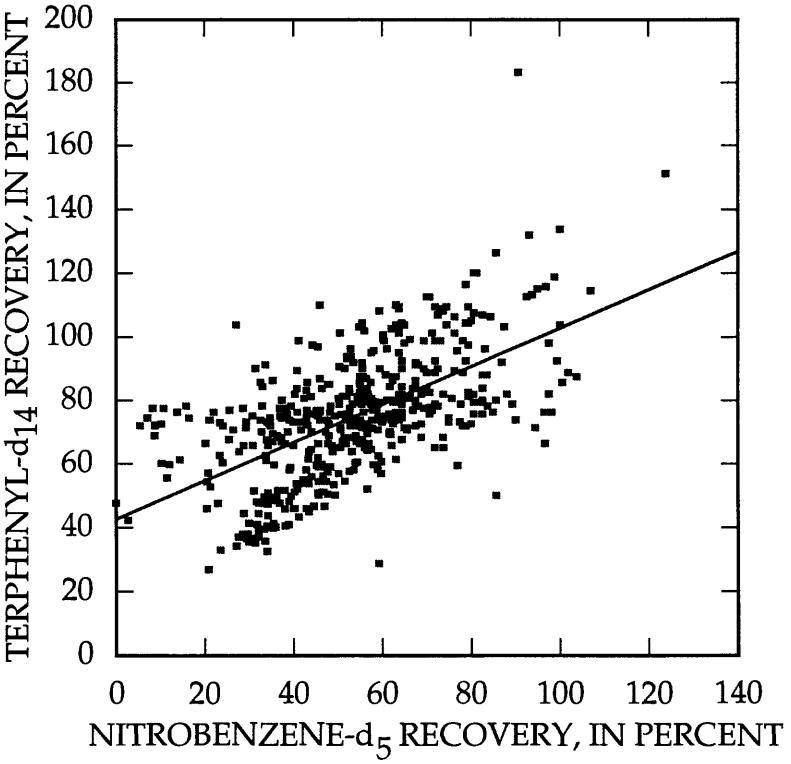


Figure 9. Correlation of method surrogate recoveries.

[Line drawn through each plot is the best-fit linear correlation.]

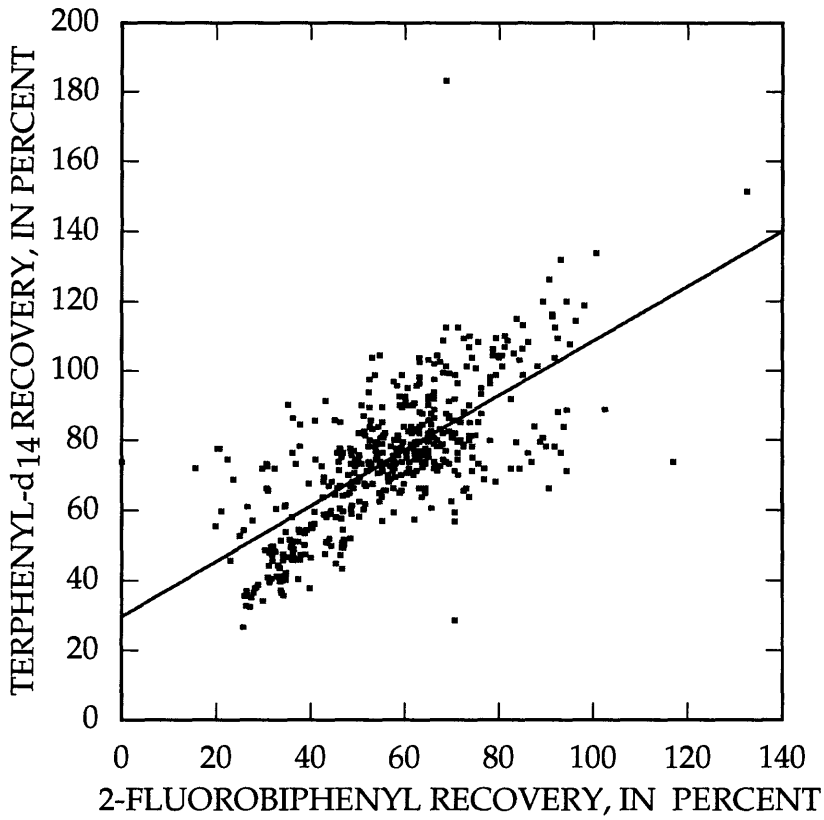
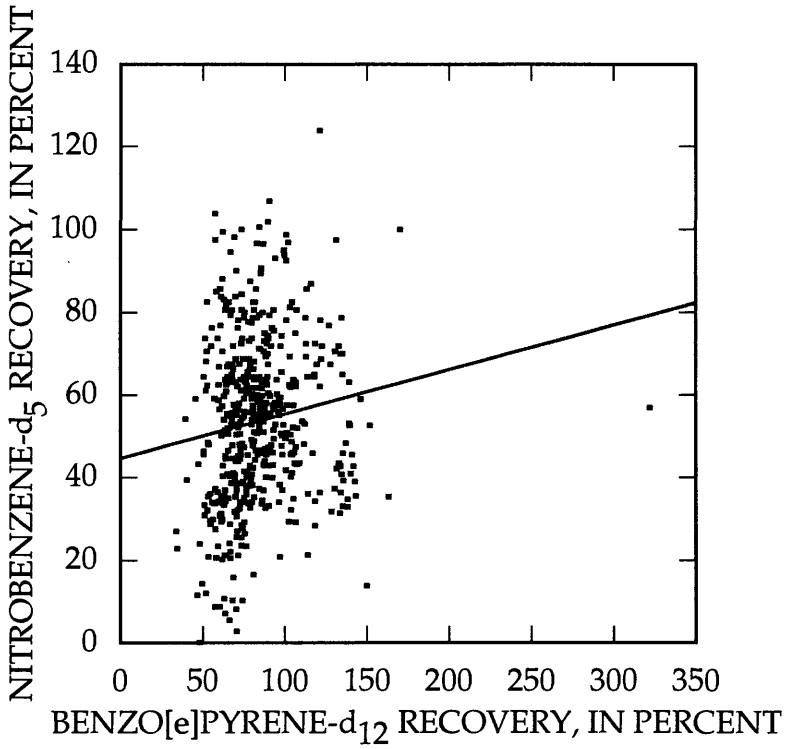


Figure 9. Correlation of method surrogate recoveries--Continued.

[Line drawn through plot is the best-fit linear correlation.]



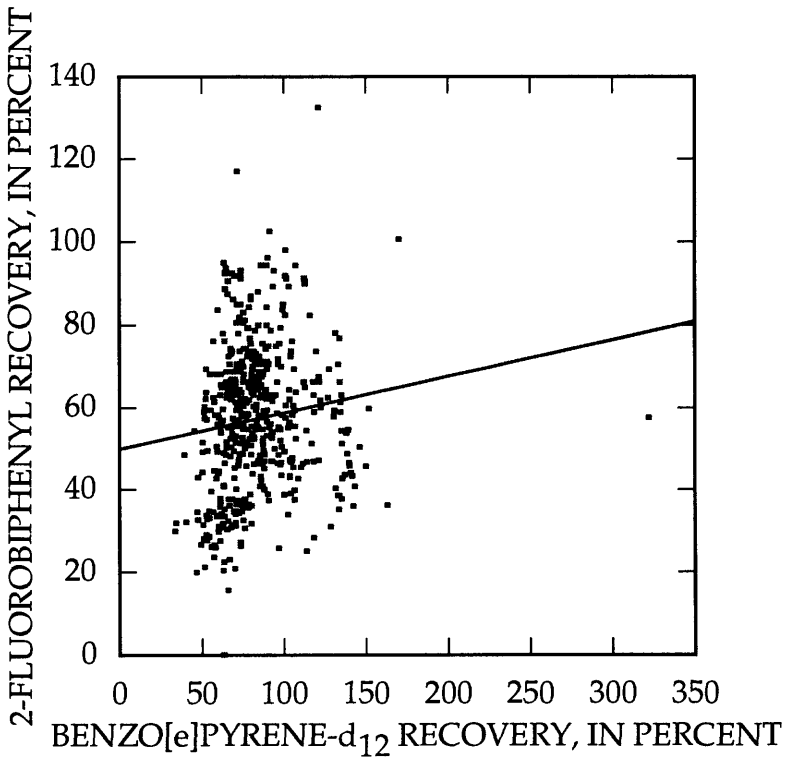


Figure 10. Correlation of gel permeation chromatography and method surrogate recoveries.

[Line drawn through each plot is the best-fit linear correlation.]

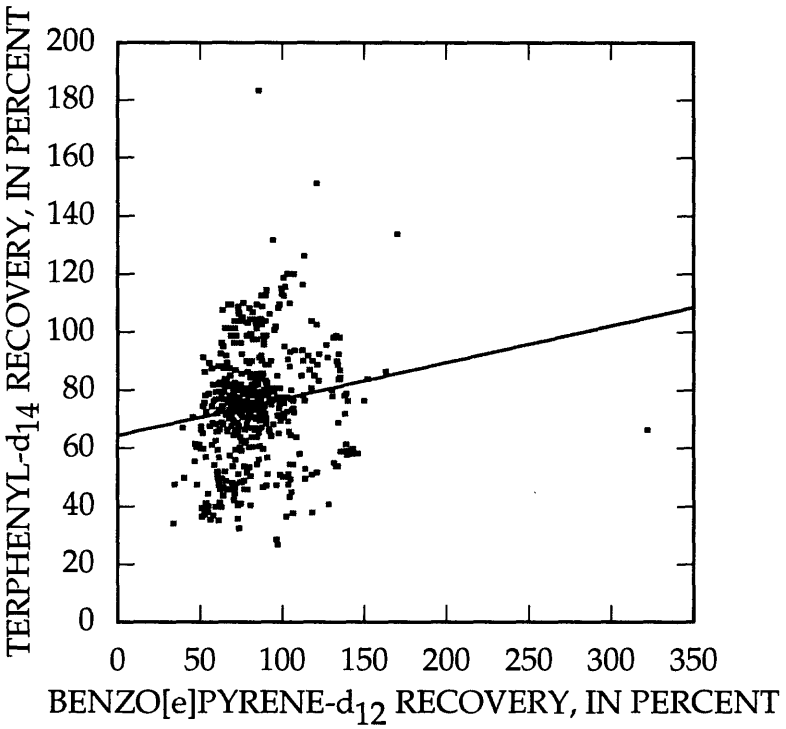


Figure 10. Correlation of gel permeation chromatography and method surrogate recoveries--Continued.

[Line drawn through plot is the best-fit linear correlation.]

Table 9. *Compounds detected in blanks using this method*

[µg/kg, micrograms per kilogram. Data are from 68 set blanks analyzed in 1993 and 1994. Concentrations are expressed as an equivalent dry weight of 25 grams]

Compound (in elution order)	Number of detections	High concentration (µg/kg)	Mean concentration (µg/kg)
Phenol	16	29.8	9.6
bis(2-Chloroethyl)ether	0		
2-Chlorophenol	2	15.9	15.9
1,3-Dichlorobenzene	0		
1,4-Dichlorobenzene	1	.7	.7
1,2-Dichlorobenzene	1	1.9	1.9
bis(2-Chloroisopropyl)ether	0		
Hexachloroethane	0		
N-Nitrosodi-*n*-propylamine	0		
p-Cresol	1	8.7	8.7
Nitrobenzene	0		
Isophorone	0		
2-Nitrophenol	0		
C8-Alkylphenol	0		
bis(-2-Chloroethoxy)methane	0		
2,4-Dichlorophenol	0		
3,5-Dimethylphenol	0		
1,2,4-Trichlorobenzene	0		
Naphthalene	0		
2,4,6-Trimethylphenol	0		
Hexachlorobutadiene	0		
Quinoline	0		
Isoquinoline	1	7.4	7.4
4-Chloro-3-methylphenol	2	13.2	13.2
Hexachlorocyclopentadiene	0		
2,4,6-Trichlorophenol	0		
2,3,5,6-Tetramethylphenol	0		
2-Chloronaphthalene	0		
2-Ethylnaphthalene	1	2.7	2.7
2,6-Dimethylnaphthalene	1	1.8	1.8
1,6-Dimethylnaphthalene	0		
Acenaphthylene	1	2.6	2.6
1,2-Dimethylnaphthalene	1	.2	.2
Dimethylphthalate	1	4.1	4.1
2,6-Dinitrotoluene	0		

Table 9. *Compounds detected in blanks using this method*--Continued

Compound (in elution order)	Number of detections	High concentration (µg/kg)	Mean concentration (µg/kg)
Acenaphthene	1	1.1	1.1
2,4-Dinitrophenol	0		
2,4-Dinitrotoluene	0		
4-Nitrophenol	0		
2,3,6-Trimethylnaphthalene	0		
9H-Fluorene	1	1.8	1.8
4-Chlorophenyl-phenylether	0		
Diethylphthalate	19	27.8	12.4
4,6-Dinitro-2-methylphenol	0		
N-Nitrosodiphenylamine	1	3.0	3.0
Azobenzene	0		
4-Bromophenyl-phenylether	0		
1-Methyl-9H-fluorene	1	1.9	1.9
Hexachlorobenzene	0		
Pentachloroanisole	1	6.4	6.4
Dibenzothiophene	0		
Pentachlorophenol	0		
Pentachloronitrobenzene	1	32.0	32.0
Phenanthrene	1	1.2	1.2
Anthracene	1	1.0	1.0
Acridine	0		
Phenanthridine	0		
9H-Carbazole	1	.7	.7
2-Methylanthracene	1	.7	.7
Benzo[*c*]cinnoline	0		
4,5-Methylenephenanthrene	1	2.8	2.8
1-Methylphenanthrene	1	3.4	3.4
Di-*n*-butylphthalate	56	82.2	31.5
Anthraquinone	0		
Fluoranthene	1	.7	.7
Pyrene	1	1.6	1.6
1-Methylpyrene	1	1.4	1.4
Butylbenzylphthalate	37	77.2	19.2
Benz[*a*]anthracene	1	3.0	3.0
Chrysene	1	2.9	2.9

Table 9. *Compounds detected in blanks using this method*--Continued

Compound (in elution order)	Number of detections	High concentration (µg/kg)	Mean concentration (µg/kg)
bis(2-Ethylhexyl)phthalate	43	321.0	40.2
2,2'-Biquinoline	6	63.9	30.3
Di-*n*-octylphthalate	2	7.6	4.0
Benzo[*b*]fluoranthene	1	2.1	2.1
Benzo[*k*]fluoranthene	0		
Benzo[*a*]pyrene	1	.1	.1
Indeno[1,2,3-*cd*]pyrene	1	4.4	4.4
Dibenz[*a,h*]anthracene	0		
Benzo[*ghi*]perylene	1	4.1	4.1

a riverine sediment that is highly contaminated with polychlorinated biphenyls. Only five of the SOCs determined in this method were reported in the certification of SRM 1939, and these are uncertified values. The reported concentrations for SRM 1939 also are near the method detection limits estimated for this method. Consequently, recovery determinations for samples of SRM 1939 are not reliable. Concentrations of SOCs determined in SRM 1939 and reported in their certification or determined but not reported are contained in table 10, since SRM 1939 was used as part of the method quality control at a time when more suitable materials were not available. These data can be compared with data for SRM 1941, a more appropriate reference material that was also used to develop this method. Data for SRM 1941 are discussed in section 11.2.5.

11.2.5 The NIST SRM 1941 is an estuarine sediment. The numbers of certified and uncertified SOCs and their concentrations are more appropriate for this method. Results for 35 SRM 1941 determinations made in 1993 and 1994 are listed in tables 11 and 12. Results comparing reported and certified SOC concentrations with the mean concentrations determined using this method in routine operation in 1993 and 1994 are listed in table 11. Mean concentrations of SOCs determined using this method, but which are not reported in the SRM certification documents supplied with SRM 1941, are listed in table 12.

11.2.6 The recoveries of certified and reported SOCs from SRM 1941 ranged from 51 to 122 percent, with a mean of 83 percent. The relative standard deviation of recovery ranged from 20 to 104 percent, with a mean of 53 percent. These high recoveries and high variability suggest that the method, on average, is performing as well as the method used by NIST to extract, isolate, and analyze SRM 1941 for SOCs. The high observed variability reflects the variability associated with the extraction, isolation, and analysis of SOCs by multiple technicians and chemists using different instruments, all performed over a period of nearly 1 year.

Table 10. *Semivolatile organic compounds detected in Standard Reference Material 1939*

[µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate mean and standard deviation. Summary results for 22 analyses of Standard Reference Material 1939 determined in 1993 and 1994 . Compounds determined, five of which are reported in the National Institute of Standards and Technology certificate of analysis]

Compound	Expected concentration in SRM 1941 (µg/kg)	Mean concentration (µg/kg)	Standard deviation (µg/kg)	Relative standard deviation (percent)	*n*
Phenol		64	78	122	13
p-Cresol		87	52	59	9
Naphthalene		24	14	58	7
Acenaphthylene		64	51	80	14
Diethylphthalate		66	47	72	11
Phenanthrene	130	98	50	51	21
Anthracene		70	65	92	18
Di-*n*-butylphthalate		225	128	57	19
Fluoranthene	190	193	102	53	22
Pyrene	170	192	109	57	21
Butylbenzylphthalate		185	168	90	16
Benz[*a*]anthracene	46	154	109	70	21
Chrysene	51	183	100	55	20
bis(2-Ethylhexyl)phthalate		747	456	61	22
Benzo[*b*]fluoranthene		197	123	62	22
Benzo[*k*]fluoranthene		167	113	67	22
Benzo[*a*]pyrene		169	119	71	20
Indeno[1,2,3-*cd*]pyrene		170	158	93	18
Benzo[*ghi*]perylene		111	75	67	13

11.2.7 The concentrations of nonreported SOCs in SRM 1941 (table 12) are reported so that other users of SRM 1941 can make independent assessments of method performance for these compounds. The observed SOC types and concentrations are what would be expected in sediment samples from a contaminated, urban estuarine site.

11.3 *Method detection limits*

11.3.1 Method detection limits (MDLs) were established by using procedures outlined by the U.S. Environmental Protection Agency (1992). For this method, the MDL was determined by analyzing a set of seven replicate reagent spike samples spiked at 200 µg/kg. For the set of seven samples, the sample standard deviation was computed and the MDL calculated from the following formula:

$$MDL = S \times t(n\text{-}1, 1\text{-}\alpha = 0.99) \quad (10)$$

Table 11. Compound concentrations certified by the National Institute of Standards and Technology for Standard Reference Material 1941 and determined using this method

[SRM, Standard Reference Material; µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate mean and standard deviation. Summary results for 35 analyses determined in 1993 and 1994 (also see table 12). Compounds are those with certified and noncertified concentrations reported in the National Institute of Standards and Technology (NIST) certificate of analysis]

Compound	Expected concentration in SRM 1941 (µg/kg)	Measured mean concentration in SRM 1941 (µg/kg)	Standard deviation of concentration in SRM 1941 (µg/kg)	Relative standard deviation (percent)	*n*	Recovery (percent)	Standard deviation of recovery (percent)	Relative standard deviation of recovery (percent)
Acenaphthene	52	48	9	19.5	11	91.8	17.9	19.5
Acenaphthylene	115	116	72	62.0	29	100.5	62.3	62.0
Anthracene[1]	202	185	86	46.4	35	91.8	42.6	46.4
Benz[*a*]anthracene[1]	550	387	164	42.4	34	70.4	29.8	42.4
Benzo[*a*]pyrene[1]	670	393	177	45.0	34	58.6	26.4	45.0
Benzo[*b*]fluoranthene[1]	780	590	280	47.5	34	75.7	35.9	47.5
Benzo[*ghi*]perylene[1]	516	298	180	60.2	34	57.8	34.8	60.2
Benzo[*k*]fluoranthene[1]	444	540	268	49.6	34	121.7	60.4	49.6
Chrysene (plus coeluting triphenylene)	641	533	227	42.7	35	83.2	35.4	42.5
2,6-Dimethylnaphthalene	198	162	90	55.7	32	81.6	45.5	55.7
Fluoranthene[1]	1,220	862	388	45.0	35	70.6	31.8	45.0
9H-Fluorene	104	98	101	103.5	23	93.9	97.2	103.5
Indeno[1,2,3-*cd*]pyrene[1]	569	477	260	54.5	34	83.9	45.7	54.5
2-Methylanthracene	66	77	64	82.9	19	116.3	96.5	82.9
4,5-Methylenephenanthrene	109	99	64	64.5	17	91.1	58.8	64.5
Naphthalene	1,322	669	283	42.3	35	50.6	21.4	42.3
Phenanthrene[1]	577	429	175	40.7	35	74.3	30.3	40.7
Pyrene[1]	1,080	772	317	41.0	35	71.5	29.3	41.0

[1]Indicates compounds whose concentrations are certified by NIST. The remaining concentrations are reported by NIST but are not certified.

Table 12. *Semivolatile organic compounds detected in Standard Reference Material 1941 not reported by the National Institute of Standards and Technology*

[µg/kg, micrograms per kilogram; *n*, number of determinations used to calculate mean and standard deviation. Summary results for 35 analyses of Standard Reference Material 1941 determined in 1993 and 1994 (also see table 11). Compounds determined but not reported in the National Institute of Standards and Technology certificate of analysis]

Compound	Mean concentration (µg/kg)	Standard deviation (µg/kg)	Relative standard deviation (percent)	*n*
Acridine	69	38	55.1	11
Anthraquinone	153	85	55.3	19
bis(2-Ethylhexyl)phthalate	1,677	814	48.6	35
Butylbenzylphthalate	171	107	62.6	28
p-Cresol	144	132	91.7	22
Dibenz[*a*,*h*]anthracene	195	166	85.1	15
Dibenzothiophene	68	39	56.4	25
Di-*n*-butylphthalate	332	217	65.4	35
Diethylphthalate	66	27	40.7	16
1,2-Dimethylnaphthalene	58	36	61.5	15
1,6-Dimethylnaphthalene	143	78	54.7	33
2-Ethylnaphthalene	59	28	47.5	12
1-Methyl-9H-fluorene	59	21	35.7	20
1-Methylphenanthrene	118	75	63.6	27
1-Methylpyrene	94	59	62.8	28
Phenol	131	67	51.5	31
2,3,6-Trimethylnaphthalene	84	45	53.2	19

where S = standard deviation of replicate analyses, in micrograms per kilogram;

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

n = number of replicate analyses.

A concentration of 200 µg/kg was used because the documented USEPA recommendation is to bracket the concentration of the spike to between two and five times the anticipated MDL.

11.3.2 The calculated MDLs for each SOC in the method at a 200 µg/kg spiking concentration (25 g assumed dry weight) are shown in table 13. As described by the U.S. Environmental Protection Agency (1992), this MDL estimate is provisional, because most of the calculated individual MDLs are less than one-fifth of the spiking concentration. These provisional results indicate that an additional MDL determination experiment, using a reagent spike concentration lower than 200 µg/kg, would result in MDLs acceptable by U.S. Environmental Protection Agency (1992) criteria. The MDLs in table 13 are thus conservative estimates.

Table 13. *Calculated method detection limits (MDLs)*

[All MDLs calculated for single-operator analysis. The calculated F-ratio must be less than 3.05 for pooled MDLs to be valid when seven replicates are used. MS Engine, MDLs determined using a Hewlett-Packard MS Engine gas chromatograph/mass spectrometer; MSD, MDLs determined using a Hewlett-Packard MSD gas chromatograph/mass spectrometer; µg/kg, micrograms per kilogram; *n*, the number of samples in the statistic; b.d., bad data; NA, not applicable; %, percent; GPC, gel permeation chromatography]

Compound (in elution order)	MS Engine method detection limit (µg/kg) spiked at 200 µg/kg *n*=7	MSD method detection limit (µg/kg) spiked at 200 µg/kg *n*=7	F-ratio (MS Engine to MSD) for 200 µg/kg standard deviation of recovery	Pooled method detection limit (µg/kg) spiked at 200 µg/kg *n*=14
Phenol	23.5	23.8	1.03	20.2
bis(2-Chloroethyl)ether	40.5	35.4	1.31	32.4
2-Chlorophenol	27.8	27.7	1.01	23.7
1,3-Dichlorobenzene	36.8	32.3	1.30	29.5
1,4-Dichlorobenzene	49.9	35.0	2.04	36.8
1,2-Dichlorobenzene	37.1	28.0	1.76	28.0
bis(2-Chloroisopropyl)ether	33.9	22.9	2.18	24.7
Hexachloroethane	32.3	30.9	1.09	26.9
N-Nitrosodi-*n*-propylamine	37.3	27.8	1.81	28.1
p-Cresol	41.2	33.4	1.51	32.0
Nitrobenzene	37.9	34.3	1.22	30.8
Isophorone	31.5	31.9	1.03	27.1
2-Nitrophenol	45.6	29.6	2.37	32.8
C8-Alkylphenol	30.9	38.8	1.57	29.9
bis(2-Chloroethoxy)methane	35.8	43.5	1.48	34.0
2,4-Dichlorophenol	31.3	26.4	1.41	24.7
3,5-Dimethylphenol	34.7	37.4	1.16	30.8
1,2,4-Trichlorobenzene	25.8	34.2	1.76	25.8
Naphthalene	29.6	32.0	1.17	26.3
2,4,6-Trimethylphenol	39.4	35.3	1.24	31.9
Hexachlorobutadiene	22.5	27.0	1.44	21.2
Quinoline	34.3	37.0	1.16	30.4
Isoquinoline	33.4	33.0	1.02	28.3
4-Chloro-3-methylphenol	31.6	29.2	1.17	26.0
Hexachlorocyclopentadiene*	17.1	4.8	12.48	10.7

Table 13. *Calculated method detection limits (MDLs)*--Continued

Compound (in elution order)	MS Engine method detection limit (µg/kg) spiked at 200 µg/kg *n*=7	MSD method detection limit (µg/kg) spiked at 200 µg/kg *n*=7	F-ratio (MS Engine to MSD) for 200 µg/kg standard deviation of recovery	Pooled method detection limit (µg/kg) spiked at 200 µg/kg *n*=14
2,4,6-Trichlorophenol	65.6	47.9	1.88	49.0
2,3,5,6-Tetramethylphenol	b.d.	b.d.	NA	NA
2-Chloronaphthalene	34.0	33.2	1.05	28.6
2-Ethylnaphthalene	35.2	30.2	1.36	28.0
2,6-Dimethylnaphthalene	32.6	28.6	1.29	26.2
1,6-Dimethylnaphthalene	35.9	28.3	1.61	27.6
Acenaphthylene	33.2	33.9	1.04	28.6
1,2-Dimethylnaphthalene	33.3	31.0	1.16	27.4
Dimethylphthalate	33.8	30.1	1.26	27.3
2,6-Dinitrotoluene	44.7	39.9	1.25	36.2
Acenaphthene	36.1	36.3	1.01	30.9
2,4-Dinitrophenol*	81.3	159.7	3.86	108.1
2,4-Dinitrotoluene	39.5	26.5	2.21	28.7
4-Nitrophenol	19.1	b.d.	NA	NA
2,3,6-Trimethylnaphthalene	34.7	39.6	1.30	31.7
9H-Fluorene	35.7	40.2	1.27	32.5
4-Chlorophenyl-phenylether	32.7	37.9	1.35	30.2
Diethylphthalate	37.7	35.6	1.12	31.3
4,6-Dinitro-2-methylphenol	30.5	b.d.	NA	18.4
N-Nitrosodiphenylamine	29.3	34.5	1.39	27.3
Azobenzene	32.8	40.7	1.54	31.6
4-Bromophenyl-phenylether	33.8	33.3	1.03	28.6
1-Methyl-9H-fluorene	33.8	41.0	1.47	32.0
Hexachlorobenzene	32.1	26.8	1.43	25.2
Pentachloroanisole	35.9	31.5	1.30	28.8
Dibenzothiophene	31.1	34.6	1.24	28.1
Pentachlorophenol	148.4	b.d.	NA	89.5
Pentachloronitrobenzene	31.9	24.1	1.75	24.1
Phenanthrene	32.5	37.0	1.30	29.7
Anthracene	32.2	32.5	1.01	27.6

Table 13. *Calculated method detection limits (MDLs)*--Continued

Compound (in elution order)	MS Engine method detection limit (µg/kg) spiked at 200 µg/kg n=7	MSD method detection limit (µg/kg) spiked at 200 µg/kg n=7	F-ratio (MS Engine to MSD) for 200 µg/kg standard deviation of recovery	Pooled method detection limit (µg/kg) spiked at 200 µg/kg n=14
Acridine	25.8	30.3	1.37	24.0
Phenanthridine	27.9	32.1	1.33	25.7
9H-Carbazole	29.8	34.5	1.34	27.5
2-Methylanthracene	29.6	29.7	1.01	25.3
Benzo[*c*]cinnoline	26.5	30.2	1.30	24.2
4,5-Methylenephenanthrene	29.4	37.1	1.59	28.5
1-Methylphenanthrene	34.6	35.6	1.06	29.9
Di-*n*-butylphthalate	31.6	33.6	1.13	27.8
Anthraquinone	29.7	38.9	1.71	29.6
Fluoranthene	28.2	38.5	1.87	28.8
Pyrene	29.0	33.2	1.30	26.6
1-Methylpyrene	28.8	28.8	1.00	24.6
Butylbenzylphthalate	33.2	29.2	1.29	26.7
Benz[*a*]anthracene	25.7	27.2	1.12	22.6
Chrysene	30.3	25.4	1.42	23.8
bis(2-Ethylhexyl)phthalate	41.4	31.5	1.73	31.4
2,2'-Biquinoline*	37.9	72.8	3.69	49.5
Di-*n*-octylphthalate	22.0	34.3	2.42	24.6
Benzo[*b*]fluoranthene	23.4	22.4	1.09	19.5
Benzo[*k*]fluoranthene	44.0	31.8	1.92	32.8
Benzo[*a*]pyrene	17.1	26.9	2.49	19.2
Indeno[1,2,3-*cd*]pyrene	27.3	31.0	1.28	24.9
Dibenz[*a,h*]anthracene	27.5	30.6	1.24	24.8
Benzo[*ghi*]perylene	60.1	87.9	2.14	64.2
Nitrobenzene-d_5 (method surrogate)	39.4	40.3	1.05	34.0
2-Fluorobiphenyl (method surrogate)	28.0	32.8	1.36	26.0
Terphenyl-d_{14} (method surrogate)	26.5	30.5	1.33	24.4
Benzo[*e*]pyrene-d_{12} (GPC surrogate)	55.8	32.9	2.87	39.1
Mean MDL-All Compounds	35.4	35.1		30.4
Standard Deviation of MDL-All Compounds	15.9	17.1		12.9

* For these compounds, the F-ratio exceeded 3.05 and failed the test for pooling MDLs. For consistency, the pooled MDL is used as the MDL for all compounds.

11.3.3 These provisional MDLs are calculated from data for a single set of replicate reagent spike samples. Ideally, the most representative MDL is determined from data collected from a group of reagent spike samples that are processed at different times and by different technicians. However, the MDLs in table 13 were determined using data from two different instruments, a Hewlett-Packard MS Engine and a Hewlett-Packard MSD. Each extract was analyzed with each instrument type. Both of these mass spectrometers are used in routine analysis for this method, so it was deemed appropriate that an MDL be presented for each instrument platform. Table 13 also contains pooled MDLs for each compound, combining the two platform-specific MDLs. Calculated F-ratios indicate that the platform-specific MDLs are not significantly different from each other for all but three SOCs (hexachlorocyclopentadiene, 2, 4-dinitrophenol, and 2,2'-biquinoline), justifying the use of the pooled MDL as the method reporting limit. Pooled MDLs are used for all SOCs, including the three noted above, for consistency. Under current routine production conditions, it is impossible to identify the specific instrument or instrument models used to determine SOC concentrations and so the pooled MDL is most appropriate. The platform-specific and pooled MDLs are based on seven replicate reagent spike samples, and thus do not include effects resulting from coextracted matrix interferences.

CONCLUSIONS

A new method has been developed for the determination of semivolatile organic compounds from bottom sediment. Method improvements include lower method detection limits, an expanded range of SOCs included in the method, and the ability to determine organochlorine pesticides and polychlorinated complex mixtures from the same sample extract. The method consists of a sediment dewatering step, extraction with dichloromethane, an automated GPC step for partial SOC isolation from coextracted interferences, and automated GC/MS instrumental analysis.

Validation data demonstrate that this method is suitable for the determination of a wide range of SOCs in sediment samples. Most SOCs in this method have acceptable recovery and precision for routine quantitative use. A small subset of the SOCs tested using this method was found to be irreproducibly recovered so that quantitative determination is not possible, but estimated concentrations can be reported.

Quality-control samples (reagent spikes, blanks, and SRM samples) in this method are used to quantitatively monitor performance under routine production conditions. These data suggest that over a period of 1 year, the method provides acceptable quantitative data for most SOCs. Surrogate compounds added to samples at the time of extraction and at the time of GPC isolation indicate that recovery variation is most likely caused by individual sample matrix effects. MDLs determined for this method indicate better sensitivity (as low as 18.4 µg/kg) than by previous USEPA and USGS analytical methods.

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