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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Bottom and Suspended Sediment by Gas Chromatography with Electron-Capture Detection

Water-Resources Investigations Report 03–4293

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

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Gale A. Norton, Secretary

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Conversion Factors

Multiply	By	To obtain
	Length	
centimeter (cm)	3.94×10^{-1}	inch
micrometer (µm)	3.94×10^{-5}	inch
millimeter (mm)	3.94×10^{-2}	inch
meter (m)	3.28×10^{0}	foot
nanometer (nm)	3.94×10^{-8}	inch
	Mass	
gram (g)	3.53×10^{-2}	ounce, avoirdupois
kilogram (kg)	3.53×10^{1}	ounce, avoirdupois
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
picogram (pg)	3.53×10^{-14}	ounce, avoirdupois
	Volume	
liter (L)	2.64×10^{-1}	gallon
liter (L)	3.38×10^{-1}	ounce, fluid
microliter (µL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon
	Pressure	
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch

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

$$°F = (1.8 \times °C) + 32$$

ABBREVIATED WATER-QUALITY UNITS

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

ABBREVIATIONS AND ACRONYMS

CAS	Chemical Abstracts Service
CCV	continuing calibration verification
ECD(s)	electron-capture detector(s)
F1(s)	fraction 1(s)
F2(s)	fraction 2(s)
FEP	tetrafluoroethylene-hexafluoropropylene copolymer
GC	gas chromatography (or gas chromatograph)

GC/ECD	gas chromatography/electron-capture detection
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HCB	hexachlorobenzene
HPLC	high-performance liquid chromatography
ID	inside diameter
IRL(s)	interim reporting level(s)
K-D	Kuderna-Danish
LRB	laboratory reagent blank
LRS(s)	laboratory reagent spike(s)
MDL(s)	method detection limit(s)
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
N-EVAP™	nitrogen gas evaporator
OC(s)	organochlorine(s)
OCIIS	organochlorine internal-injection standard
PAH(s)	polycyclic aromatic hydrocarbon(s)
PCB(s)	polychlorinated biphenyl(s)
PEM	performance evaluation mix
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
rpm	revolutions per minute
RPD(s)	relative percent difference(s)
SRM(s)	standard reference material(s)
S-EVAP™	steam evaporator
TPC(s)	third-party check(s)
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
±	plus or minus
≥	greater than or equal to
≤	less than or equal to

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory–Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Bottom and Suspended Sediment by Gas Chromatography with Electron-Capture Detection

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Abstract

A method applicable for the determination of 19 organochlorine (OC) pesticides, including total toxaphene as a complex mixture, and 3 polychlorinated biphenyl (PCB) mixtures as Aroclor® equivalents—Aroclor 1016/1242, 1254, and 1260—in soil, aquatic bottom sediment, and suspended sediment is described. Method performance data are presented. The solvent system is designed to extract simultaneously selected OC pesticides and PCBs from the same sample matrix. The compounds are extracted by conventional Soxhlet extraction with dichloromethane, followed by partial isolation using gel permeation chromatography (GPC) to remove inorganic sulfur and large naturally present molecules from the sediment extract. The aliquot of extract collected from the GPC for OCs (OC pesticides and PCBs) is split into two sample fractions by alumina/silica combined-column chromatography, followed by Florisil adsorption chromatography to remove interfering compounds in the second fraction. The OC fractions are analyzed by dual capillary-column gas chromatography with electron-capture detection (GC/ECD). This report is limited to the determination of selected OC pesticides and PCBs by GC/ECD using this method. Interim reporting levels (IRLs) have been set at 0.400 to 3.12 micrograms per kilogram (µg/kg) for 18 individual OC pesticides, 200 µg/kg for toxaphene, and 4.04 to 4.68 µg/kg for the PCBs, based on a sample size of 25-gram equivalent dry weight. These reporting levels may change following additional determinations of method detection limits.

Introduction

Most organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) have low water solubilities; thus, these organic contaminants typically are associated with soil, bottom sediment, and suspended sediment in hydrologic environments that possess a measurable total of organic carbon. The method described in this report was designed to extract OC pesticides and PCBs from a sediment or soil matrix and to isolate the contaminants from co-extracted natural organic matter by gel permeation and adsorption chromatography prior to instrumental analysis by dual capillary-column gas chromatography (GC) with electron-capture detection (ECD).

The determination of selected OC pesticides and PCBs as Aroclor equivalents was implemented as a custom method at the National Water Quality Laboratory (NWQL) in July 1996 at the request of the Reconstructed Trends Program for a study as part of the National Water-Quality Assessment (NAWQA) Program (Van Metre and others, 1997, 2000). The custom method developed into the present (2004) new method described in this report. The new method is based largely on USGS method O-5129-95 (Foreman and others, 1995, p. 4–49) originally developed for the NAWQA Program. The new method includes a Florisil clean-up step for fraction-2 extracts to minimize interferences that would compromise the performance of the GC columns used for quantifying the selected OCs determined by this method. The extensive preparation protocol provides cleaner extracts, thus increasing signal-to-noise ratios and improving method detection limits compared to the method by Foreman and others (1995). The new method also determines fewer compounds in a shorter gas chromatographic analysis time compared to the method by Foreman and others (1995). The selected OCs in the new method are determined by using a GC oven temperature program that is 42 minutes shorter per sample fraction than the gas chromatographic program described by Foreman and others (1995, p. 30), which was

lengthened to enhance PCB congener and OC pesticide separations and to determine the permethrin isomers. Furthermore, the new method specifically reports PCBs as Aroclor equivalent concentrations at the request of the Reconstructed Trends Program.

Before 2004, the NWQL reported PCBs eluting in the Aroclor 1242 region of the gas chromatogram as Aroclor 1242 only. However, Aroclor 1242 and Aroclor 1016 have nearly identical PCB congener composition, and, thus, practically indistinguishable gas chromatographic profiles. Therefore, in the new method, PCBs eluting in this region will be classified and the concentration will be reported as Aroclor 1016/1242 (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum No. 99.10, 1999) to minimize misclassification of these two Aroclors in environmental and quality-assurance samples. In the method-performance evaluation, PCB Aroclor 1242 (and not Aroclor 1016) was determined; however, the results for Aroclor 1242 are reported as Aroclor 1016/1242 (see section 14). The new method was approved October 2003. The method was implemented at NWQL in March 2004.

Purpose and Scope

The purpose of this report is to describe an analytical method for the determination of 19 OC pesticides and 3 PCB mixtures in soil, aquatic bottom sediment, and suspended sediment. An aliquot of the concentrated, filtered extract is injected quantitatively onto two polystyrene-divinylbenzene gel permeation chromatography (GPC) columns connected in series. The compounds are eluted with dichloromethane. A specific range of time is set on the GPC for the collection of the OC aliquot containing the OC pesticides and PCBs. An adsorption chromatography step using an alumina/silica combined column separates the OCs into two sample fractions; the second fraction undergoes an additional adsorption chromatography step using a Florisil column for cleanup. These two adsorption chromatography steps reduce interferences that might produce a response in the electron-capture detector, or contribute to degradation of analytes in the injection port of the gas chromatograph. Each fraction then is analyzed by dual capillary-column GC/ECD.

This method combines elements of U.S. Geological Survey (USGS) methods outlined in OC pesticides and PCBs in bottom sediment (Foreman and others, 1995). In addition, this method adapts components of U.S. Environmental Protection Agency (USEPA) method 3620C (Florisil cleanup) (U.S. Environmental Protection Agency, 2000).

A description of the method from sampling protocol through calculation and reporting of results for OC pesticides and PCBs, estimated method detection limits, laboratory quality assurance and quality control, and bias and precision data from a method-performance evaluation are presented.

Acknowledgments

The authors note the substantial contributions made by Dan Bottinelli, Troy Engstrom, and Deborah Vaught of the NWQL's Analytical Services Section for much of the sample preparation for the data presented in this report. The authors also wish to acknowledge the following NWQL staff members for their assistance and contributions leading to the design, development, testing, and implementation of this method: Edward T. Furlong of the Methods Research and Development Program, and Sonja Abney, Dawn Fulton, Jana L. Iverson, Virendra Jha, Leslie (Merten) Kanagy, Dennis Markovchick, Mary C. Olson, and Michael Schroeder, Analytical Services. Additional thanks to Barbara Kemp for assistance with manuscript preparation and to Jon Raese for report editing.

Safety Considerations

This method involves the handling of known, suspected, and possibly unknown hazardous chemicals and reagents. The method uses substantial volumes of dichloromethane, a suspected carcinogen, during sample extraction and some extract clean-up steps. Wear SilverShield® (also known as Norfoil®) gloves for the most resistance to dichloromethane; most other gloves (including nitrile gloves) do not provide adequate protection when handling the solvent. Carefully follow all standard safety practices regarding the use of solvents, compressed gases, OC pesticides, PCBs, polycyclic aromatic hydrocarbons, and other method-related chemicals. Consult material safety data sheets and chemical labels for proper storage, handling, and additional safety information. The USEPA has special regulations covering the handling and disposal of PCBs. Always wear appropriate protective clothing, gloves, and eye wear, and use adequate ventilation when preparing samples or standard solutions. Electron-capture detectors contain radioactive ^{63}nickel and are cleaned by trained personnel only.

Analytical Method

Organic Compounds and Parameter Codes: Organochlorine pesticides, polychlorinated biphenyls, soil, bottom and suspended sediment by mass per mass, high-performance gel permeation chromatography, dual capillary-column gas chromatography, electron-capture detection, O-5504-03; and suspended sediment by mass per volume, O-7504-03 (see table 1)

1. Scope and Application

This method is suitable for the determination of 19 individual OC pesticides, including total toxaphene as a complex OC pesticide mixture, and 3 PCB mixtures as Aroclor equivalents—Aroclor1016/1242, 1254, and 1260—in soil, bed sediment, suspended sediment, and dry sludge. This method is applicable to samples with OC compounds that are (1) efficiently extracted from the solid matrix by methanol or dichloromethane, (2) adequately separated from natural co-extracted compounds by gel permeation chromatography (GPC), (3) efficiently recovered from the alumina-over-silica adsorption chromatography clean-up/fractionation step and the Florisil adsorption chromatography clean-up step, (4) sufficiently volatile and thermally stable for gas chromatographic analysis, and (5) responsive to electron-capture detection. This method is applicable to a 25-g equivalent dry-weight sample size for extraction. A minimum of 0.1-g dry-weight sample size can be used, with reporting levels raised accordingly. This method also is applicable to suspended-sediment samples collected on glass-fiber filters, with concentrations reported in micrograms per liter for known sample-volume filtered (Mahler and others, 2001).

2. Summary of Method

A flowchart for the method is shown in figure 1. In brief, a bottom-sediment sample is centrifuged to remove excess water. A sample size of 25-g equivalent dry weight is extracted overnight with dichloromethane (93 percent) and methanol (7 percent). The sample extract is concentrated and first filtered through a 1.0-µm polytetrafluoroethylene syringe filter, then through a 0.2-µm polytetrafluoroethylene syringe filter connected in series. For the determination of OC pesticides and PCBs, a 1,100-µL aliquot of the sample extract is injected quantitatively onto two serial polystyrene-divinylbenzene GPC columns. Compounds are eluted with dichloromethane at a flow rate of 1 mL/min and are collected in a distinct fraction time window. Interferences elute first from the GPC columns and are not collected. The method compounds then are collected in a GPC fraction for about 8.9 minutes. Sulfur elutes immediately after this GPC fraction and is not collected. The collected GPC fraction of OCs is concentrated and solvent exchanged, then undergoes cleanup using alumina/silica combined column adsorption chromatography and further split into two OC fractions. The second OC fraction undergoes additional cleanup using a Florisil column. Both OC fractions are analyzed by dual capillary-column gas chromatography with electron-capture detection (GC/ECD). The GC/ECD is calibrated for both capillary columns by the external standard method using multipoint calibration standards. The OCs subsequently are quantitated against the calibration curve processed for each column.

3. Interferences

This method is designed to minimize false positives through dual-column confirmation. However, nonmethod organohalogen, oxygenated, and other ECD-sensitive compounds that are co-extracted, collected in the GPC fraction and the adsorption chromatography fractions, and have GC retention times identical to those of the selected OCs of interest potentially can interfere with the analytical method. Hydrocarbon contamination from oils on the analytical instrument or in sediments, polychlorinated napthalenes, phthalates, and inorganic sulfur that is incompletely removed during the GPC step can interfere with qualification and quantification of method compounds. Follow-up analysis by mass-spectral confirmation also may be used to confirm identification, if uncertain. For some samples, reliable detection might not be possible because of the levels of interferences in the matrix, and interim reporting levels might have to be raised. Furthermore, the shorter GC oven temperature program in contrast with that described by Foreman and others (1995, p. 30) causes some recognizable coelutions, for example, dieldrin and *p,p'*-DDE on the Rtx® –5 primary column (5.10.1.1), and *p,p'*-DDE and a PCB congener on the Rtx® –1701 secondary column (5.10.1.2). Consequently, high PCB concentrations might interfere with *p,p'*-DDE determination.

4. Apparatus and Equipment

The apparatus and equipment required for this method, listed as follows, are grouped by the specific preparation step or analysis but are not repeated if used in

Table 1. Laboratory codes, parameter codes, and Chemical Abstracts Service registry numbers for method compounds.

[NWQL, National Water Quality Laboratory; P-code, parameter code; CAS, Chemical Abstracts Service; --, not assigned]

Compound name	Abbreviation	Method O-5504-03 Dry-weighted sediment		Method O-7504-03 Wet-weighted sediment		CAS number
		NWQL result code	P-code	NWQL result code	P-code	
Aldrin	--	4450	39333B	4550	39332B	309-00-2
cis-Chlordane (*alpha*-Chlordane)	--	4451	62802A	4551	62956A	5103-71-9
trans-Chlordane (*beta*-Chlordane)	--	4452	62803A	4552	62957A	5103-74-2
4,4'-Dichlorodiphenyldichloro-ethane	*p,p'*-DDD	4453	39363B	4553	39362B	72-54-8
4,4'-Dichlorodiphenyldichloro-ethene	*p,p'*-DDE	4454	39368B	4554	39367B	72-55-9
4,4'-Dichlorodiphenyltrichloro-ethane	*p,p'*-DDT	4455	39373B	4555	39372B	50-29-3
Dieldrin	--	4456	39383B	4556	39382B	60-57-1
Endosulfan I	--	4457	39389B	4557	34363B	959-98-8
Endrin	--	4458	39393B	4558	39392B	72-20-8
Heptachlor	--	4459	39413B	4559	39412B	76-44-8
Heptachlor epoxide (Isomer B)	--	4460	39423B	4560	39422B	1024-57-3
Hexachlorobenzene	HCB	4547	39701B	4561	34402A	118-74-1
alpha-Hexachlorocyclohexane	α-HCH	4461	39076B	4562	34254A	319-84-6
beta-Hexachlorocyclohexane	β-HCH	4462	34257B	4563	34256A	319-85-7
gamma-Hexachlorocyclohexane (Lindane)	γ-HCH	4463	39343B	4564	39342B	58-89-9
p,p'-Methoxychlor	--	4464	39481B	4565	82351B	72-43-5
Mirex	--	4465	39758B	4566	39757B	2385-85-5
trans-Nonachlor	--	4466	62804A	4567	62958A	39765-80-5
Polychlorinated biphenyl Aroclor 1016/1242	PCB Aroclor 1016/1242	4548	46343A	4568	62959A	--
Polychlorinated biphenyl Aroclor 1016	PCB Aroclor 1016	--	--	--	--	12674-11-2
Polychlorinated biphenyl Aroclor 1242	PCB Aroclor 1242	--	--	--	--	53469-21-9
Polychlorinated biphenyl Aroclor 1254	PCB Aroclor 1254	4468	39507A	4569	39506A	11097-69-1
Polychlorinated biphenyl Aroclor 1260	PCB Aroclor 1260	4469	39511A	4570	39510A	11096-82-5
Toxaphene (technical)	--	4471	39403B	4572	39402B	8001-35-2
Surrogates						
alpha-Hexachlorocyclohexane-d_6	α-HCH-d_6	4472	62837A	4573	99990A	--
Isodrin	--	4473	62836A	4574	99991A	465-73-6
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	PCB-207	4474	62838A	4575	99992A	53742-07-7

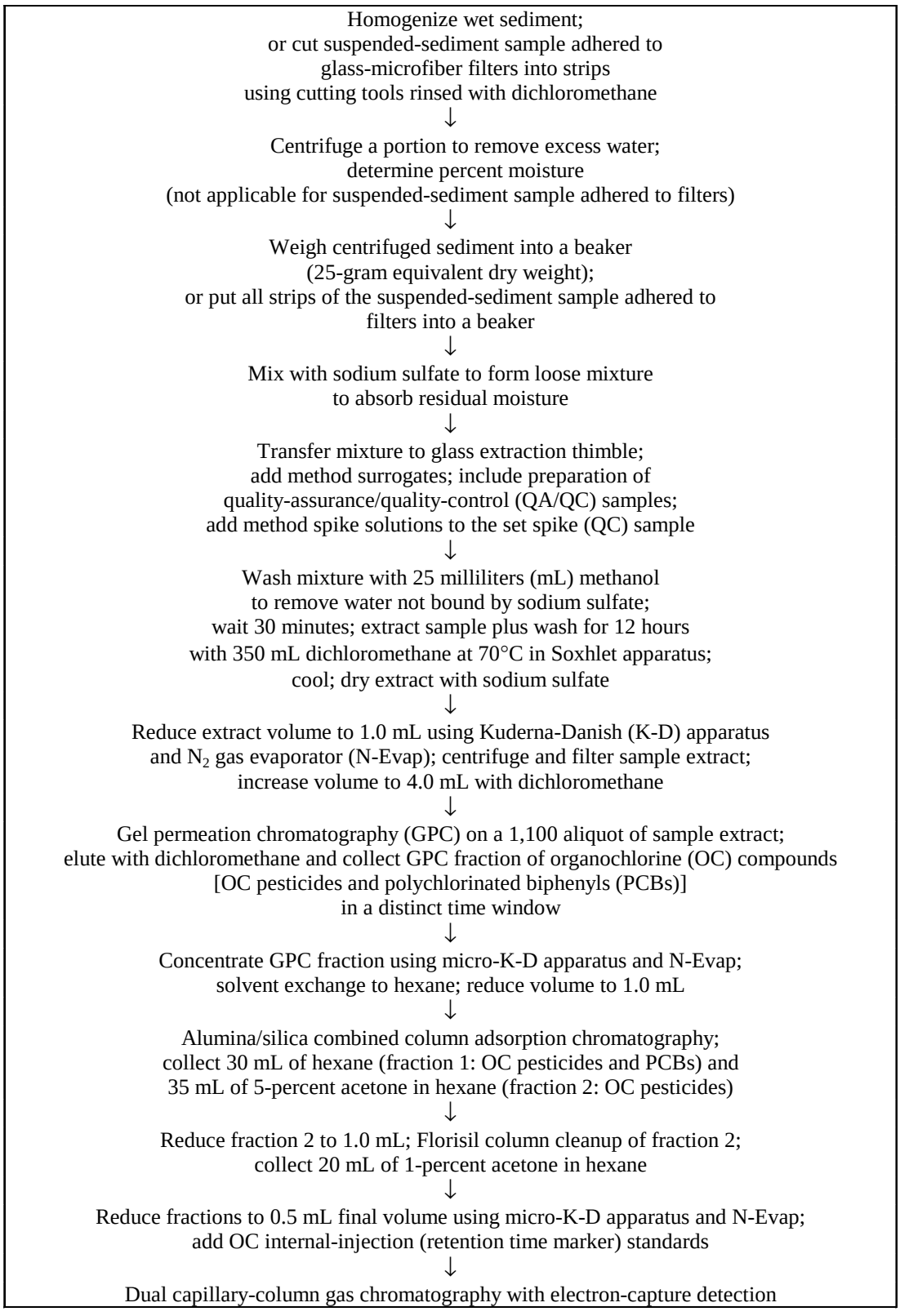

Figure 1. Flowchart showing the analytical method. Details are in the text of this report.

more than one part of the method. Specific models and sources that were used to develop or implement this method also are listed, as appropriate.

Prior to use, wash all glassware (except class–A volumetric glassware) with phosphate-free detergent, rinse sequentially with tap and distilled water, and heat to 450°C for a minimum of 2 hours. With the exception of vials, micropipet bores, and Pasteur pipets, prerinse all glassware with the solvent used in the procedure requiring the glassware. Clean class–A volumetric glassware by rinsing with acetone followed by triple rinsing with pesticide-grade dichloromethane. Solvent-rinsing steps may be substituted for the final heating step for other glassware.

Unless otherwise indicated, prerinse all nonglass items that will be in contact with the sample or sample extract with the solvent used in the procedural step or with pesticide-residue grade acetone.

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 swinging bucket rotor and buckets capable of centrifuging 250-mL centrifuge bottles at up to 5,000 revolutions per minute; International Equipment Co. Model EXD or comparable.

4.1.3 *Centrifuge bottles*—250-mL capacity made of a tetrafluoroethylene-hexafluoropropylene copolymer (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 *Drying (or 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 comparable.

4.1.6 *Glass beakers*—borosilicate, 50- and 400-mL volumes.

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 water-cooled extractor condenser with 45/50 bottom joint.

4.2.2 *Soxhlet extraction sample thimble*—borosilicate glass, 35 x 90 mm, extra-coarse glass frit; Kontes, Inc. Model K-586500-0022EC or comparable.

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

4.2.4 *Fixed volume micropipet*—10- and 100-µL; Drummond micropipetor-microdispenser or comparable.

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 tube (see 4.3.2), all with 19/22 standard taper joints.

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

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

4.3.4 *Nitrogen manifold sample concentrator*—Organomation Associates, Inc. Model 124 N-EVAP™ or comparable.

4.4 *Sediment extract filtration*

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

4.4.2 *Syringe*—5- or 10-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 Corp. or comparable:

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 built tube holder capable of holding thirty-six, 25-mL K-D receiver tubes.

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

4.5.2 *Column heater*—set at 27.0°C; Jones Chromatography Ltd. or comparable.

4.5.3 *Nitrogen pressurization system*—consisting of a regulated grade 5 nitrogen source, polytetrafluoroethylene (PTFE) tubing, a 23-gage needle, and associated metal fittings and Vespel® ferrule for connecting the needle to the nitrogen source by the tubing.

4.5.4 *Helium sparging system*—used for deoxygenating the dichloromethane solvent prior to GPC.

4.5.5 *HPLC pump priming syringe*—25-mL; Hamilton Gas-Tight 1,000 Series, Model 82520 or comparable.

4.5.6 *Balance*—capable of weighing to 200 ±0.0001 g; Mettler-Toledo Model AT 200 or comparable.

4.5.7 *K-D receiver tube, 25-mL*—graduated to 25 mL, with 19/22 ground-glass stopper.

4.6 ***GPC OC fraction solvent exchange and reduction***

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 ***Adsorption chromatography and cleanup***

4.7.1 *Nitrogen head-pressure system*—an eight-column, in-house built system designed to deliver nitrogen gas head pressure from 0 to 70 kilopascals (kPa) gage pressure and to allow precise and accurate control of solvent flow at 1 mL/min through each column at less than 70 kPa delivery pressure. The system uses eight Norgen Model 11-018-146 relieving regulators or comparable, fitted with pressure gages, along with associated hardware to connect the regulators to the columns, including 3.2-mm inside diameter (ID) PTFE tubing, shut-off valves, tubing fittings, ferrules, and pinch clamps. The system also includes a molecular sieve/activated-charcoal filter that is used to purify the nitrogen gas, and an in-house built eight-position rack for holding the 40-mL K-D receiver tubes (see 4.7.3).

4.7.2 *Glass alumina/silica adsorption chromatography clean-up column*—30-cm long by 10-mm ID fitted with coarse glass frit, PTFE stockcock, solvent reservoir top capable of holding at least 60 mL of solvent, and fitted with a 28/15 female ball joint for connection to the nitrogen head pressure system (4.7.1) by a 28/15 male ball joint; Allen Scientific Glassblowers, Inc., items ASG-201-01 and ASG-202-01 or comparable.

4.7.3 *K-D receiver tube, 40-mL*—custom-made using a 25-mL K-D receiver tube modified with a top reservoir capable of containing 40 mL of solvent, graduated at 25, 30, 35, and 40 mL, and has a 19/22 joint; Allen Scientific Glassblowers, Inc., item ASG-210-01 or comparable.

4.7.4 *Bottle-top solvent dispenser*—5- or 10-mL; Brinkmann Dispensette or comparable.

4.7.5 *Glass Florisil column*—11-cm long by 5-mm ID with top reservoir capable of containing 15 mL of solvent; Allen Scientific Glassblowers, Inc., item ASG-MC01 or comparable.

4.8 ***Fraction concentration***

4.8.1 *Micropipet*—10-µL fixed-volume, calibrated; Hamilton Co. Model 80366 or comparable; for addition of internal-injection standard solution.

4.9 ***Gas chromatography/electron-capture detection analysis***

4.9.1 *Gas chromatograph/electron-capture detector*—Hewlett-Packard 5890 or Perkin-Elmer Autosystem, equipped with two electron-capture detectors, an autosampler, a split/splitless injector, and a computer controller (Perkin-Elmer's Turbochrom® Client/Server instrument control software and Thru-Put System's Target® data review software) or comparable. The GC system needs to be suitable for use with single injection, dual capillary-column GC analysis.

4.9.2 *Syringe*—10-µL volume; Hamilton Co. Model 80377 for GC autosampler or comparable.

4.10 ***Instrument calibration and spike standards solution preparation***

4.10.1 *Volumetric flasks*—class A, varied volumes from 25- to 100-mL.

4.10.2 *Micropipets*—10- to 250-µL fixed- and variable-volume, calibrated.

4.10.3 *Syringes*—variable volumes from 10- to 500-µL, calibrated.

4.10.4 *Pipets*—class A, varied volumes from 1- to 5-mL.

4.10.5 *Disposable pipets*—Pyrex®, sterile, pack plugged, 1-mL volume, graduated in 1/100.

5. Reagents and Consumable Materials

The reagents and consumable materials required for this method, listed as follows, are grouped by the specific preparation step or analysis 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 at 150°C in a stoppered, prebaked Erlenmeyer flask until used.

5.2 *Sediment extraction*

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

5.2.2 *Boiling chips*—bake at 450°C for 8 hours. Store in sealed, prebaked glass jar until used.

5.2.3 *Disposable glass capillaries*—for the 10-, 25-, 50-, 100-, 200-, and 250-µL fixed- and variable-volume micropipets described in sections 4.2.4 and 4.10.2.

5.2.4 *OC surrogate solution*—contains isodrin, nonachlorobiphenyl (PCB-207), and deuterium-labeled alpha-hexachlorocyclohexane (*alpha*-HCH-d_6), commercially obtained as concentrated solutions in hexane; Protocol Analytical Supplies, Inc. or comparable, except isodrin, which is commercially obtained as a concentrated solution in methanol; Absolute Standards, Inc. or comparable. Dilute an aliquot of each solution to a final single solution concentration (C_a) of 0.5 ng/µL of each OC surrogate in methanol. Other appropriate surrogate compounds may be added or substituted into this method after demonstrating acceptable method performance.

Note: Surrogate and other standard solutions (spike, OC internal-injection, calibration, and quality-control solutions) typically are prepared in advance but can become concentrated. Therefore, prepare all standard solutions every 6 months, or sooner if any one of the solutions becomes concentrated. Store all standard solutions at –15°C in a freezer specified for OC standards and free from samples.

5.2.5 *Individual OC-pesticide spike solution*—contains the individual OC pesticides listed in table 1, commercially obtained as concentrated solutions in hexane or other solvent; Absolute Standards, Inc. or comparable. Dilute in hexane an aliquot of each solution to an intermediate single solution concentration of 10 ng/µL of each component. Dilute the intermediate solution further to a final solution concentration ($C_{b)}$ of 0.5 ng/µL of each individual OC pesticide in methanol.

Note: Currently (2004), OC surrogate (section 5.2.4) and individual OC-pesticide spike solutions (section 5.2.5) also are used in water extraction methods at the NWQL. Consequently, the latter solution contains additional (water-method or commercially present) compounds (endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone, delta-HCH, and perthane) that are not suitable for this sediment method (Foreman and others, 1995, p. 53). The polarity of the methanol solvent renders the solutions applicable to the water methods. Ideally, n-hexane is the suggested solvent for preparing all surrogate and spike (and calibration) solutions to help ensure proper compound dissolution, especially of the higher molecular-weight OC compounds [see PCB (5.2.6) and toxaphene (5.2.7) spike solutions]. Use of some higher boiling intermediate polarity solvents (for example, toluene or ethyl acetate) in the spike solutions is not suggested because of potential fraction irreproducibilities during adsorption chromatography.

5.2.6 *PCB spike solution*—contains PCB Aroclor 1242, 1254, and 1260, each commercially obtained as concentrated solutions in isooctane; NSI Solutions, Inc. or comparable. Dilute an aliquot of each solution to a single final solution concentration (C_b) of 25 ng/µL of each Aroclor in hexane.

5.2.7 *Toxaphene spike solution*—contains toxaphene at a final solution concentration (C_b) of 250 ng/µL in hexane, prepared by diluting an aliquot of a commercially obtained concentrated solution of toxaphene in methanol; NSI Solutions, Inc. or comparable.

5.2.8 *Standard reference materials (SRMs) or other quality-assurance (QA) reference materials*—any SRM consisting of naturally present organochlorine compounds, interlaboratory comparison sample, or other (spiked) sediment or soil reference material available to test the method for recovery of some or all of the method compounds may be an appropriate QA material. Spiked soil from Environmental Resource Associates—PriorityPollutnT® Certified Reference Material (CRM), catalog number 720—predominately was used in this method. An example of a natural material is SRM 1941b from The National Institute of Standards and Technology.

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 *Filters*—0.2- and 1.0-µm pore sizes, 25-mm diameter disposable PTFE membrane syringe filters, Gelman Sciences' Acrodiscä CR or comparable.

5.4.2 *Pasteur pipets*—14.6- and 22.9-cm-long disposable pipets with rubber bulbs. Clean by baking at 450°C for 8 hours, no solvent rinse.

5.4.3 *GPC vials*—4-mL, amber glass, with open-top screw cap and PTFE-faced silicone rubber septum. Clean by baking at 450°C for 8 hours, no solvent rinse.

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 comparable. Connect the columns in series with a low dead-volume union.

5.5.3 *GPC–OC fraction test solution*—contains *trans*-permethrin, hexachlorobenzene, and elemental sulfur each at about a concentration of 20 ng/µL in dichloromethane. The components in the GC–OC fraction test solution are the same as those used by Foreman and others (1995, p. 13).

Note: Compound *trans*-permethrin has not been tested as a method compound in this method; however, *trans*-permethrin is a method compound in the analytical method O-5129-95 (Foreman and others, 1995, p. 5). The GPC–OC fraction test solution is shared between these two methods.

5.6 *GPC fraction concentration and solvent exchange*

5.6.1 *Hexane*—pesticide-residue grade or higher purity.

5.7 *Alumina/silica adsorption chromatography cleanup and fractionation*

5.7.1 *Alumina*—Woelm Alumina N Activity I, 50 to 200 mesh, finer particle size preferred; Scientific Adsorbents, Inc., catalog number 02087 or comparable, lot number E1002-2 tested (see note in section 7.7).

5.7.2 *Silica gel*—Woelm Active, 100 to 200 mesh, finer particle size preferred; Scientific Adsorbents, Inc., catalog number 02747 or comparable, lot number K18P3 tested (see note in section 7.7).

5.7.3 *Acetone*—pesticide-residue grade or higher purity.

5.7.4 *Water*—ASTM Type I reagent water (American Society for Testing and Materials, 2001, p. 107–109).

5.7.5 *Fraction-2 elution solvent for alumina/silica cleanup*—Prepare a 5-percent acetone and 95-percent hexane solution by combining 30 mL of acetone with 570 mL of hexane.

Note: Carefully prepare the 5-percent acetone and 95-percent hexane solution. Slight variations from the specified mixture composition might result in fractionation differences in the alumina/silica fractionation process.

5.8 *Florisil adsorption chromatography cleanup*

5.8.1 *Florisil*® —adsorbent for gas chromatography, 60 to 100 mesh; EM Science, catalog number FX0284-1 or comparable, lot number 37300940 tested.

5.8.2 *Fraction-2 elution solvent for Florisil cleanup*—Prepare a 1-percent acetone and 99-percent hexane solution by combining 10 mL of acetone with 990 mL of hexane.

Note: Carefully prepare the 1-percent acetone and 99-percent hexane solution. Slight variations from the specified mixture might result in unwanted interferences in the fraction-2 extract.

5.8.3 Glass wool—plug, deactivated borosilicate.

5.9 *Fraction concentration*

5.9.1 *Vial*—1.8- or 2-mL, amber glass, screw top, with hole-top screw caps that have PTFE-faced silicone septa, 0.5-mL marked calibration preferred. Clean by baking at 450°C for 8 hours, no solvent rinse.

5.9.2 *OC internal-injection standard (OCIIS) solution*—contains tetrachloro-*m*-xylene and decachlorobiphenyl, commercially obtained as a concentrated solution of tetrachloro-*m*-xylene and decachlorobiphenyl in acetone; Supelco, Inc. or comparable. Dilute the concentrated solution to a final concentration of 10,000 pg/µL in hexane.

5.10 *Gas chromatography/electron-capture detection analysis*

5.10.1 *Capillary GC columns:*

5.10.1.1 *Primary column*—fused-silica, 30-m by 0.25-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.'s Rtx®-5 or comparable.

5.10.1.2 *Secondary column*— fused-silica, 30-m by 0.25-mm ID, internally coated with a 14-percent cyanopropylphenyl- and 86-percent dimethyl-polysiloxane stationary phase having a 0.25-µm film thickness; Restek Corp.'s Rtx®-1701 or comparable.

Note: Other column types can be used after demonstration of acceptable separation and quantitation performance.

5.10.2 *Column connector*—glass Y-type; Restek Corp. catalog number 20405 or comparable.

5.10.3 *GC guard column*—deactivated, uncoated fused-silica tubing, 5-m by 0.32-mm ID; Restek Corp. catalog number 10044 or comparable.

5.10.4 *GC injection-port liners*—glass. Use any instrument-specific splitless or direct injection-port liner that provides minimal breakdown of endrin, *p,p'*-DDT, and *p,p'*-methoxychlor following deactivation with a silanization reagent, and that provides acceptable peak shape and detector response.

5.10.5 *Silanizing reagent*—for deactivating GC injection-port liners; Supelco, Inc. Sylon-CT® solution (5-percent dimethyldichlorosilane in toluene) or comparable.

5.11 ***GC/ECD calibration and quality-control solutions***

Note: Prior to analysis, add 10 µL of the OCIIS solution (5.9.2) to each of the GC/ECD calibration standard (5.11.1) and quality-control (5.11.2) solutions listed below. The OCIIS solution is added to a known volume (for example, 0.5 mL) of solution in a 1.8-mL amber vial to allow for compound dilution correction and for use of internal-injection standard quantitation (see option in section 9.1). Use the same lot number or NWQL standard solution number of the OCIIS solution that will be added to the sample extracts under section 7.9.5.

5.11.1 *GC/ECD calibration standard solutions:*

5.11.1.1 *Individual OC pesticide calibration standard solutions*—Prepare working calibration standard solutions containing the individual OC pesticides listed in table 1 and the surrogates at 1, 2, 5, 10, 20, 50, 100, and 200 pg/µL in hexane, using commercially prepared higher concentration, single- or mixed-compound stock solutions; Absolute Standards, Inc. or comparable.

5.11.1.2 *PCB calibration standard solutions*—Prepare separate working calibration standard solutions for Aroclor 1242, Aroclor 1254, and Aroclor 1260 at 100 pg/µL in hexane, using commercially prepared higher concentration stock solutions; NSI Solutions, Inc. or comparable. Aroclor 1016 typically is not used as a calibration standard solution because its peak pattern of polychlorinated biphenyl congeners is nearly identical to Aroclor 1242 (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum No. 99.10, 1999). See section 9.2 for PCB calibration and section 9.2.1 for guidance on PCB peak selection.

5.11.1.3 *Toxaphene calibration standard solution*—Prepare a working calibration standard solution of toxaphene at 1,000 pg/µL in hexane, using a commercially prepared higher concentration stock solution; NSI Solutions, Inc. or comparable. See section 9.2 for toxaphene calibration and section 9.2.2 for guidance on toxaphene peak selection.

5.11.2 *GC/ECD quality-control (QC) solutions:*

5.11.2.1 *Performance evaluation mix (PEM)*—used to monitor the degradation of problem compounds in the GC injection port. The PEM typically contains *p,p'*-DDT (100 pg/µL), endrin (50 pg/µL), and *p,p'*-methoxychlor (250 pg/µL) at a minimum; Supelco, Inc. pesticide PEM catalog number 48397 or comparable.

5.11.2.2 *Continuing calibration verification (CCV) standard solution*—used to monitor calibration stability. The CCV contains the entire suite of individual OC pesticides listed in table 1, typically prepared at 20 pg/µL in hexane. The individual OC pesticide calibration standard solution at 20 pg/µL (5.11.1.1) typically is used for the CCV.

5.11.2.3 *Third-party check (TPC) solution*—an independent, commercially available standard solution that is used to verify the accuracy of the concentrations of the calibration standard components. The TPC contains selected OC pesticides of interest, typically with its component concentrations equivalent to the CCV. Prepare the TPC solution to a final working concentration of 20 pg/µL in hexane, using a commercially prepared higher concentration multicomponent stock solution; Supelco, Inc. or comparable.

5.11.2.4 *600-each Aroclor solution*—used to monitor the PCB calibration linearity. Prepare a 1:1:1 mixture of Aroclor 1242, 1254, and 1260 at 600 pg/µL for each Aroclor in hexane, using the commercially prepared higher concentration stock solutions that were used to make the PCB calibration standard solutions (5.11.1.2). Additional 1:1:1 mixtures at higher concentrations may be used to monitor the PCB calibration linearity.

6. Collection, Shipment, and Storage of Sediment Samples

6.1 ***Sampling methods and sample-collection equipment***—Use sampling methods that will collect bottom-sediment and suspended-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 used to collect representative bottom-sediment samples as well as procedures for sampling and postcollection processing are contained in the USGS National Field Manual (Radtke, 1998), and specifically for the USGS National Water-Quality Assessment Program, in Shelton and Capel (1994). A method for the collection of a suspended-sediment sample on glass-fiber filters, where the volume of water pumped is recorded, is described by Mahler and others (2001).

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 PTFE

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 (precleaned by baking at 450°C for at least 2 hours) with PTFE-lined lids or other NWQL-approved containers, on ice by overnight carrier to the NWQL as soon as possible following collection. Decant excess water to allow space in the jars for expansion from freezing.

6.4 ***Sample storage***—Following login at the NWQL, samples are stored at –15°C in freezers dedicated to OC sediment samples 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). Foil may be wrapped around the glass jars to prevent breakage and possible contamination. After analysis, the remaining sample materials are stored at –15°C for a minimum of 3 years; however, the sample extracts are stored indefinitely at –15°C.

7. Sample Preparation Procedure

Samples are grouped into sets of 16 total samples, including QA/QC samples, because two extraction units accommodate up to 16 samples. Typically, 13 field samples are included in a set, depending on the number of laboratory QC samples.

7.1 ***Sample dewatering and percent dry-weight 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 about a 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 about 150 g of homogenized sample into a 250-mL PTFE centrifuge bottle and record sediment weight (W_a). 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 revolutions per minute (rpm). **CAUTION:** Make sure the centrifuge is balanced properly prior to operation. 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. Record weight of sediment after decanting water (W_b).

Note: If there is an unpaired sample in the centrifuge, add a centrifuge bottle of water of equal weight to counterbalance.

7.1.5 Thoroughly rehomogenize the sediment sample in the centrifuge bottle. Using the drying balance (4.1.5), determine the percent moisture content to ±0.1 percent on a 1.8- to 2.2-g aliquot of the centrifuged sediment. The wet-weight fraction (f_w) is calculated by dividing the percent moisture content by 100. Calculate the dry-weight fraction of sediment (f_d):

$$f_d = 1 - f_w \quad (1)$$

Option: Set the drying balance (4.1.5) to display percent dry weight (P_d) (for example, on the Model YTC O1L drying balance, select the setting "100 – 0%" to display "P_d" on the balance screen). Record the percent dry weight to ±0.1 percent on a 1.8- to 2.2-g aliquot of the centrifuged sediment. Calculate the dry-weight fraction of sediment (f_d) by dividing P_d by 100.

7.1.6 Weigh a maximum of 30 g of wet, centrifuged sediment sample into a tared 400-mL beaker. Record the weight as actual sample (wet) weight (W_w).

7.1.7 Add 130 g of anhydrous sodium sulfate to the beaker. Mix thoroughly, and, if necessary, add additional sodium sulfate to ensure that the mixture is dry and loose.

7.1.8 For suspended sediment collected in the field on burned, glass-microfiber filters, sample dewatering and percent dry-weight determinations do not apply. On a clean watch glass, cut the filters to quarter-inch-wide strips with razor blades rinsed with dichloromethane. Transfer the strips to a beaker and tare to zero on the top-loading analytical balance (4.1.4). Add 70 g of anhydrous sodium sulfate to the beaker. Mix thoroughly, and, if necessary, add additional sodium sulfate to ensure that the mixture is dry and loose, so that the strips are not clinging to each other.

7.2 ***Sediment extraction***

7.2.1 Add all of the sediment-sodium sulfate mixture (7.1.7 or 7.1.8) to a Soxhlet extraction sample thimble (4.2.2). Repeat for all field-sediment samples.

7.2.2 Prepare the following QA/QC samples as required, depending on types of analyses to be performed:

7.2.2.1 *Reagent blank sample (laboratory reagent blank or set blank)*—Place 125 g of sodium sulfate into an extraction thimble.

7.2.2.2 *Reagent OC spike sample (laboratory reagent spike or set spike)*—Place 125 g of

sodium sulfate into an extraction thimble, and spike the sodium sulfate with 100 µL (V_b) of individual OC-pesticide spike solution (5.2.5), using a calibrated micropipet or syringe. The expected final spiked concentration for the individual OC pesticides is 2 µg/kg, assuming a 25-g equivalent dry weight (see following second note). Additional set spike solutions: In addition to the individual OC-pesticide spike solution, spike either 10 µL (V_b) of the PCB spike solution (5.2.6), or spike 100 µL (V_b) of the toxaphene spike solution (5.2.7) as desired into the set spike. The expected final spiked concentration is 10 µg/kg for each PCB Aroclor, or 1,000 µg/kg for toxaphene, assuming a 25-g equivalent dry weight. Preparation of a set spike sample containing both the PCB and toxaphene spike solutions generally is not used because of the complexity of the PCB and toxaphene mixtures.

Note: When possible, implement all new spiking standard solutions in one sample set and keep in synchrony with new calibration standard solutions to avoid undesirable data shifts.

Note: This same laboratory reagent spike (LRS) typically is fortified with spiking solutions used for other sediment methods, for example, organophosphate analysis (Jha and Wydoski, 2003) and polycyclic aromatic hydrocarbon (PAH) analysis (Olson and others, in press). Compound HCB is currently (2004) a component in a PAH spike solution at a final solution concentration of 6 ng/µL in dichloromethane. If the LRS is fortified with 100 µL of this PAH spike solution in addition to the individual OC-pesticide spike solution, then the expected final spiked concentration for HCB in the LRS is 26 µg/kg—2 µg/kg from the individual OC-pesticide spike solution and 24 µg/kg from the PAH spike solution, assuming a 25-g equivalent dry weight.

7.2.2.3 Standard reference material (SRM) sample—Place 1 to 25 g of appropriate SRM (5.2.8) into an extraction thimble; the amount extracted will depend on SRM availability, compound concentrations relative to the reporting level, and cost. Mix in 123 g of anhydrous sodium sulfate for 2 g of SRM 1941b, for example, to simulate step 7.1.7. (SRMs usually do not contain much water so a separate dry-weight determination is unnecessary.)

7.2.3 Extract and process the QA/QC samples through the remainder of the method exactly as for the field-sediment samples.

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

7.2.5 Add 100 µL (V_a) of OC surrogate solution (5.2.4) on top of each sample contained in a thimble, using a calibrated micropipet or syringe.

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

Note: 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 note in section 7.3.2).

7.2.7 Attach the Soxhlet apparatus to the condenser, adjust coolant flow to 1,500 cubic centimeters per minute, and extract the sample at 70°C on the steam bath (4.2.3) for at least 12 hours.

7.2.8 Following extraction, cool the extract to room temperature, then add about 20 g of anhydrous 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 the flask with a ground-glass stopper and store sodium sulfate-containing extract in a refrigerator for at least 2 hours.

7.3 *Sediment extract concentration*

7.3.1 Transfer the extract (but not the sodium sulfate) from the flask to a K-D evaporative 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 using the K-D combined steam bath/condenser unit (4.3.3), then remove the extract from the unit and allow to cool.

Note: Remove all methanol during this K-D concentration step, otherwise the solvent will cause problems during the GPC cleanup (7.5). Methanol is removed completely 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 in the receiver tube to 1.0 mL using a gentle stream of nitrogen gas (4.3.4). Cap tube and store the extract at 4°C until step 7.4.

7.4 ***Sediment extract filtration***

7.4.1 Centrifuge (4.4.1) paired sets of extracts, contained in uncapped centrifuge receiver tubes, at 2,150 rpm for 10 minutes. Centrifugation improves the filtration process described in 7.4.2 to 7.4.6.

7.4.2 Weigh a labeled, 4-mL GPC vial with cap and septum attached (5.4.3) to ±0.0001 g and record the vial weight (W_v).

7.4.3 Attach a 1.0-µm PTFE filter (5.4.1) to a 5-mL Luer-Lok syringe (4.4.2). Attach a 0.2-µm PTFE filter (5.4.1) to the 1.0-µm PTFE filter. Remove the syringe plunger and place a tared GPC vial under the 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 the GPC vial as in 7.4.5.

7.4.7 Repeat step 7.4.6.

7.4.8 The extract volume should be at 2 mL with the above additions (steps 7.4.6 and 7.4.7). Using dichloromethane, bring extract volume up to 4 mL. Cap the GPC vial.

7.4.9 Weigh the extract contained in the capped GPC vial to ±0.0001 g and record vial-plus-extract weight (W_G). Calculate the weight of extract before GPC (W_1):

$$W_1 = W_G - W_v \quad (2)$$

where

W_G = weight of GPC vial with cap, septum, and extract, in grams; and

W_v = weight of empty GPC vial with cap and septum, in grams (7.4.2).

7.4.10 Store the extract at 4°C 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 configuration for elution fractions 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. The chromatographic conditions are the same as those used for similar USGS method O-5129-95 (Foreman and others, 1995, p. 20–23).

7.5.1 The GPC data system remains turned on continuously. Other system components (4.5.1), including the pump, autosampler, detector, fraction collector, and column heater (4.5.2), are 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 establishing start and end fraction collection times (7.5.7).

Note: 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 extract (7.4.10) to room temperature.

7.5.5 The GPC vial headspace of all sample extracts and GPC test solutions contained in 4-mL GPC vials is pressurized with nitrogen gas prior to beginning a GPC autosequence. This pressurization assists the syringe in withdrawing the correct aliquots of extract and test solutions for injection into the GPC. Pierce the vial septum with the pressurization needle (4.5.3), and pressurize with 200 kPa nitrogen for 1 minute. **CAUTION:** Do not place the needle into the liquid. Rinse the needle with dichloromethane between vial pressurizations.

7.5.6 For OCs, establish GPC system cleanliness and baseline stability by injecting a 1,100-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.

7.5.7 Perform GPC fraction calibration. Elution times might vary between analyses of a sample set because of GPC column aging, the presence of residual methanol from sample extraction, and other factors. Therefore, prior to beginning a GPC autosequence, establish start and end fraction collection times for the OCs to allow final configuration of the fraction collector.

7.5.7.1 Establish OC fraction collection times by injecting 1,100 µL of the GPC–OC fraction test solution (5.5.3) and monitoring the elution times of the peaks at low attenuation. Repeat injections of the GPC–OC fraction test solution as necessary to ensure chromatographic reproducibility. Fractions typically are

not collected for the GPC–OC fraction calibration test analyses. An example gel permeation chromatogram resulting from the analysis of the GPC–OC fraction test solution is shown in figure 2 (from Foreman and others,1995, p. 22).

7.5.7.1.1 Set the "start time" on the fraction collector for the GPC–OC fraction at least 10 seconds earlier from the beginning of the *trans*-permethrin peak (the first OC compound that elutes from the GPC; see fig. 2).

Note: Large natural substances that are being removed from the extract during the GPC step mostly elute prior to the method compounds. Therefore, do not set the collection "start time" much earlier than about 10 seconds before the beginning of the *trans*-permethrin peak; otherwise, the natural material may not be successfully eliminated from the collected fraction.

7.5.7.1.2 Set the "end time" on the fraction collector for the GPC–OC fraction at least 10 seconds later from the end of the hexachlorobenzene (HCB) peak (the last OC compound that elutes from the GPC before the sulfur peak; see fig. 2). The HCB peak is expected to be at least baseline separated from the sulfur peak, otherwise there might be some sulfur detected during GC/ECD analysis. Typically, small amounts of sulfur carry over into the collected GPC–OC fraction,

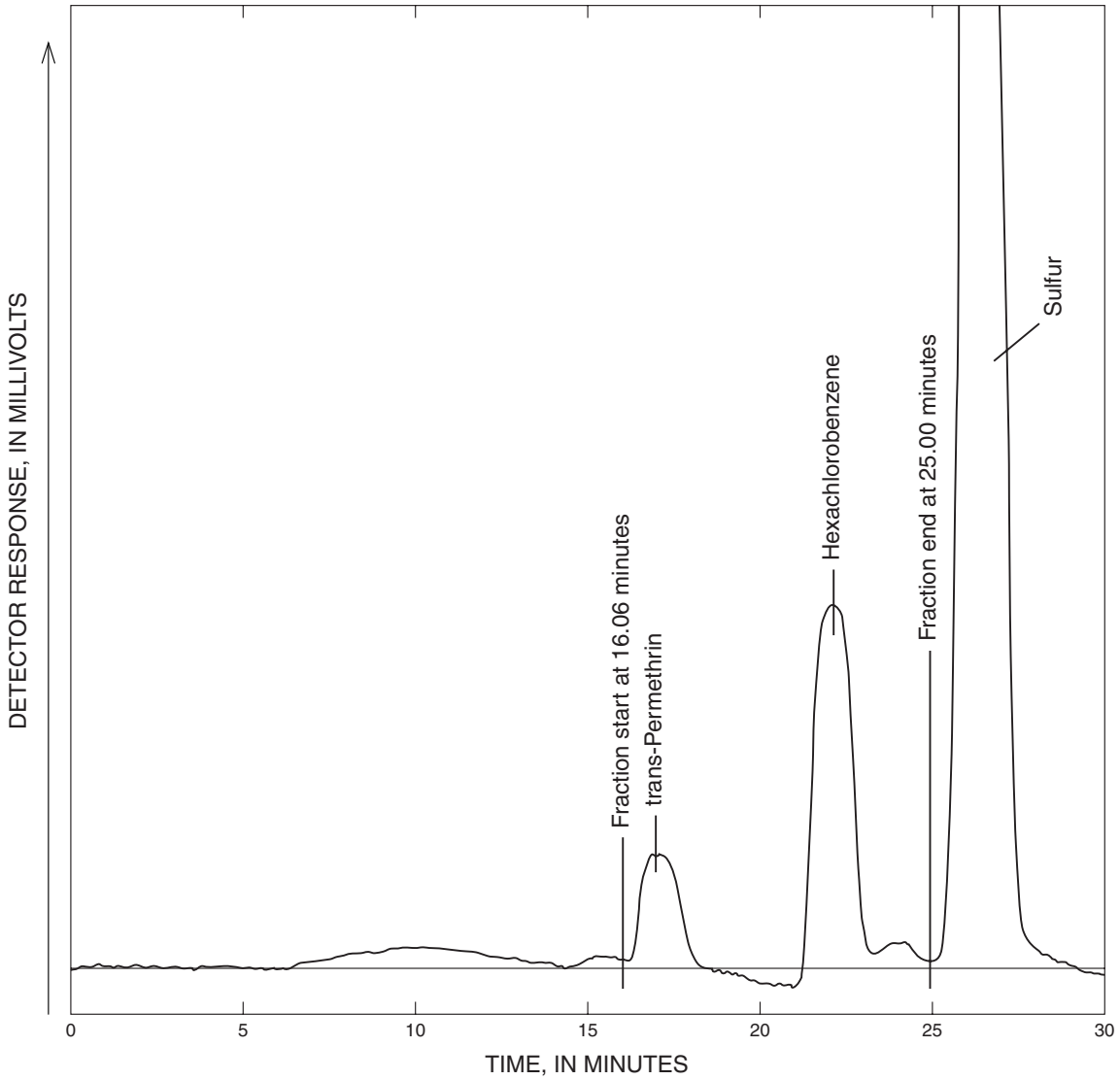

Figure 2. Gel permeation chromatogram of the fraction test solution at attenuation 8 showing the analyst-determined collection start and end times for the organochlorine pesticide fraction (from Foreman and others, 1995). Chromatographic conditions are listed in the text.

which result in a small sulfur peak in the GC/ECD that does not interfere with the determination of any compounds (except for selected individual PCB congeners). Carryover of larger amounts of sulfur might result in a large, broad peak or a severe baseline rise in the GC/ECD chromatogram, which might interfere with compound determinations. Thus, it is important to establish GPC conditions and set up OC fraction collection times so that sulfur is eliminated (or at least greatly minimized) in the collected GPC–OC fraction.

7.5.8 Perform a GPC automated separation to collect the OC fraction. Inject 1,100 µL of the sample extract and collect the GPC–OC fraction in a 25-mL K-D receiver tube (4.5.7). Use a 30-minute total separation time per sample. A suggested GPC autosequence, assuming one reagent blank sample, a reagent OC spike sample, an SRM sample, 12 field samples, and one field sample duplicate or additional field sample, is listed in table 2. Repeated injections of the GPC–OC fraction test solution and the system blank help to ensure continued fraction calibration and system cleanliness.

7.5.9 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 an overnight automated analysis, and record this weight as the weight of vial plus extract after GPC injection (W_H). Calculate the weight of OC extract processed through the GPC (W_2):

$$W_2 = W_G - W_H \quad (3)$$

where

W_G = weight of GPC vial with cap, septum, and extract before GPC, in grams (7.4.9); and

W_H = weight of GPC vial with cap, septum, and extract after GPC, in grams.

7.5.10 Cap K-D receiver tube containing the GPC–OC fraction and refrigerate until the solvent exchange step (7.6).

7.5.11 Replace the septum on the GPC sample vial and store the remaining portion of the extract not processed through the GPC in a freezer for possible reanalysis of an OC fraction, if necessary.

7.6 *GPC–OC fraction solvent exchange and reduction*

7.6.1 Add 4 mL hexane and two to three small boiling chips to the GPC extract (7.5.10), and attach a 3-ball micro-Snyder column to the top of the 25-mL K-D receiver tube.

7.6.2 Slowly introduce the 25-mL K-D receiver tube to a water bath (4.6.1) maintained at 70°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 hexane to the 25-mL K-D receiver tube, vortex, and place into the water bath. Reduce solvent volume to 4 mL.

7.6.4 Remove the 25-mL K-D receiver tube from water bath and reduce the extract to 1 mL using a gentle stream of nitrogen (4.3.4). Cap and store the OC sample extract at 4°C until step 7.7.

Table 2. Suggested gel permeation chromatography autosequence.

[OC, organochlorine; GPC, gel permeation chromatography; SRM, Standard Reference Material]

Sequence	Sample type
1	System blank (7.5.6) [1]
2	Reagent blank (7.2.2.1)
3	Reagent OC spike (7.2.2.2)
4	Sample 1
5	Sample 2
6	Sample 3
7	GPC–OC fraction test solution (5.5.3) [1]
8	System blank [1]
9	Sample 4
10	Sample 5
11	Sample 6
12	Sample 7
13	Sample 8
14	GPC–OC fraction test solution [1]
15	System blank [1]
16	Sample 9
17	Sample 10
18	Sample 11
19	Sample 12
20	Sample duplicate or additional sample
21	SRM (7.2.2.3)
22	GPC–OC fraction test solution[1]
23	System blank [1]

[1]Fractions typically not collected for the GPC test solution and system blank injections.

7.7 *Alumina/silica adsorption chromatography cleanup and fractionation for OCs*

This procedure removes additional unwanted interferences and separates method compounds into the alumina/silica fractions 1 and 2. The alumina/silica fractionation of method compounds in the analyses of a limited number of set spikes processed through the sample preparation procedure described in this section is listed in table 3.

Table 3. Alumina/silica fractionation and mean percent recovery of method compounds from the analyses of three to seven set spikes processed through the entire analytical procedure.

[±, plus or minus; --, not detected]

Compound[1]	Mean recovery ± standard deviation	
	Fraction 1[2] (percent)	Fraction 2[3] (percent)
Aldrin	62 ± 10	--
cis-Chlordane	--	63 ± 5
trans-Chlordane	--	63 ± 6
p,p'-DDD	--	61 ± 8
p,p'-DDE	75 ± 11	8 ± 6
p,p'-DDT	--	61 ± 8
Dieldrin	--	64 ± 6
Endosulfan I	--	53 ± 7
Endrin	--	71 ± 10
Heptachlor	54 ± 13	--
Heptachlor epoxide	--	62 ± 6
Hexachlorobenzene	51 ± 8	--
alpha-Hexachlorocyclohexane	--	52 ± 8
beta-Hexachlorocyclohexane	--	68 ± 8
gamma-Hexachlorocyclohexane	--	57 ± 7
p,p'-Methoxychlor	--	78 ± 13
Mirex	67 ± 11	--
trans-Nonachlor	--	66 ± 6
PCB Aroclor 1016/1242	75 ± 12	--
PCB Aroclor 1254	94 ± 20	--
PCB Aroclor 1260	94 ± 15	--
Toxaphene (technical)	--	70 ± 5
Surrogates		
alpha-HCH-d_6	--	76 ± 5
Isodrin	67 ± 10	--
PCB-207	87 ± 24	3 ± 1

[1]Individual pesticides were spiked at 50 nanograms per column, PCB Aroclors at 250 nanograms per column, and toxaphene at 5 micrograms per column.

[2]Fraction 1 is 30 milliliters (mL) of hexane. The number of observations (n) for the fraction-1 compounds was 7, except for hexachlorobenzene (n=5).

[3]Fraction 2 is 35 mL of 5-percent acetone and 95-percent hexane. The number of observations (n) for the fraction-2 compounds was 7, except for *p,p'*-DDE (n=3), and PCB-207 (n=5).

Note: The adsorption chromatography procedure used the specific lots of alumina and silica listed in section 5.7 at the specified levels of sorbent (heat) activation and sorbent (water) deactivation (7.7.1 and 7.7.2) for the fractionation listed in table 3. Use of different sources of sorbents or even different lots from the same source can alter the fractionation of method compounds. Ensure that sorbent materials are composed primarily of the finer particle sizes for acceptable fractionations. Verification of fraction recoveries is required prior to routine use of sorbent materials for samples and can be conducted using column-spike experiments of the method compounds solvent exchanged in hexane (Foreman and others, 1995, p. 24–26).

7.7.1 Sorbent (heat) activation

7.7.1.1 Weigh out into a 500-mL Erlenmeyer flask two times the total amount of alumina (5.7.1) and silica gel (5.7.2) required to process one set of samples.

Suggested amount of alumina =
2 x (3 g x number of samples)
Suggested amount of silica =
2 x (5 g x number of samples)

7.7.1.2 Activate the sorbents for at least 12 hours in an oven at 150°C. Store sorbents in the 150°C oven until ready to begin deactivation.

7.7.2 Sorbent (water) deactivation

7.7.2.1 Following activation, place the unstoppered flasks in a desiccator and allow the sorbents to cool to room temperature.

7.7.2.2 Sorbents are deactivated on a weight-to-weight basis using ultrapure water. Alumina is 8.5-percent deactivated, and silica gel is 2-percent deactivated. For example, if 100 g of 8.5-percent deactivated alumina is desired, weigh 91.5 g of alumina into a 500-mL Erlenmeyer flask on the analytical balance (4.1.4) and add 8.5 g water using a Pasteur pipet. Immediately cap the flask with ground-glass stopper and vigorously shake by hand for 10 minutes.

Note: Minimize contact of the sorbent to ambient air because the sorbents rapidly adsorb air moisture that can affect the level of deactivation.

Note: Unused deactivated sorbents may be reused at a later time; simply reactivate the unused portion at 150°C (7.7.1).

7.7.2.3. Place flasks on a mechanical shaker for 2 hours to equilibrate. Secure the stopper of each flask with a rubber band wrapped around the stopper and the shaker clamp.

Note: Fractionation could be affected if a flask is fractured while on the mechanical shaker. If breakage occurs, repeat steps 7.7.1 and 7.7.2 for the sorbent.

7.7.2.4. Store the flasks in a desiccator until ready to use.

7.7.3 Dry pack the chromatography columns in the following order:

Note: Open the stopcock prior to packing the column, especially before adding solvent (7.7.4). This procedure minimizes back-pressure problems that disrupt the packing during solvent addition.

7.7.3.1 Add about 1 cm of sodium sulfate (5.1.3) to the chromatography column (4.7.2). (The sodium sulfate helps prevent clogging of the column frit by silica fines.)

7.7.3.2 Add 3.0 g of 2-percent deactivated silica gel. Assist the packing step by gently tapping the column above the sorbent layer.

7.7.3.3 Overlay with 5.0 g of 8.5-percent deactivated alumina. Gently tap the column above the sorbent layer to facilitate packing.

7.7.3.4 Add about 1 cm of sodium sulfate to the top of the packing.

7.7.4 Using the solvent dispenser, immediately add 40 mL hexane to the column. Collect the hexane prerinse in a 50-mL beaker.

Note: Carefully add all solvents down the side of the column wall so as not to disturb the packing.

7.7.5 Attach a ball joint to the column and apply sufficient nitrogen gas pressure to pass the hexane rinse though the column in about 5 minutes. This helps drive out air and pack the sorbent. Take the solvent layer just into the top sodium sulfate layer; close stopcock.

CAUTION: At no time after wetting the column packing is the solvent level to fall below the top sodium sulfate layer and into the sorbents. If it does so prior to the addition of the sample extract (7.7.9), discard the column packing and repack with new deactivated sorbent.

7.7.6 Add another 10 mL hexane. **Option:** If 30 mL of hexane is added instead of 10 mL here, the packed columns can sit unused, with stopcock closed and ball joint attached, for as many as 4 hours.

7.7.7 Pass the final hexane prerinse through at a flow rate of 2 to 5 mL/min based on packing, prerinsing, and running of simultaneous columns. When about 2 to 3 mL of hexane prerinse remain, stop nitrogen pressure, and maintain solvent flow comparable to gravity flow (1 mL/min) until the hexane goes just into the top sodium sulfate layer; close stopcock.

7.7.8 Discard the prerinse and position a clean, hexane-rinsed 40-mL K-D receiver tube (4.7.3) labeled "fraction 1" (F1) at the column outlet.

7.7.9 Vortex the sample extract in the 25-mL K-D receiver tube (7.6.4), then carefully add the sample extract to the column head using a 22.9-cm Pasteur pipet. Position the pipet just above the top of the sodium sulfate layer and introduce the extract onto the sodium sulfate. Do not disturb the packing.

Note: At the time of sample addition, the sample must be in a completely nonpolar solvent (for example, hexane) and at a volume ranging from 0.5 (minimum) to 1.5 mL (maximum). The presence of residual dichloromethane or other "polar" solvent will produce undesirable and irreproducible compound separations. Consequently, dichloromethane or other "polar" solvent must be completely removed from the extract prior to adsorption chromatography.

7.7.10 Open stopcock and allow the sample to drop just into the top sodium sulfate layer; close stopcock.

Note: With GPC cleanup, the extracts generally are clean enough that application of nitrogen pressure during this and subsequent steps is not necessary. However, some sediment extracts might require application of slight nitrogen pressure to maintain adequate solvent flow; only use sufficient pressure to achieve previously unobstructed gravity-like flow rates (1 mL/min for hexane).

7.7.11 Rinse the 25-mL K-D receiver tube with 1 mL hexane, then carefully pipet the solvent onto the

column. Open stopcock and allow the rinse to drop just into the top sodium sulfate layer; close stopcock.

7.7.12 Repeat step 7.7.11. (The extract and two 1-mL rinses of the 25-mL K-D receiver tube are now loaded onto the column.)

7.7.13 Carefully add 27 mL of hexane down the inside wall of the column (do not disturb the packing), cap the ball joint, open the stopcock, and collect solvent into the F1 receiver tube until the hexane just reaches the top sodium sulfate layer; close stopcock. The total volume of F1 is 30 mL.

7.7.14 Replace the F1 receiver tube with another clean, hexane-rinsed 40-mL K-D receiver tube labeled "fraction 2" (F2) at the column outlet.

7.7.15 Carefully add 35 mL (5 mL seven times) of the 5-percent acetone and 95-percent hexane mixture (see 5.7.5 note) down the inside wall of the column, cap the ball joint, open the stopcock, and collect the solvent into the F2 receiver tube until the solvent just reaches the top of the sodium sulfate layer; close stopcock. The total volume of F2 is 35 mL.

7.7.16 Cap and store the F1 and F2 extracts at 4°C until step 7.9 and step 7.8, respectively.

7.7.17 Remove remaining solvent from used columns using 35-kPa nitrogen pressure; the dried packing is easily discharged from the column and discarded.

7.8 ***Fraction-2 solvent reduction and Florisil adsorption chromatography cleanup for OCs***

7.8.1 Fraction-2 reduction

7.8.1.1 Attach a 3-ball micro-Snyder column to the top of the 40-mL K-D receiver tube containing the F2 extract (7.7.15) and several small boiling chips.

7.8.1.2 Place the F2 receiver tube into a water bath (4.6.1) maintained at 85 to 87°C, and reduce the solvent volume to 4 mL.

7.8.1.3 Remove the F2 receiver tube from the water bath and reduce the F2 extract to 1 mL using a gentle stream of nitrogen (4.3.4). Cap and store the F2 extract at 4°C until step 7.8.2.

7.8.2 Florisil adsorption chromatography cleanup

7.8.2.1 Sorbent (heat) activation

7.8.2.1.1 Weigh into separate 500-mL Erlenmeyer flasks two times the total amount of Florisil required to process one set of samples.

Suggested amount of Florisil =
2 x (0.5 g x number of samples)

7.8.2.1.2 Activate the sorbent for at least 24 hours in an oven at 150°C. Store the Florisil sorbent at 150°C until ready to use.

7.8.2.2 Dry pack the Florisil columns in the following order:

7.8.2.2.1 Insert a small plug of glass wool into the narrow end of the glass Florisil column (4.7.5).

7.8.2.2.2 Add about 0.5 g of activated Florisil cooled to room temperature in a desiccator.

7.8.2.2.3 Overlay 1 cm of anhydrous sodium sulfate to the top of the packing.

7.8.2.3 Prerinse the column by adding 5 mL of hexane. Collect the hexane prerinse in a 50-mL beaker.

CAUTION: At no time after wetting the column packing is the solvent level to fall below the top sodium sulfate layer and into the sorbent.

7.8.2.4 Discard the prerinse and position a clean, hexane-rinsed 40-mL K-D receiver tube (4.7.3) labeled "fraction 2" (F2) at the column outlet.

7.8.2.5 Vortex the F2 extract in the F2 receiver tube (7.8.1.3), then carefully add the F2 extract to the column head, using a Pasteur pipet. Do not disturb the packing.

7.8.2.6 Allow the extract to drop just into the top sodium sulfate layer.

7.8.2.7 Rinse the F2 receiver tube (7.8.2.5) with 1 mL of 1-percent acetone and 99-percent hexane solution (5.8.2) and carefully pipet the rinse onto the column. Allow the solution to drop just below the top sodium sulfate layer.

7.8.2.8 Repeat step 7.8.2.7. (The extract and two 1-mL rinses of the F2 receiver tube are now loaded onto the column.)

7.8.2.9 Add 17 mL of the 1-percent acetone and 99-percent hexane solution down the inside wall of the column, and collect the solvent into the 40-mL K-D receiver tube labeled "fraction 2" positioned at the column outlet (7.8.2.4). The total volume of F2 is now 20 mL.

7.8.2.10 Cap and store the F2 extract at 4°C until step 7.9.

7.9 ***Fraction concentration for OCs***

7.9.1 Add two small boiling chips to the F2 extract (7.8.2.9), attach a 3-ball micro-Snyder column to the top of the K-D receiver tube, place the tube in a 80°C water bath, and reduce the solvent volume to 4 mL. Remove the tube from the bath and cool.

7.9.2 Raise water bath to 85 to 87°C. Add one small boiling chip to the K-D receiver tube, vortex, and place into the water bath. Reduce the solvent volume to no less than 1 mL, or until solvent evaporation dramatically decreases. Remove the tube from the bath and cool.

7.9.3 Further reduce the fraction to 0.5 mL using a gentle stream of nitrogen (4.3.4). Record the final extract volume (V_E) of the fraction.

7.9.4 Carefully transfer the fraction to a 1.8-mL amber vial (5.9.1), using a Pasteur pipet.

7.9.5 Add 10 µL of OCIIS (5.9.2) to the fraction in the vial, using a micropipet (4.8.1). Cap the vial and vortex. Mark on the vial the level of the extract and store at 4°C until GC/ECD analysis (see section 8).

Note: Exactly match the lot number or NWQL standard solution number of the OCIIS solution to that added in the calibration and quality-control solutions in section 5.11.

7.9.6 Repeat steps 7.9.2 through 7.9.5 for the F1 extract (7.7.13), which requires the higher water bath temperature.

8. Gas Chromatography/Electron-Capture Detection Analysis

8.1 ***Setup***—Analyze the sample extracts by gas chromatography with electron-capture detection (GC/ECD) using a dual capillary-column system (4.9.1) equipped with an autosampler, one split/splitless injection port (operated in the splitless mode), a 5-m section of deactivated, uncoated guard column (5.10.3), a Y-type column connector (5.10.2) to connect the guard column to the primary (5.10.1.1) and secondary (5.10.1.2) capillary columns, and two electron-capture detectors. Use a computer system to control the autosampler, GC operational conditions, and to acquire and process responses from the dual detectors. Complete details of GC/ECD operation are beyond the scope of this report. The following procedure outlines the suggested GC conditions and autosequence used in this method. Consult the appropriate instrument manuals for additional details regarding general GC/ECD system operation.

8.2 ***Suggested GC operational conditions***—Use any operational conditions that provide acceptable levels of compound separation, identification, quantitation, bias, and precision.

8.2.1 Injection port temperature: 220°C.

8.2.2 Splitless injection split time: 60 seconds. Split flow rate: about 50 mL/min. Septum purge flow rate: about 3 mL/min.

8.2.3 Sample injection volume: 2 µL.

8.2.4 Oven temperature program: initial temperature 60°C (hold for 1 minute).

Ramp 1—30°C/min to 180°C

Ramp 2—1°C/min to 210°C

Ramp 3—4°C/min to 280°C, hold for 10 to 30 minutes to allow for sufficient column bake-out.

Note: The GC temperature program is 42 minutes shorter than that used in USGS method O-5129-95 (Foreman and others, 1995), which, for that method, was lengthened to allow for improved separation of PCB congeners and the additional analytes.

8.2.5 Electron-capture detector temperature: 350°C (Hewlett-Packard); 380°C (Perkin-Elmer).

8.2.6 Carrier gas: helium at about 131 kPa pressure at the head of the column for a linear velocity of about 24 cm/s at 280°C.

8.2.7 Makeup gas: nitrogen at about 40 mL/min flow rate.

8.3 ***Determine compound identifications***—Typical peak separations for the individual OC pesticides and the PCB Aroclors in analyzing fraction 1 of a laboratory reagent spike (LRS) using the GC operating conditions in section 8.2 are shown in figures 3 and 4 on the Rtx-5 and Rtx-1701 columns, respectively. Peak separations on the Rtx-5 and Rtx-1701 columns for fraction 2 of the same LRS are shown in figures 5 and 6, respectively. Toxaphene patterns obtained on the Rtx-5 and Rtx-1701 columns from the analysis of the calibration standard solution, made using a stock standard solution from NSI Solution, Inc., are shown in figures 7and 8, respectively. Peak identifications and retention times for the method compounds are listed in table 4.

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

8.4 ***Coelution problems***—Coelutions among compounds in the individual OC pesticide calibration solutions (5.11.1.1) were observed on the GC/ECD instrument using the chromatographic conditions described in 8.2. Those compound coelutions that were commonly observed are listed in table 5. Coelution conditions require special identification (8.5.2) and calibration (9.1) considerations.

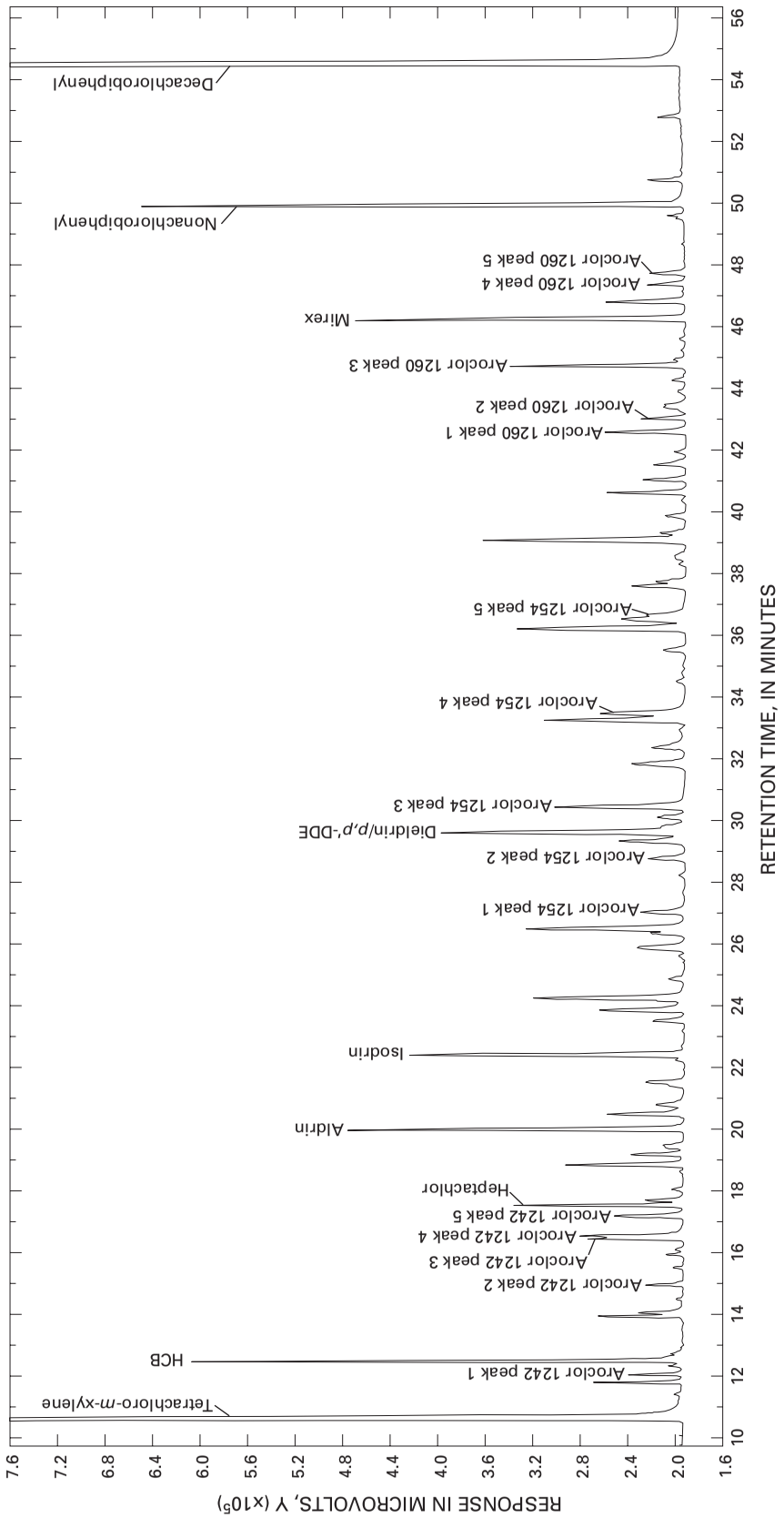

Figure 3. Gas chromatogram showing electron-capture detection of a fraction-1 extract from a laboratory reagent spike fortified with 50 nanograms of individual organochlorine pesticides and 250 nanograms of PCB Aroclors 1242, 1254, and 1260 on a Restek Rtx-5 column. Compound identifications and retention times are listed in table 4. Chromatographic conditions are given in the text.

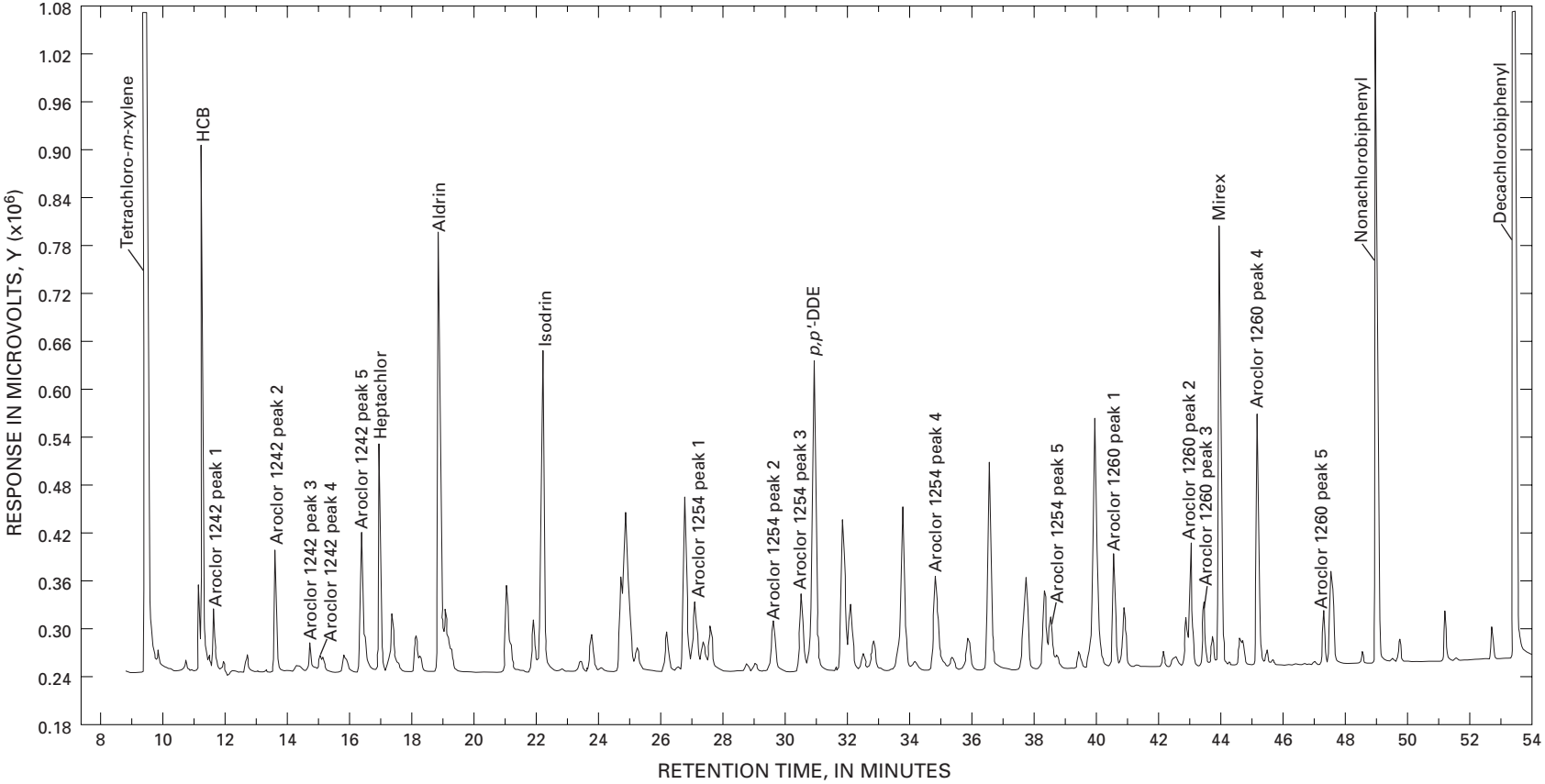

Figure 4. Gas chromatogram showing electron-capture detection of a fraction-1 extract from a laboratory reagent spike fortified with 50 nanograms of individual organochlorine pesticides and 250 nanograms of PCB Aroclors 1242, 1254, and 1260 on a Restek Rtx-1701 column. Compound identifications and retention times are listed in table 4. Chromatographic conditions are given in the text.

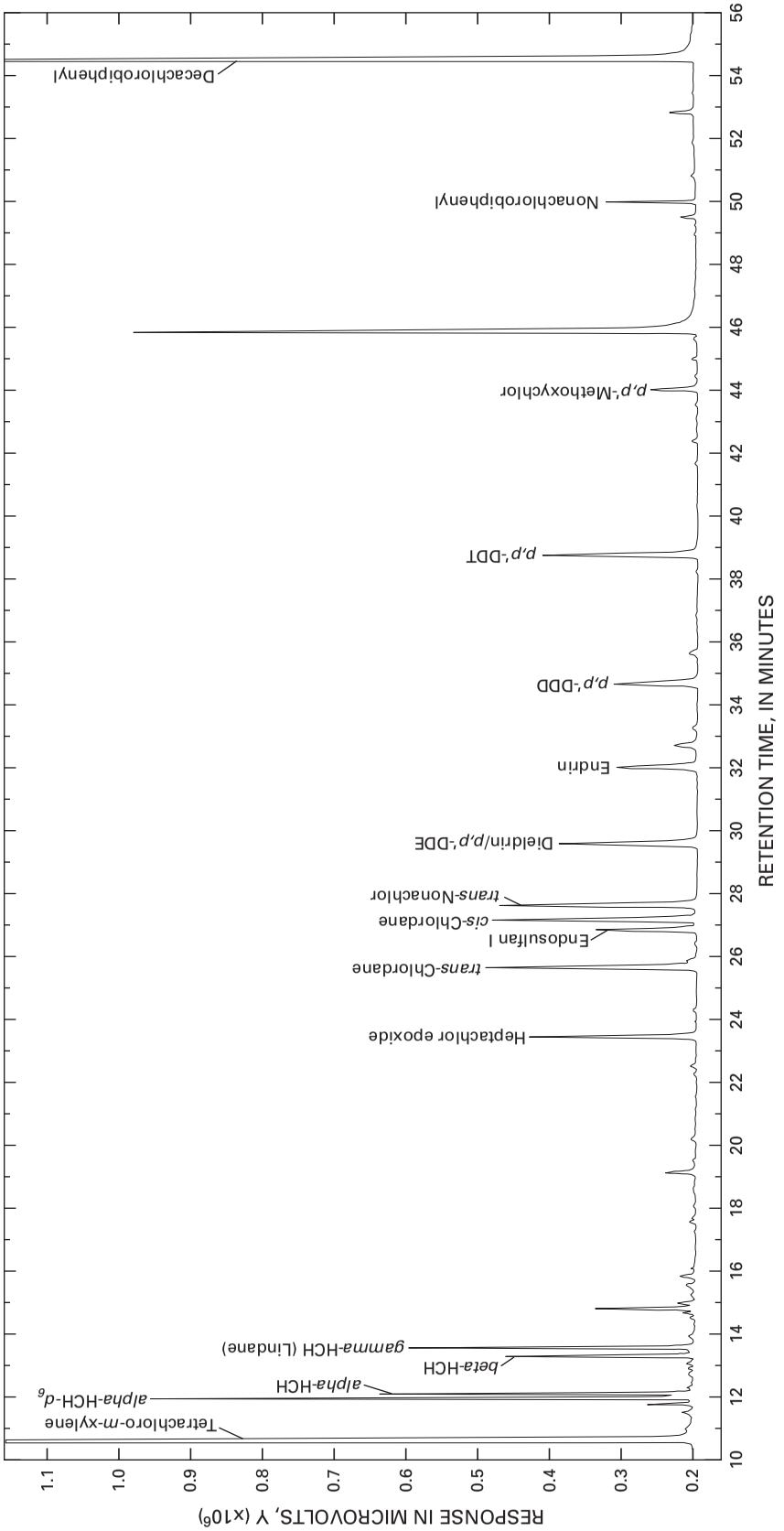

Figure 5. Gas chromatogram showing electron-capture detection of a fraction-2 extract from a laboratory reagent spike fortified with 50 nanograms of individual organochlorine pesticides and 250 nanograms of PCB Aroclors 1242, 1254, and 1260 on a Restek Rtx-5 column. Compound identifications and retention times are listed in table 4. Chromatographic conditions are given in the text.

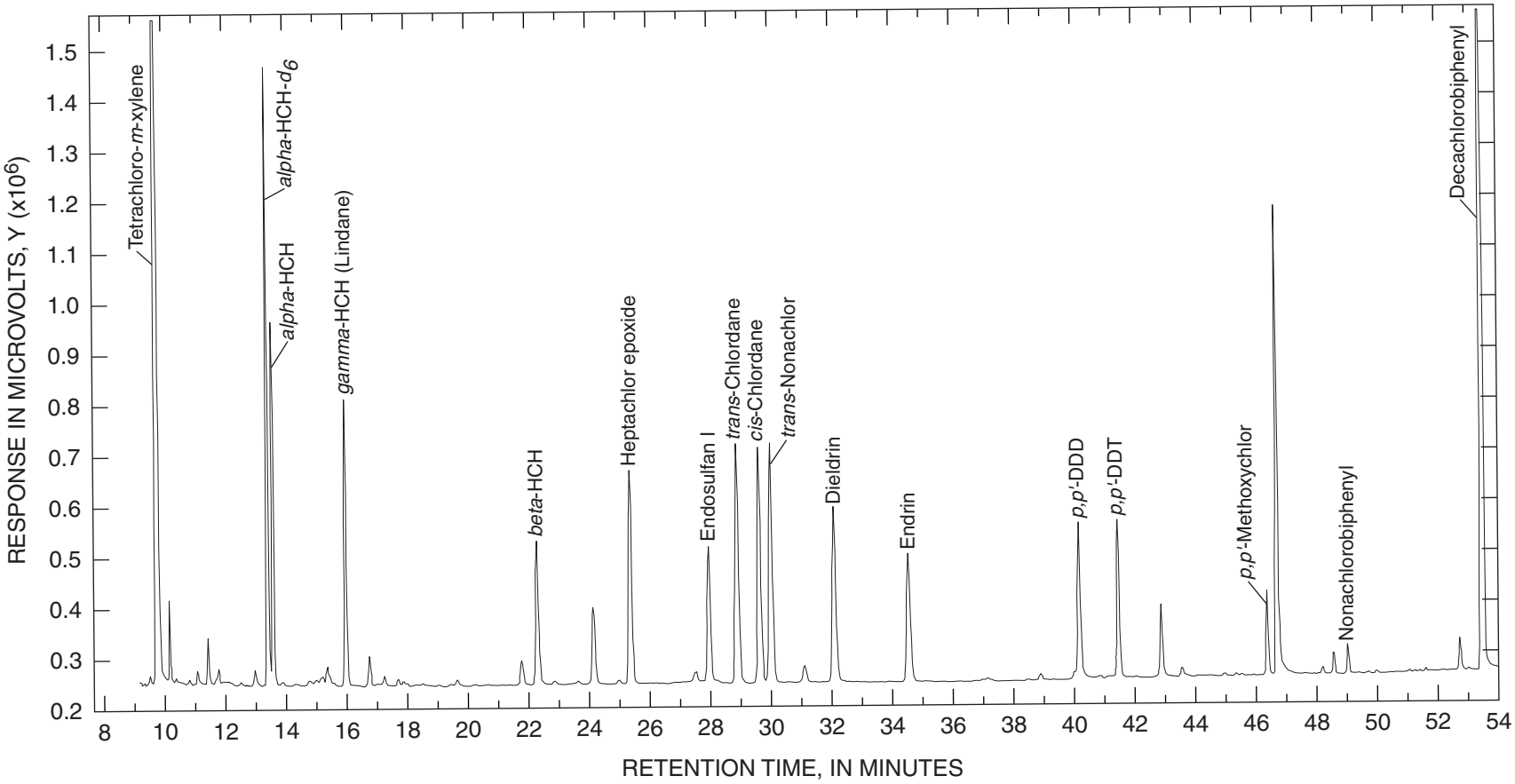

Figure 6. Gas chromatogram showing electron-capture detection of a fraction-2 extract from a laboratory reagent spike fortified with 50 nanograms of individual organochlorine pesticides and 250 nanograms of PCB Aroclors 1242, 1254, and 1260 on a Restek Rtx-1701 column. Compound identifications and retention times are listed in table 4. Chromatographic conditions are given in the text.

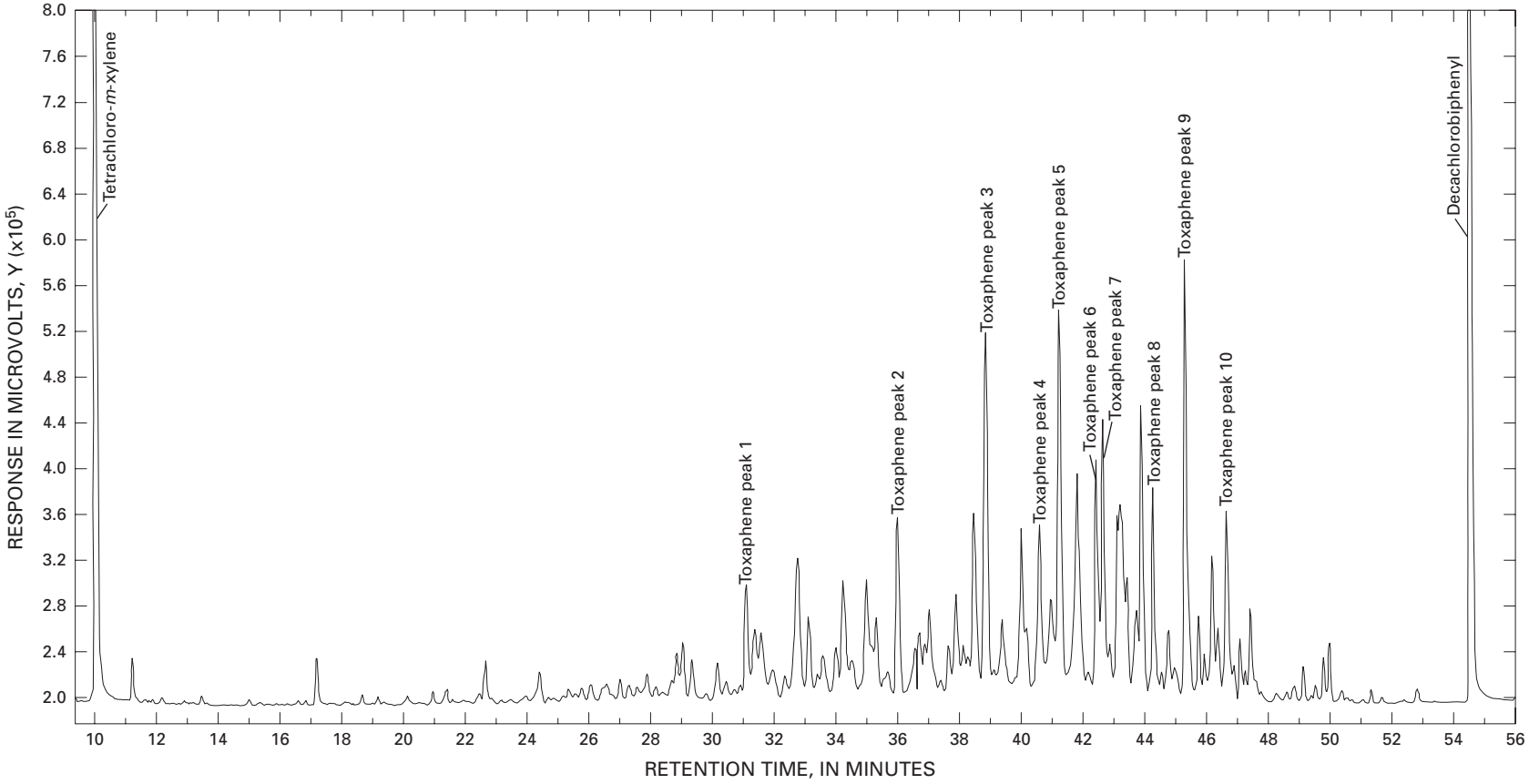

Figure 7. Gas chromatogram showing electron-capture detection a 1,000-picograms-per-microliter toxaphene calibration standard solution prepared from an NSI Solutions, Inc. stock solution on a Restek Rtx-5 column. Retention times of 10 selected peaks are listed in table 4. Chromatographic conditions are given in the text.

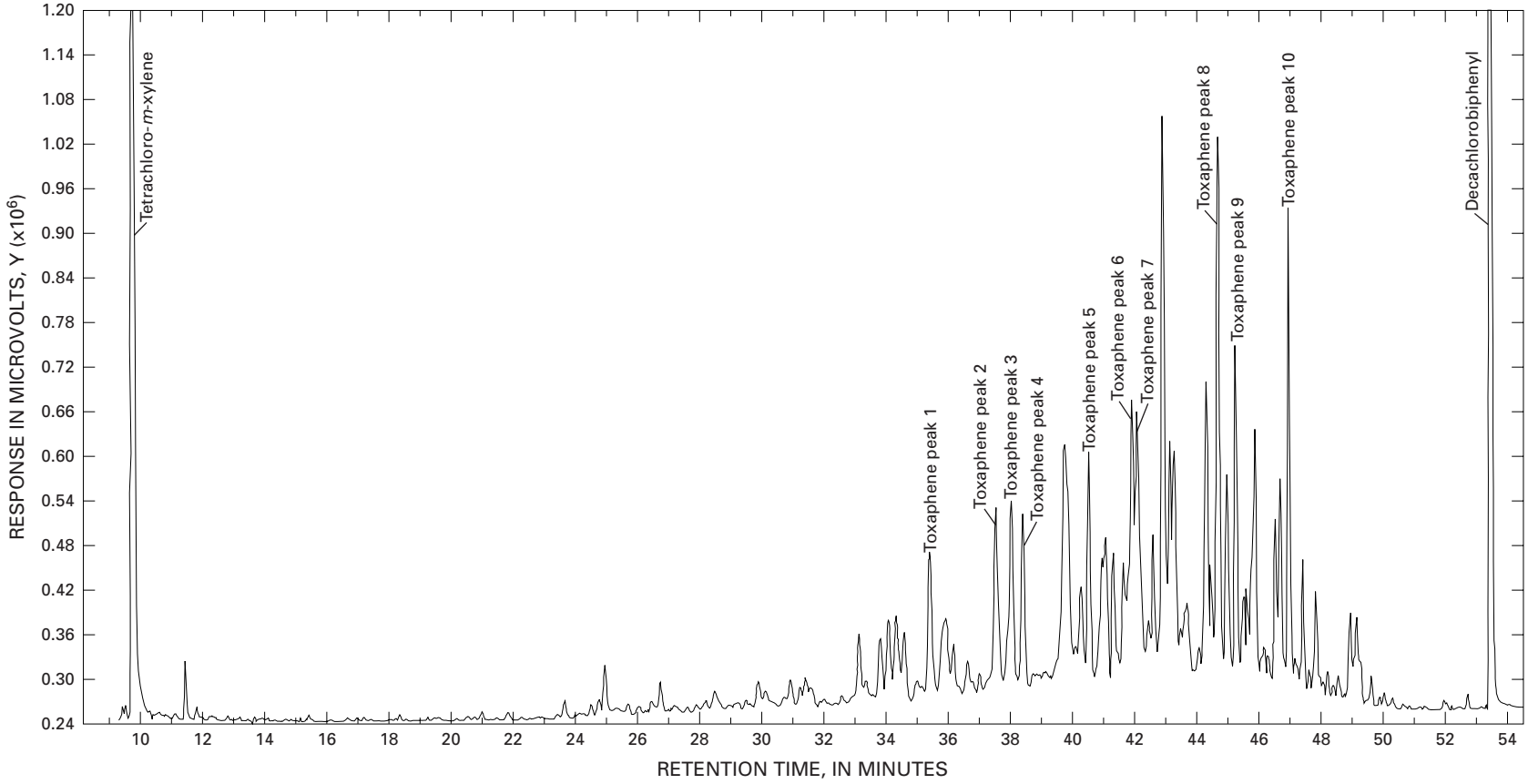

Figure 8. Gas chromatogram showing electron-capture detection of a 1,000-picograms-per-microliter toxaphene calibration standard solution prepared from an NSI Solutions, Inc. stock solution on a Restek Rtx-1701 column. Retention times of 10 selected peaks are listed in table 4. Chromatographic conditions are given in the text.

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Table 4. Retention times of individual organochlorine method compounds, selected peaks for PCB Aroclor 1016/1242, 1254, 1260, and toxaphene on the Rtx-5 and Rtx 1701 columns from figures 3 through 8 example gas chromatograms (listed in Rtx-5 retention-time order).

[±, plus or minus]

Compound	Retention time (minutes)		Suggested width of retention time window (minute)
	Rtx-5	Rtx-1701	
Tetrachloro-*m*-xylene[1]	10.65	9.77	± 0.05
alpha-HCH-d_6 [2]	11.98	13.42	± .05
PCB Aroclor 1016/1242 peak 1	12.05	11.93	± .07
alpha-HCH	12.14	13.60	± .05
Hexachlorobenzene (HCB)	12.49	11.57	± .05
beta-HCH	13.32	[3,4] 22.28	± .05
gamma-HCH (Lindane)	13.60	15.96	± .05
PCB Aroclor 1016/1242 peak 2	14.97	13.90	± .07
PCB Aroclor 1016/1242 peak 3	16.48	15.02	± .07
PCB Aroclor 1016/1242 peak 4	16.57	15.34	± .07
PCB Aroclor 1016/1242 peak 5	17.21	16.66	± .07
Heptachlor	17.57	17.24	± .07
Aldrin	20.04	19.12	± .07
Isodrin[2]	22.41	[3,4] 22.41	± .07
Heptachlor epoxide	23.41	25.34	± .07
trans-Chlordane	25.62	28.92	± .07
Endosulfan I	26.82	27.97	± .07
PCB Aroclor 1254 peak 1	27.05	27.22	± .07
cis-Chlordane	27.14	29.62	± .07
trans-Nonachlor	27.61	30.00	± .07
PCB Aroclor 1254 peak 2	28.78	29.76	± .07
Dieldrin	[3,4] 29.62	32.05	± .07
p,p'-DDE	[3,4] 29.62	31.06	± .07
PCB Aroclor 1254 peak 3	30.46	30.65	± .07
Toxaphene peak 1	31.42	35.42	± .07
Endrin	32.00	34.43	± .07
PCB Aroclor 1254 peak 4	33.49	34.97	± .07
p,p'-DDD	34.62	40.12	± .07
Toxaphene peak 2	36.25	37.60	± .07
PCB Aroclor 1254 peak 5	36.65	38.86	± .07
p,p'-DDT	38.73	41.40	± .07
Toxaphene peak 3	39.09	38.09	± .07
Toxaphene peak 4	40.80	38.46	± .07
Toxaphene peak 5	41.42	40.60	± .07
Toxaphene peak 6	42.60	41.93	± .07
PCB Aroclor 1260 peak 1	42.62	40.69	± .07
Toxaphene peak 7	42.81	42.14	± .07
PCB Aroclor 1260 peak 2	43.05	43.12	± .07
p,p'-Methoxychlor	43.98	46.37	± .07
Toxaphene peak 8	44.42	44.73	± .07
PCB Aroclor 1260 peak 3	44.76	43.52	± .07
Toxaphene peak 9	45.46	45.29	± .07
Mirex	46.25	44.05	± .07
Toxaphene peak 10	46.78	47.00	± .07
PCB Aroclor 1260 peak 4	47.36	45.24	± .07
PCB Aroclor 1260 peak 5	47.70	47.34	± .07
PCB-207 [2]	49.94	49.06	± .1
Decachlorobiphenyl[1]	54.57	53.48	± .1

[1]Organochlorine internal-injection standard compound.

[2]Surrogate compound.

[3]Compound largely or completely coelutes with another individual organochlorine compound on this column.

[4]Compound is separated (baseline resolved) in similar U.S. Geological Survey method O-5129-95 (Foreman and others, 1995) using the gas chromatograph temperature program described.

Note: Improved separations of some compounds may be achieved with temperature program modifications, but usually at the expense of other method compound separations (Foreman and others, 1995, p. 30).

Table 5. Compound coelutions commonly observed on the gas chromatography capillary columns used in this analytical method.

Column Rtx-5	Column Rtx-1701
Dieldrin and *p,p'*-DDE	*beta*-HCH and isodrin[1]

[1]Isodrin is a surrogate compound.

8.5 ***Positive identification of a compound***—A compound is positively identified if it is found within the expected retention time window (see 8.5.1) on both columns and in similar amounts (see 8.5.2).

8.5.1 *Retention time window*—The size of the retention time window is compound dependent. For single-component compounds and selected congener peaks from the multicomponent compounds (PCBs and toxaphene, see sections 9.2.1 and 9.2.2), set the center of the retention time window using the average of at least three retention time determinations from the initial calibration of a GC/ECD autosequence (see table 6). Suggested widths of the retention time windows are listed in table 4. A ±0.1-minute width is suggested for the selected congener peaks used to quantitate PCBs and toxaphene. Alternatively, window widths can be set at plus or minus three times the standard deviation of the average retention time computed from injections of the calibration standard solutions.

8.5.2 *Detection of a compound in similar amounts*—Amounts typically within 30-percent relative percent difference (RPD) on both columns help to confirm compound identification. The RPD is calculated as follows:

$$RPD = \left| \frac{C_1 - C_2}{(C_1 + C_2)/2} \right| \times 100 \qquad (4)$$

where

C_1 and C_2 are the compound concentrations from each column, or, in the case of duplicate samples (see 13.5), the compound concentrations in the duplicate and original analyses.

Compound coelutions, and, especially, sediment-matrix-specific GC interference problems, are commonly observed in this method, often resulting in RPDs greater than 30 percent. Under these conditions, an analyst's judgment is required for compound identification, and the data are qualified appropriately (raising the reporting level or labeling the concentration as estimated with an "E" code, for example). When applicable, consider the presence of other "family" compounds in the sample to assist in compound identification. (For example, if considering *trans*-chlordane, expect the detection of *cis*-chlordane in the sample; if considering *p,p'*-DDT, expect the detection of *p,p'*-DDD and *p,p'*-DDE in the sample.) Compounds that show coelution with another method compound (or interference from an unknown compound) on one column are quantified on the other column where no coelution (or interference) problem occurs. Typically, the compound concentration is reported from the column with the lower calibrated response (see 12.1). The compound still must be found within the expected retention time window on both columns for positive identification.

8.6 ***GC/ECD autosequence***—A suggested sequence for an automated analysis of OC fractions F1 and F2 in one analysis for 16 samples is listed in table 6.

Note: Synchronize new calibration standard and quality-control solutions with new spiking standard solutions in a sample set to avoid undesirable data shifts.

9. Gas Chromatography/Electron-Capture Detection Compound Calibration

9.1 ***Multipoint external standard calibration for single-component compounds***—For calibrating individual OC pesticides, multipoint curves are produced by analyzing the 1- to 200-pg/µL calibration standard solutions (5.11.1.1). Plot the GC/ECD peak area for the compound (A_c) in relation to the mass (in picograms) of the compound in each of the 1- to 200-pg/µL calibration standards injected. Calculate a calibration curve for this plot using a simple linear regression model {of the form $Y = m \times X + b$; where $X = (C_c \times V_1)$}

$$A_c = m \times (C_c \times V_1) + b \qquad (5)$$

where

A_c = GC/ECD peak area of the compound in the calibration standard solution;

m = compound-specific slope, in area per picogram;

C_c = concentration of the compound in the calibration standard solution, in picograms per microliter (5.11.1.1);

V_1 = volume of calibration standard solution injected into the GC/ECD, in microliters (8.2.3); and

b = compound-specific *y*-intercept, in area.

Note: Other regression models may be used as appropriate.

Table 6. Suggested gas chromatography/electron-capture detection autosequence.

[pg/µgL, picogram per microliter, F1, fraction1; F2, fraction 2]

Standard or sample type
Hexane gas chromatograph injection blank
Performance evaluation mix (PEM) (5.11.2.1)
Organochlorine pesticide calibration standard solutions at 1, 2, 5, 10, 20, 50, 100, and 200 pg/µL or other appropriate concentration (5.11.1.1)
Third-party check solution (5.11.2.3)
Multicomponent polychlorinated biphenyl (PCB) Aroclor 1242 calibration standard solution (F1) at 100 pg/µL or other appropriate concentration (5.11.1.2)
Multicomponent PCB Aroclor 1254 calibration standard solution (F1) at 100 pg/µL or other appropriate concentration (5.11.1.2)
Multicomponent PCB Aroclor 1260 calibration standard solution (F1) at 100 pg/µL or other appropriate concentration (5.11.1.2)
Polychlorinated biphenyl 600 solution (F1) at 1,800 pg/µL total PCBs (5.11.2.4)
Multicomponent toxaphene calibration standard solution (F2) at 1,000 pg/µL (5.11.1.3)
Reagent blank sample (7.2.2.1)
Reagent organochlorine spike sample (7.2.2.2)
Standard reference material sample (7.2.2.3)
Continuing calibration verification (CCV) standard solution (5.11.2.2)
PEM
Six field samples (F1s)
CCV
PEM
Seven field samples (F1s)
CCV
PEM
Six field samples (F2s)
CCV
PEM

If compounds coelute on both analytical columns, calibrate as described by using one or more separate standard solutions that contain only one of the coeluting compounds. Identification and quantification of compounds that coelute both columns require careful consideration by the analyst. In most cases, the compound that coelutes on both columns will need to be reported as either an upper-limit value, as a raised reporting-limit value, or not reported because of coeluting interference (Foreman and others, 1995, p. 37).

Note: None of the compounds tested by this method coeluted on both analytical columns. The corrective action described in 9.1 is presented in case the complication occurs, for example, in replacing of a consumable material or in evaluating additional compounds by this method.

Option: The internal-injection standard method of calibration and compound quantitation may be used by selecting either one of the OCIIS compounds, tetrachloro-*m*-xylene or decachlorobiphenyl, provided that there are no chromatographic interferences with these compounds in the standard solutions and samples. Details regarding internal-injection standard quantitation are not presented here but are provided in USEPA method 8000B (U.S. Environmental Protection Agency, 1996). (In the external standard calibration method, the OCIIS compounds are used as retention time markers to assist in compound identification.)

9.2 ***External standard calibration for PCBs and toxaphene***—One-point calibrations are produced for PCB Aroclor 1016/1242, 1254, 1260, and toxaphene. Compute the response factor (*RF*) by summing the GC/ECD peak areas of five representative peaks for the Aroclor, or 10 representative peaks for toxaphene, and dividing by the concentration of the PCB or toxaphene calibration standard solution. Representative peaks are selected on the basis of adequate peak intensity and separation from other congener, method compound, and interfering peaks (see sections 9.2.1 and 9.2.2). Calculate the response factor using

$$RF = \frac{\text{Sum of selected peak areas in the PCB or toxaphene calibration standard solutions}}{C_C \times V_1} \quad (6)$$

where

RF = Aroclor-specific or toxaphene response factor, in area per picogram;

C_c = concentration of the PCB calibration standard solution (5.11.1.2) or toxaphene calibration standard solution (5.11.1.3), in picograms per microliter; and

V_1 = volume of the calibration standard solution injected into the GC/ECD, in microliters (8.2.3).

9.2.1 *PCB peak selection*—Carefully compare the PCB gas chromatographic profiles of each Aroclor with the profiles of the individual OC pesticide calibration standard solutions and field samples. Select PCB peaks that show minimal interference problems in the standard and samples. This comparison may result in the selection of different PCB peaks for different field samples, depending on matrix-specific interference or other chromatographic separation problems. The peaks selected for calculating the response factor for each Aroclor (equation 6) must be the same peaks that are selected in calculating the peak-area response amount on the analytical instrument (equation 9, section 10) for final quantitation of PCBs in a given field sample (equation 10, section 10).

9.2.1.1 *Selection of PCB peaks on the Rtx-5 column*—Figure 3 shows an example gas chromatogram on the Rtx-5 column for a fraction-1 extract of a laboratory reagent spike fortified with individual OC-pesticide spike solution (5.2.5) and PCB spike solution (5.2.6) containing a 1:1:1 mix of PCB Aroclor 1242, 1254, and 1260. Suggested selection of peaks from a mixed PCB standard solution on the Rtx-5 column and tentative identification of congeners present in the suggested peaks from the stationary phase are described in USGS method O-5129-95 (Foreman and others, 1995, p. 41), referencing publications by Mullin and others (1984), Eganhouse and others (1989), and Schulz and others (1989). More recently, Frame (1997a, 1997b) has reported coelution profiles on the Rtx-5 stationary phase (and other phases) for all 209 PCB congeners and 6 Aroclors. Typically PCB peaks in the method described in this report are selected from the individual gas chromatogram of the PCB calibration standard solution for each Aroclor (5.11.1.2) on the column to facilitate the identification of Aroclors. Peaks selected from the Rtx-5 column for the Aroclor determinations presented in this report are listed in table 4.

9.2.1.2 *Selection of PCB peaks on the Rtx-1701 column*—Figure 4 shows an example gas chromatogram on the Rtx-1701 column for a fraction-1 extract of a laboratory reagent spike fortified with individual OC pesticide spike solution (5.2.5) and PCB spike solution (5.2.6) containing a 1:1:1 mix of PCB Aroclor 1242, 1254, and 1260. Typically PCB peaks in the method described in this report are selected from the individual gas chromatogram of the PCB calibration standard solution for each Aroclor (5.11.1.2) on the column to facilitate the identification of Aroclors. Peaks selected from the Rtx-1701 column for the Aroclor determinations presented in this report are listed in table 4.

9.2.2 *Toxaphene peak selection*—Select 10 peaks for toxaphene using the approach described for PCBs (9.2.1). Toxaphene peak selection is left to an analyst's discretion after careful comparison of sample and toxaphene standard gas chromatographic patterns.

Note: GC/ECD analysis of toxaphene in bed-sediment samples typically is much more complicated than the analysis of PCBs. Toxaphene reportedly contains hundreds of compounds (Jansson and Wideqvist, 1983; Saleh, 1991; Vetter and Luckas, 1995), and, unlike PCBs, has not been well characterized (Swackhamer and others, 1987; Bidleman and others, 1993). Avoid selecting toxaphene peaks that might coelute with other commonly observed method compounds (especially *p,p'*-DDT, *p,p'*-DDD, dieldrin, *cis*- and *trans*-chlordane, and *trans*-nonachlor). Toxaphene also undergoes considerable environmental weathering, primarily because of differential environmental partitioning as a result of the widely varying physicochemical properties of its components. Additionally, many toxaphene components are susceptible to reductive dechlorination reactions in anoxic bed sediments. These environmental weathering processes (especially the dechlorination process) often produce an enrichment in earlier eluting components, resulting in chromatographic patterns that are not characteristic of the chromatogram obtained with the technical toxaphene calibration standard solution (Williams and Bidleman, 1978; Harder and others, 1983). In this method, determination of toxaphene relies on visual pattern recognition of toxaphene in a sample chromatogram relative to the toxaphene standard solution. Therefore, an analyst may not readily recognize heavily altered toxaphene in a field sample by GC/ECD. The presence of toxaphene can be confirmed using GC with electron-capture negative ionization mass spectrometry or electron-impact ionization combined with high-resolution mass spectrometry (for example, see Swackhamer and others, 1987; Patton and others, 1989; Lau and others, 1996; Glassmeyer and others, 1999). Because of its complexity in pattern recognition, toxaphene concentration is qualified as estimated with an "E" code in this method.

10. Calculation of Results

10.1 Calculate the dry weight of sediment extracted (W_s), in grams:

$$W_s = W_w \times f_d \quad (7)$$

where

W_w = wet weight of sediment, in grams (7.1.6); and

f_d = dry-weight fraction of sediment (calculated from equation 1).

10.2 Calculate the peak-area response amounts in the sample extract and concentrations of compounds in the sample.

10.2.1 Calculation of peak-area response amount

10.2.1.1 For individual OC compounds, use the compound-specific regression parameters *m* and *b* (equation 5) from the calibration curve to calculate the peak-area response amount (*RA*) of identified compound in the analyzed sample extract:

$$RA = \frac{(A_s - b)}{m \times V_2} \quad (8)$$

where

RA = peak-area response amount (or on-column amount) of identified compound in the sample extract, in picograms per microliter;

A_s = GC/ECD peak area of the identified compound in the sample extract; and

V_2 = volume of the sample extract injected into the GC/ECD, in microliters (8.2.3).

10.2.1.2 For PCBs and toxaphene, sum the GC/ECD peak areas of the selected peaks eluting in the range of the particular Aroclor or toxaphene in the sample that match the retention times of those peaks selected from the chromatogram of the PCB or toxaphene calibration standard solution (see sections 9.2.1 and 9.2.2 for PCB and toxaphene peak selections, respectively). Calculate the peak-area response amount (*RA*) of the Aroclor or toxaphene analyzed in the sample extract by using

$$RA = \frac{\text{Sum of selected peak areas for the Aroclor or toxaphene in the sample extract}}{RF \times V_2} \quad (9)$$

where

RA = peak-area response amount (or on-column amount) of the Aroclor or toxaphene in the sample extract, in picograms per microliter;

RF = Aroclor-specific or toxaphene response factor, in area per picogram (calculated from equation 6); and

V_2 = volume of the sample extract injected into the GC/ECD, in microliters (8.2.3).

10.2.2 Calculate the concentration (C_s) of the identified compound in the sample by using

$$C_s = \frac{RA \times V_E \times (W_1 / W_2)}{W_s} \quad (10)$$

where

C_s = determined concentration of compound in the sample, in micrograms per kilogram (equivalent to nanograms per gram); or, for suspended sediment of known sample volume filtered, in micrograms per liter (equivalent to nanograms per milliliter);

RA = peak-area response amount of compound in the sample extract, in nanograms per milliliter (equivalent to picograms per microliter) (calculated from equation 8 or 9, as appropriate);

V_E = final volume of sample extract prior to GC/ECD analysis, in milliliters (7.9.3);

W_1 = weight of extract before GPC, in grams (calculated from equation 2);

W_2 = weight of OC extract processed through the GPC, in grams (calculated from equation 3); and

W_s = dry weight of sample extracted, in grams (calculated from equation 7).

Note: For the reagent blank and reagent OC spike samples, assume a dry weight (W_s) of 25 g in equation 10.

Note: For suspended-sediment samples submitted on filters, substitute the volume of sample filtered in the field (V_f), in milliliters, for W_s in equation 10.

10.3 Calculate the percent recovery of the surrogate compounds in each sample by using

$$R_a = \frac{C_s}{(C_a \times V_a)/W_s} \times 100 \quad (11)$$

where

R_a = recovery of surrogate in sample, in percent;

C_s = determined concentration of surrogate in sample, in nanograms per gram (equivalent to micrograms per kilogram) or, for suspended sediment, in nanograms per milliliter (equivalent to micrograms per liter) (calculated from equation 10);

C_a = concentration of compound in the OC surrogate solution added to the sample, in nanograms per microliter (5.2.4);
V_a = volume of OC surrogate solution added to the sample, in microliters (7.2.5); and
W_s = dry weight of sample extracted, in grams (calculated from equation 7).

Note: For the reagent blank and reagent OC spike samples, assume a dry weight (W_s) of 25 g in equation 10.

Note: For suspended-sediment samples submitted on filters, substitute the volume of sample filtered in the field (V_f), in milliliters, for W_s in equation 10.

10.4 Calculate the percent recovery of compounds in reagent OC spike sample by using

$$R_b = \frac{C_s}{(C_b \times V_b)/W_s} \times 100 \qquad (12)$$

where
R_b = recovery of spiked compound in the reagent OC spike sample, in percent;
C_s = determined concentration of compound in reagent OC spike sample, in nanograms per gram (calculated from equation 10);
C_b = concentration of individual compound in the OC-pesticide spike solution added to sample, in nanograms per microliter (5.2.5); concentration of Aroclor in the PCB spike solution added to sample, in nanograms per microliter (5.2.6); or concentration of toxaphene spike solution added to sample, in nanograms per microliter (5.2.7);
V_b = volume of individual OC-pesticide, PCB, or toxaphene spike solution added to the sample, in microliters (7.2.2.2); and
W_s = specified method dry weight, 25 g.

Note: The assumed sample weight (W_s) of the matrix used for preparing the reagent spike sample is equivalent in equations 10 and 12.

10.5 Calculate the percent degradation of *p,p'*-DDT and endrin on the GC/ECD from injections of the PEM (5.11.2.1) by using the following equations:

Percent *p,p'–DDT* loss =

$$\frac{A_{p,p'-DDD} + A_{p,p'-DDE}}{A_{p,p'-DDT} + A_{p,p'-DDD} + A_{p,p'-DDE}} \times 100 \qquad (13)$$

and

Percent endrin loss =

$$\frac{A_{endrin\ aldehyde} + A_{endrin\ ketone}}{A_{endrin} + A_{endrin\ aldehyde} + A_{endrin\ ketone}} \times 100 \qquad (14)$$

where
$A_{compound}$ = peak area of given compound in the PEM chromatogram.

10.6 Compute the CCV percent difference.

10.6.1 Calculate the peak-area response amount for each compound in the CCV standard solution (RA_{ccv}) by using equation 8.

10.6.2 Calculate the percent difference between the determined and expected CCV concentrations by using

$$\text{CCV percent difference} = \frac{RA_{ccv} - C_e}{C_e} \times 100 \qquad (15)$$

where
RA_{ccv} = calculated peak-area response amount of compound in the CCV standard solution, in picograms per microliter (from 10.6.1); and
C_e = expected concentration of compound in the CCV standard solution, in picograms per microliter (5.11.2.2).

10.7 Calculate the percent moisture of the uncentrifuged sediment (7.1.4) by using

Percent moisture in uncentrifuged sediment =

$$\frac{(W_a - W_b) + (W_b \times f_w)}{W_a} \times 100 \qquad (l6)$$

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 in 7.1.5).

Note: 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 16 does not include the amount of 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 the sediment samples on site.

10.8 Compute the revised reporting levels for a suspended-sediment sample submitted on filters if known sample volume filtered is less than 63 L.

10.8.1 Calculate the lowest suspended-sediment revised reporting level for the compound of lowest reporting level (for example, *gamma*-HCH in table 9, section 14) based on a 2-pg/µL calibration by using

$$SSRL_{lowest} = \frac{2 \times V_E \times (W_1 / W_2)}{V_f} \qquad (17)$$

where

$SSRL_{lowest}$ = lowest suspended-sediment revised reporting level, in micrograms per liter (equivalent to picograms per microliter) for compound of lowest reporting level (see table 9, section 14);

2 = lowest calibrator for determining concentration of compounds in a suspended-sediment sample of known sample volume filtered, in picograms per microliter;

V_E = final volume of sample extract just prior to GC/ECD, in milliliters (7.9.3);

W_1 = weight of extract before GPC, in grams (calculated from equation 2);

W_2 = weight of OC extract processed through the GC, in grams (calculated from equation 3); and

V_f = volume of sample filtered in the field, in milliliters.

10.8.2 Calculate the suspended-sediment revised reporting levels for all other compounds by using

$$SSRL_{other} = \frac{SSRL_{lowest} \times IRL_{other}}{IRL_{lowest}} \qquad (18)$$

where

$SSRL_{other}$ = compound-specific suspended-sediment revised reporting level, in micrograms per liter, for compound of other-than-lowest reporting level (see table 9, section 14);

$SSRL_{lowest}$ = lowest suspended-sediment revised reporting level, in micrograms per liter (calculated from equation 17);

IRL_{other} = compound-specific interim reporting level (IRL), in micrograms per kilogram, for compound of other-than-lowest IRL (see table 9, section 14); and

IRL_{lowest} = lowest interim reporting level, in micrograms per kilogram (see table 9, section 14).

Note: A laboratory reporting level (Childress and others, 1999) may be substituted for the IRL when established.

11. Gas Chromatography/Electron-Capture Detection Performance

11.1 ***GC/ECD instrument system***—For GC/ECD instrumental analysis, performance of the gas chromatograph is indicated by peak shape, the efficiency of separation for closely eluting compound pairs, and by the variation in detector response over time for compounds from calibration and CCV standard solutions. Daily assessments of these characteristics are made relative to the performance obtained with new capillary columns and GC inlet liner, and by using freshly prepared standard calibration solutions. When peak shape, separation efficiency, or response fail to meet performance criteria, instrument maintenance is required. Routine maintenance includes replacement of the injection port liner (5.10.4) and septum. If this does not result in acceptable performance, short lengths (0.3 m) of the guard column (5.10.3) are removed first to try to restore the chromatographic performance. Continued poor chromatographic performance might require replacement of the entire guard column and Y-connector (5.10.2), and removal of short lengths (0.3 to 1 m) of the capillary columns (5.10.1), or complete replacement of the capillary columns. Continued decrease or instability in response factor also can be caused by instability in electron-capture detector performance. Refer to the appropriate instrument manual for operating the detector system and controlling signal output. If the aforementioned steps do not improve response factors, then electron-capture detector maintenance might be required.

11.2 ***GC/ECD performance criteria***

11.2.1 *Calibration standards*—Calibration standards containing the individual component

compounds should bracket the compound concentrations expected in the sample extracts. Stock solutions used in preparing the individual OC pesticide calibration standard solutions (5.11.1.1) were obtained from Absolute Standards, Inc. Prepare calibration standards at eight different concentrations (1, 2, 5, 10, 20, 50, 100, and 200 pg/µL) containing the individual OC pesticide and surrogate compounds by adding known volumes of stock standard solutions to a volumetric flask. Dilute to volume with hexane. Typically multicomponent compounds—the PCB Aroclors and toxaphene—each have one calibration standard solution. Stock solutions used in preparing the PCB and toxaphene calibration standard solutions (5.11.1.2, and 5.11.1.3, respectively) were obtained from NSI Solutions, Inc. Prepare the PCB calibration standard solutions at 100 pg/µL for each Aroclor and the toxaphene calibration standard solution at 1,000 pg/µL by adding a known volume of stock standard solution to the respective volumetric flask of each multicomponent compound. Dilute to volume with hexane.

11.2.2 *Calibration curve*—Starting with the lowest concentration, each calibration standard solution (5.11.1) is analyzed in the sample set prior to analyzing the samples (table 6), and the response (peak area) is tabulated in relation to the concentration in the standard. This method is an external standard quantitation method and uses multipoint external standard calibration for individual component compounds. PCB Aroclors and toxaphene are one-point, external standard calibrations. External standard calibrations for all the OC compounds are described in section 9. The multipoint calibration curve contains a minimum of four to eight concentrations. For multipoint calibrations, use the results to prepare a calibration curve by a linear regression model (equation 5) for each compound. If a linear calibration relation cannot be achieved, especially at low concentrations, then a quadratic calibration may be used. The calibration curve should have a correlation coefficient (r^2) equal to or greater than 0.995. The determined concentration for each individual OC pesticide and surrogate is expected to be within ±20 percent of the known concentration for each compound on at least one column, especially at the 2-pg/µL calibration level, before proceeding with sample quantitation. If the instrument does not meet these calibration criteria, correct the problem by maintaining the GC or by preparing new calibration standards and reanalyzing the new standards.

11.2.3 *Third-party check (TPC)*—One TPC solution (5.11.2.3) is analyzed in each GC/ECD autosequence after the calibration standards to verify the calibration curve. The original sources for the compounds in the TPC solution are independent of those used in creating the calibration curve. The determined concentration for all compounds in the TPC solution is expected to be within ±30 percent of the known concentration. If the determined concentrations fall outside of the acceptance criteria, reanalysis of the samples might be required. The source of the problem needs to be identified and resolved before continuing analyses. Maintain the instrument as necessary, or prepare a new TPC solution or new calibration standard solutions if one or the other is suspect. Report SRM and field sample data as suspect with an estimated (E-code) qualifier for the compounds that fail recovery in the TPC.

11.2.4 *Performance evaluation mix (PEM)*—The PEM (5.11.2.1) is injected at the beginning of a GC/ECD autosequence and is injected after each continuing calibration verification in the autosequence (table 6) to monitor the degradation of labile compounds (especially *p,p'*-DDT and endrin) in the GC injection system. The calculated percent loss of *p,p'*-DDT (equation 13) or endrin (equation 14) is not to exceed 20 percent on more than one column. If losses exceed 20 percent, replace the injection port liner with a clean, deactivated liner (5.10.4), followed by other GC maintenance (11.1) as required to reduce the losses to acceptable levels.

Note: Foreman and Gates (1997) reported that substantial sample-matrix specific degradation (or signal enhancement) beyond that indicated by the PEM can occur for *p,p'*-DDT (and presumably other thermolabile compounds), even though the PEM is within acceptance criteria.

11.2.5 *Continuing calibration verification (CCV)*—CCV standard solutions (5.11.2.2) are injected typically every six to seven samples throughout the GC/ECD autosequence (table 6) to monitor the calibration of the GC/ECD for bias and precision. The calculated CCV percent difference (equation 15) is expected to be within ±30 percent for each compound on at least one column. If CCV percent differences are outside of the acceptance criteria, reanalysis of the affected field samples might be required, especially if there is a loss of detection capability. Maintain the GC/ECD as needed to return to acceptable CCV performance. If CCV recoveries continue to fall outside of the acceptance criteria, then qualify the sample data as suspect with an estimated (E-code) qualifier for compounds affected by the CCV recoveries for the samples bracketed by the CCV (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

Note: There are no CCVs for the multicomponent compounds—PCBs and toxaphene. PCBs use the

600-each Aroclor solution (5.11.2.4) to check linearity (11.2.6) beyond the calibration at 100 pg/µL (5.11.1.2). Toxaphene, on the other hand, is a permanently E-coded compound in this method, with its estimated final concentration in the sample quantitated from the one-point calibration at 1,000 pg/µL (5.11.1.3).

11.2.6 *PCB calibration linearity check*—The 600-each Aroclor solution (5.11.2.4) is injected after the PCB calibration standard solutions in the GC/ECD autosequence (table 6). The recovered concentration for each Aroclor is expected to be within ±20 percent of the concentration in the solution on at least one column for linearity. If the acceptance criteria are not met, reanalysis of the affected field samples might be required. If the recovered concentration for the Aroclor continues to fall outside of the acceptance criteria, then qualify the sample data as suspect with an estimated (E-code) qualifier for the Aroclor affected by the recovery in the solution.

11.3 ***Other GC/ECD requirements***—Quantitate sample concentrations within the range of calibration standard concentrations. Sample concentrations that exceed the high concentration calibration standard are diluted in hexane to within the calibration range.

12. Reporting of Results

12.1 ***Column-dependent quantitation***—The quantitative value reported is column dependent. Report the lower concentration produced by the two GC columns unless it has been demonstrated by the calibration, CCV, TPC, or PEM standards that one of the columns is causing a method compound to degrade or otherwise produce errant results. Column-specific quantitation also will be necessary for those compounds that exhibit coelution or other apparent interference on one GC column (see 8.5.2). If a compound is split between fractions, add the lower concentration or the preferential column concentration of fractions 1 and 2 and report the sum.

12.2 ***Reporting units***—Compound concentrations in field samples and in the SRM sample are reported in micrograms per kilogram for dry-weighted sediment (equation 10). Compound concentrations for suspended-sediment samples collected on filters are reported in micrograms per liter for known volume filtered (equation 10). Compounds quantified in the reagent blank sample (laboratory reagent blank, or LRB) are reported in micrograms per kilogram, assuming a 25-g sample dry weight (equation 10). Surrogate data for all sample types are reported in percent recovered (equation 11). Data for the reagent OC spike sample (laboratory reagent spike, or LRS) are reported in percent recovered, assuming a 25-g sample dry weight (equation 12).

12.3 ***Reporting levels***—Estimates of method detection limits (MDLs) using the procedures outlined by the U.S. Environmental Protection Agency (1997) have been calculated for this method and are discussed further in sections 14.8 and 14.9 and are listed in table 8 (see section 14). Interim reporting levels (IRLs) for this method are listed in table 9 (see section 14) for sediment samples on a dry-weight basis and for suspended-sediment samples collected on filters. The IRLs in micrograms per kilogram are set at 2 times the estimated MDL for all compounds except toxaphene. The IRL for toxaphene is arbitrarily set in this method at 200 micrograms per kilogram to minimize false positive detections through dual GC column confirmation. For samples with dry weights $\leq$12.5 g, raise the reporting levels by a factor of $(25/W_s)$ above the IRLs based on a 25-g equivalent dry weight of the sample, where W_s is the dry weight of the sample extract, in grams (calculated from equation 7). For suspended-sediment samples of known sample volume filtered, revise the IRLs accordingly (10.8). IRLs may be replaced by laboratory reporting levels based on long-term method detection levels described by Childress and others (1999).

12.4 ***Reporting data results***—Report surrogate and LRS recoveries to three significant figures. Compounds not detected are reported as less than the IRL or as a raised reporting level (12.3). Report concentrations in the SRM, LRB, and field samples to three significant figures. If the peak-area response amount (equation 8 or 9, as appropriate) in the sample extract is greater than the highest calibration standard, or in the case of PCBs, is greater than the 1:1:1 Aroclor mixture (5.11.2.4) used in checking PCB calibration linearity, dilute the sample extract to bring the peak-area response amount within calibration range, and report the final concentration. If the peak-area response amount for a positively identified Aroclor in the extract is less than the one-point calibration at 100 µg/kg, report the final concentration of the Aroclor in the sample with the estimated (E-code) qualifier for the final concentration at or greater than the estimated MDL. Reporting less than the estimated MDL in this method is not appropriate because the method is not "information-rich" (Childress and others, 1999). Use the E-code qualifier for a data result if the recovery in the TPC or LRS is outside the acceptance criteria (sections 11.2.3 and 13.3, respectively). The E-code qualifier also is used when the CCV is outside of expected limits and the set is not reanalyzed, or any time the analyst suspects that the quantitation might not be accurate. The method

compound *p,p'*-DDE in the presence of PCB Aroclor 1254 or Aroclor 1260 interference (see 14.10) is reported with the E-code qualifier in the LRB, LRS, SRM (if PCBs are a component), and in the field samples if resolution on the GC/ECD instrument cannot be resolved with the GC conditions described in section 8.2. Likewise, PCB Aroclor 1254 and Aroclor 1260 may be reported with the E-code qualifier in the presence of *p,p'*-DDE interference. Method compounds *p,p'*-methoxychlor and toxaphene are reported permanently with the E-code qualifier in this method.

13. Laboratory Quality Assurance/Quality Control

Laboratory extraction samples are prepared in sample sets, each consisting of a laboratory reagent blank (LRB), a laboratory reagent spike (LRS), a standard reference material (SRM), and 13 field samples, which may include a laboratory duplicate. The aspects of the analytical process that the QA/QC samples monitor are described in this section.

Note: See Pirkey and Glodt (1998) for additional QA/QC practices that can be used with this method.

13.1 ***Surrogates***—Three surrogate compounds are added at the time of extraction to all sample types to monitor recoveries from the sample preparation process. Surrogate recoveries are used to measure gross sample-processing problems and matrix effects. The surrogate recoveries are not used to correct concentrations of other method compounds because the surrogates do not mimic chemically all of the method compounds. The surrogates were selected to indicate problems with the alumina/silica adsorption chromatography part of the method. The fraction-1 surrogates are isodrin and PCB-207; the fraction-2 surrogate is *alpha*-HCH-d_6 (table 3). The surrogates selected are not expected to be present in the environment. Surrogate observations that indicate errors in the alumina/silica adsorption chromatography procedure are listed in table 7. There have been no known F2 surrogate observations indicative of Florisil adsorption chromatography errors. As previously noted (section 7.7), changes in the source or lot of sorbent used can result in fractionation differences. Severe matrix effects can result in erroneous fractionations. In any case, report the sum of the recovery in fractions 1 and 2 for the surrogate compound. Statistical process control techniques (preferrably nonparametric statistics) are used to establish control limits for surrogate recoveries (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998). When surrogate recovery for a sample is greater than the upper control limits or less than the lower control limits and fractionation is accounted for, check the following: (1) calculations, to locate possible mathematical errors; (2) spike, calibration, and surrogate solutions for degradation and concentration, and notes pertaining to the solution preparation; (3) contamination, which usually produces positive bias; and (4) instrument performance (section 11.1). If those steps do not reveal the cause of the problem, reanalyze the extract. If the problem can be identified as a correctable laboratory failure, take corrective action for surrogate recovery (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written

Table 7. Surrogate observations that indicate alumina/silica adsorption chromatography errors.

[F1, fraction 1; F2, fraction 2]

Surrogate observation	Possible reason for error
alpha-HCH-d_6 in F1	Not all dichloromethane removed from extract before adsorption chromatography step. Collected more than 30 milliliters of hexane for F1. Used 5-percent acetone in hexane instead of hexane for F1. Incorrect sorbent activation or deactivation.
Isodrin and PCB-207 in F2	Collected less than 30 milliliters of hexane for F1. Incorrect sorbent activation or deactivation.
No *alpha*-HCH-d_6 in F1 or F2	Collected less than 35 milliliters of 5-percent acetone/hexane for F2. Used hexane instead of 5-percent acetone in hexane for F2. F2 elution solvent contains less than 5-percent acetone. Incorrect sorbent activation or deactivation.
No surrogates in F1 or F2	Forgot to add surrogates to sample. Incorrect sorbent activation or deactivation.

commun., 1998) before continuing analysis. If the sample extract reanalysis meets the surrogate recovery acceptance criteria, then report the sample results appropriately using the reanalyzed extract data. If sample extract continues to fail the recovery acceptance criteria, report, if necessary, the sample data as suspect with an estimated (E-code) qualifier for only those analytes affected by the surrogate recovery, or do not report the data if the unacceptable surrogate recovery might indicate that the sample results are unsalvageable (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

13.2 ***Laboratory reagent blank (LRB)***—The LRB is a sodium sulfate sample of 25-g equivalent dry weight fortified with method surrogates only. One LRB is included with each sample set and is carried through the entire sample preparation and analytical procedure. The LRB is used to monitor for impurities and contamination from reagents and glassware. Concentration of each analyte (a nonsurrogate method compound) is expected to be undetected, or less than the IRL. If the LRB contains interfering peaks that would prevent the determination of one or more compounds, then determine the source of the contamination and eliminate the interferences before continuing sample processing and analysis. If the interferences cannot be eliminated, then qualify the sample data as suspect with an estimated (E-code) qualifier for only those analytes affected by the blank contribution (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

13.3 ***Laboratory reagent spike (LRS)***—The LRS (7.2.2.2) is a sodium sulfate sample of 25-g equivalent dry weight fortified with individual OC-pesticide spike solution (5.2.5). The LRS also can be fortified with PCB spike solution (5.2.6) or toxaphene spike solution (5.2.7). (Other spike solutions might be added; see second note in section 7.2.2.2.) The expected spiked concentration for each PCB Aroclor 1242, 1254, and 1260 is 10 µg/kg; 1,000 µg/kg for toxaphene, if added; and 2 µg/kg for the individual OC pesticides (see second note in section 7.2.2.2 for method compound HCB). One LRS is included with each sample set and is carried through the entire sample preparation and analytical procedure. The concentration of each compound in the LRS needs to be within the range of the calibration standards. The LRS recoveries reflect method performance in the absence of any environmental sample matrix. These results are used to determine if overall set recoveries are acceptable, or if there are gross changes in method performance in the set. Acceptability is defined from analysis of a series of LRS samples, typically 30 or more, processed by multiple operators using different GC/ECD instruments. Statistical process control techniques (preferrably nonparametric statistics) are used to establish control limits for LRS recoveries (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998). Control limits for this method are updated annually. Failure of LRS recoveries needs to be evaluated. If the recovery of any compound does not fall within the control-limit criteria, the compound is judged out of control. Reanalysis of sample extract or sample repreparation might be required. The source of the problem needs to be identified and resolved before continuing the analyses. Report SRM and field sample data as suspect with an estimated (E-code) qualifier for the compounds that fail recovery in the LRS, or do not report the sample result if an unacceptable LRS recovery might indicate that the sample result is completely uninterpretable (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

13.4 ***Standard reference material (SRM)***—An SRM containing many compounds of interest is used to monitor performance through the sample preparation and analytical procedure in the presence of matrix interferences. One SRM is included with each sample set. The SRM results are compared to certified concentrations.

13.5 ***Laboratory duplicate***—One laboratory duplicate sample may be processed with each set of samples and selected at random from one of the field samples within the set. The duplicate analysis provides an indication of method precision within that particular matrix by the relative percent difference computation (equation 4). The NWQL has not established corrective action for laboratory duplicates. For the purpose of production efficiency, the laboratory duplicate may be replaced in this method with an additional field sample for the sample set.

13.6 ***Verification of standard solution concentrations***—This is a critical quality-assurance requirement. Verify compound concentrations in all prepared calibration and spiking standard solutions prior to use to avoid possible significant changes in determined recoveries. Determined concentrations are expected to be within ±20 percent of the known concentrations in the solutions. Third-party check standards (for example, standard reference solutions from the National Institute of Standards and Technology) can be used to assist in this verification process, provided that the original sources of the OC pesticides used to prepare the TPCs are not the same sources used to prepare the solutions being verified (11.2.3).

14. Method Performance

Method performance is tested by establishing the recoveries of the method compounds spiked at a minimum of two concentrations in at least three different matrices. A minimum of seven replicates is determined at each test condition. For this method, three concentrations were tested in three matrices, with as many as eight replicates for each test condition. Unfortunately, as few as three replicates were used for one of the method performance determinations.

14.1 The matrices used to test method performance included a reagent (sodium sulfate); a sediment sample collected from Evergreen Lake, Evergreen, Colorado; and a sediment sample collected from Clear Creek near Central City, Colorado.

14.2 The Evergreen Lake sediment was dredged as part of routine dam maintenance; the sample was collected from a mound that had been dredged several weeks prior to collection. The Evergreen Lake sediment sample was coarse with substantial sand component.

14.3 The Clear Creek sediment sample was bottom sediment that had been size-separated after collection. Particles less than 63 mm in diameter were used in this evaluation for the Clear Creek sediment sample. This sediment was light brown and was received as a dry sample from the donor, unlike the Evergreen Lake sample, which was damp.

14.4 Each of the three sample matrices was homogenized and split into twenty-four 25-g dry-weighted samples. All samples were fortified with OC surrogates at 2 µg/kg. One set of eight samples (replicates) was fortified with selected OC pesticides at 1 µg/kg (50 µL of an individual OC-pesticide spike solution at 0.5 ng/µL in methanol) and with PCB Aroclor 1242, 1254, and 1260 at 20 µg/kg each Aroclor (10 µL of a PCB spike solution at 50 ng/µL in hexane). A second set was fortified with the OC pesticides at 2 µg/kg (100 µL of an individual OC-pesticide spike solution at 0.5 ng/µL in methanol) and with each Aroclor at 40 µg/kg (20 µL of a PCB spike solution at 50 ng/µL in hexane). A third set was fortified with the OC pesticides at 10 µg/kg (100 µL of an individual OC-pesticide spike solution at 2.5 ng/µL in methanol) and with each Aroclor at 5 µg/kg (5 µL of a PCB spike solution at 25 ng/µL in hexane). Excess PCBs were added in the first two sets as an estimated guess in determining the Aroclor method detection limits (MDLs) based on the total PCB minimum reporting level at 50 µg/kg in similar USGS method O-5129-95 (Foreman and others, 1995, p. 49). After determining the estimated MDL results from the first two sets (extracted and analyzed during spring 2000), the decision was made to spike excess individual OC pesticides for a third level and to spike lower for the PCBs (extracted and analyzed during fall 2001) to obtain the estimated MDLs listed in table 8 for the Aroclors. Aroclor 1016 intentionally was not spiked.

14.5 Replicates for toxaphene were prepared separately and fortified with OC surrogates. Toxaphene was spiked at only one concentration into eight replicates of each of the three sample matrixes. One-milliliter aliquots of a 5,028-ng/µL toxaphene stock standard solution from NSI Solutions, Inc. were spiked into the replicates. The replicates were diluted 1:1,000 to obtain an expected final concentration of 201 µg/kg, assuming a 25-g equivalent dry-weight sample size. Toxaphene replicates were extracted and analyzed during winter 2003.

14.6 Replicates in a given sample set were extracted on the same day. Extracts were analyzed on one GC/ECD instrument under one operator, but different concentrations and matrices were analyzed at different times. Bias and precision data are listed in table 10 at the end of this section.

14.7 Additional 25-g dry-weighted samples (matrix blanks) for each of the three sample matrices were fortified with surrogates only, extracted with replicates, and analyzed to determine background concentrations of method compounds. Method compounds *p*,*p'*-DDT and PCB Aroclor 1254 were detected in the Evergreen Lake matrix blank at 1.24 µg/kg and 6.29 µg/kg, respectively, for the replicates spiked at 1 and 2 µg/kg for individual OC pesticides and at 20 and 40 µg/kg for each PCB Aroclor 1242, 1254, and 1260, all extracted on the same day. The background concentrations were subtracted from concentrations determined in the replicates to give the corrected results in table 10.

14.8 Estimated MDLs, determined by fortifying eight sodium sulfate reagent replicates with method compounds, and the corresponding spiked concentrations are listed in table 8. The estimated MDLs in table 8 reflect variation with replicate preparations and GC/ECD calibrations. The lot numbers of the method compounds in the spiking solutions used to prepare the replicates were the same lot numbers for the compounds in the calibration standard solutions used to make the calibration curves. Estimated MDLs were calculated by using the following equation outlined by the U.S. Environmental Protection Agency (1997):

$$MDL = S \times t_{(n-1,\,1-\alpha\,=\,0.99)} \qquad (19)$$

Table 8. Estimated method detection limits for method compounds from eight sodium sulfate reagent organochlorine-fortified replicates.

[conc., concentration; µg/kg, micrograms per kilogram; mL, milliliter; ng/µL, nanograms per microliter]

Compound	Spiked conc.[1] (µg/kg)	Mean conc. (µg/kg)	Standard deviation (µg/kg)	Relative standard deviation (percent)	Mean recovery (percent)	Number of observations[2]	Estimated method detection limit[3] (µg/kg)
Aldrin	2	1.48	0.27	18.43	74.0	7	0.859
cis-Chlordane	2	1.25	.13	10.51	62.5	8	.415
trans-Chlordane	1	.701	.06	9.42	70.1	7	.207
p,p'-DDD	2	1.64	.32	19.95	82.0	7	1.03
p,p'-DDE	1	1.36	.22	16.86	136.0	8	.688
p,p'-DDT	1	.711	.14	19.78	71.1	7	.442
Dieldrin	1	.905	.06	7.55	90.5	7	.215
Endosulfan I	2	.952	.07	7.81	47.6	7	.234
Endrin	1	1.14	.10	9.32	114.7	7	.336
HCB[4]	13	8.06	.47	5.92	62.0	8	1.43
alpha-HCH	2	1.16	.17	15.08	58.0	8	.550
beta-HCH	1	.727	.07	9.68	72.7	7	.221
gamma-HCH	1	.548	.06	11.60	54.8	7	.200
Heptachlor	1	.662	.10	15.54	66.2	8	.309
Heptachlor epoxide	2	1.53	.19	12.44	76.5	8	.601
p,p'-Methoxychlor[5]	1	6.08	.49	8.19	[6] 607.8	7	1.56
Mirex	2	1.47	.18	12.75	73.5	7	.589
trans-Nonachlor	1	.569	.12	21.58	56.9	7	.385
PCB Aroclor 1016/1242	5	4.35	.64	14.82	87.0	7	2.02
PCB Aroclor 1254	5	9.02	.66	7.38	180.4	7	2.09
PCB Aroclor 1260	5	6.93	.74	10.77	138.6	7	2.34
Toxaphene (technical)[7]	201	134	19.09	14.25	66.6	8	57.3

[1]The spiked concentrations assume a 25-gram sample size.

[2]Number of observations less than eight resulted from loss of sample in the preparation procedure.

[3]Estimated method detection limits (MDLs) were determined from these reagent organochlorine-fortified replicate results and calculated by the U.S. Environmental Protection Agency (1997) procedure using Student's *t*-values for the 99-percent confidence interval. More than one significant figure was included for the standard deviations used to calculate the estimated MDLs.

[4]Hexachlorobenzene (HCB) is a component in the individual organochlorine (OC)-pesticide spike solution and in a polycyclic aromatic hydrocarbon (PAH) spike solution, which also was spiked into the sodium sulfate reagent replicates for other performance method evaluations not shown in this report. The data represent a 1-µg/kg spiked concentration of HCB from the individual OC-pesticide spike solution and a 12-µg/kg spiked concentration from the PAH spike solution.

[5]Interference from a nonmethod compound suspected in calculating the mean recovery.

[6]The mean recovery from 18 laboratory reagent spikes in calendar year 2002 was 77.9 percent with a standard deviation of 17 percent for *p,p'*-methoxychlor spiked at 2 µg/kg.

[7]Toxaphene replicates were diluted 1:1,000 to obtain a final expected concentration of 201 µg/kg for 1-mL aliquots of a 5,028-ng/µL toxaphene solution spiked per replicate.

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 (two-tail test) with *n*-1 degrees of freedom; and

n = number of replicate analyses.

Note: More than one significant figure was included for the standard deviations used to calculate the estimated MDL.

14.9 According to the U.S. Environmental Protection Agency (1997) procedure, the fortified concentration for a compound is expected to be no more than five times the estimated MDL; otherwise, an optional iterative procedure is followed to verify the reasonableness of the MDL estimate. Because the spiked concentrations are nearly two to five times the estimated MDLs for most of the compounds in table 8, these estimated MDLs appear to be appropriate. In the method-performance evaluation, estimated MDLs lower than those listed in table 8 of about 0.1 µg/kg were obtained for the compounds aldrin, *cis*-chlordane, *p,p'*-DDD, endosulfan I, and mirex from a fortified concentration at 1µg/kg; however, that concentration did not meet U.S. Environmental Protection Agency (1997) criteria. For endosulfan I, even a fortified concentration at 2 µg/kg, being greater than five times its estimated MDL listed in table 8, does not satisfy the criteria. In the method-performance evaluation, a fortified concentration at 10 µg/kg yielded an estimated MDL of 3.21 µg/kg for endosulfan I, but that MDL was calculated from only four replicate results.

14.10 The mean recovery data for the concentrations spiked for the estimated MDL determinations also are listed in table 8. The mean recovery for *p,p'*-DDE reflects possible interferences from PCB Aroclor 1254 and 1260, which is a potential problem to *p,p'*-DDE quantitation if PCBs are present at high concentration. For example, at the spiked concentration of 1 µg/kg for *p,p'*-DDE in the sodium sulfate reagent OC-fortified replicates, PCBs also were spiked in the same replicates at 20 µg/kg, assuming a 25-g sample size. Conversely, the mean recoveries for PCB Aroclor 1254 and 1260 reflect possible interferences from *p,p'*-DDE, especially at the spiked concentration of 5 µg/kg for the Aroclors because individual OC pesticides were spiked also in the same replicates at 10 µg/kg, assuming a 25-g sample size, and from a more concentrated solution, 2.5 ng/µL in methanol in relation to 0.5 ng/µL (5.2.5). For comparison, a reagent OC spike sample (or LRS) typically is spiked at 10 µg/kg for PCB Aroclors and 2 µg/kg for most individual OC pesticides, assuming a 25-g sample size (7.2.2.2). In the analysis of 18 typical LRSs in calendar year 2002, *p,p'*-DDE mean recovery was 85.3 percent with 14.54-percent relative standard deviation, Aroclor 1254 mean recovery was 92.9 percent with 18.22-percent relative standard deviation, and Aroclor 1260 mean recovery was 91.7 percent with 13.14-percent relative standard deviation.

Through the years as a custom method, seven LRSs were not fortified with PCBs. In the absence of PCB interference in those LRSs, *p,p'*-DDE mean recovery was 69.1 percent with 20.73-percent relative standard deviation. Unfortunately, bias and precision data are not available for LRSs fortified with the PCB Aroclors in the absence of OC pesticide interference.

14.11 The abnormally high mean recovery of 608 percent for *p,p'*-methoxychlor from the reagent replicates spiked at 1 µg/kg most likely was caused by interference from a nonmethod compound in preparing the replicates. The relative standard deviation was about 8 percent in the determination of the estimated MDL listed in table 8. For the reagent replicates spiked at 2 µg/kg, the mean recovery for *p,p'*-methoxychlor was 507 percent with a much higher relative standard deviation of about 58 percent. For comparison, in the analysis of 18 typical LRSs in calendar year 2002, *p,p'*-methoxychlor mean recovery was 77.9 percent with a relative standard deviation of about 22 percent for the compound spiked at 2 µg/kg.

14.12 The interim reporting levels (IRLs) for this method are listed in table 9 for sediment samples on a dry-weight basis, assuming a 25-g sample size, and for suspended-sediment samples collected on filters based on a total of 63 L of water filtered (Mahler and others, 2001). The IRLs in micrograms per kilogram were set at 2 times the estimated MDL for all compounds except toxaphene. Considering toxaphene detectability relative to typical matrix-derived instrumental noise levels encountered in most sediment samples processed to date with this method, the IRL for toxaphene was arbitrarily set at 200 µg/kg to minimize false positive detections through dual GC column confirmation.

14.13 Bias (percent mean recovery) and precision (percent relative standard deviation) are shown for all matrices in table 10. The data presented in table 10 represent results from eight or fewer replicates. One replicate sample was rejected in the reagent sample set spiked at 2 µg/kg because the surrogate recoveries (< 35 percent in both fractions) were outside of the statistical control limits established, indicating errors in the sample preparation. One replicate sample was entirely ruined in

preparation in the reagent and Clear Creek sample sets spiked at 10 µg/kg. The second fraction (F2) for one replicate sample was ruined in preparation in the reagent sample set spiked at 1 µg/kg. Results for PCB Aroclor 1016/1242, 1254, and 1260 from one replicate sample in the reagent sample set spiked at 20 µg/kg for each Aroclor (except Aroclor 1016) were rejected because the recoveries appeared to be doubled. The rejection or ruin of the entire sample, an extracted fraction, or method compounds in these sample sets left only seven replicates to evaluate method performance. With the exception of *p,p'*-DDT, two replicate results were rejected for all F2 compounds in the Evergreen Lake sample set spiked at 1 µg/kg because of low (14 percent) recoveries for the F2 surrogate *alpha*-HCH-d_6. Correcting the *p,p'*-DDT results for the large matrix blank contribution (1.24 µg/kg) in this sample set resulted in rejecting five replicate results for *p,p'*-DDT because of low (< 26 percent) recoveries being outside of the statistical control limits used during spring 2000 (35–114 percent for *p,p'*-DDT) when the sample set was extracted and analyzed. One to three replicate results were rejected for several F2 method compounds in the reagent and Clear Creek sample sets spiked at 10 µg/kg because of low (< 26 percent) recoveries owing to problems with the GPC instrument.

14.14 In the overall method-performance evaluation, relative standard deviations for method compounds were equal to or less than 25 percent for all but two compounds (endrin and *p,p'*-methoxychlor) in the sodium sulfate reagent matrix, for all but nine compounds (*cis*- and

Table 9. Interim reporting levels for dry-weighted sediment samples, in micrograms per kilogram, assuming a 25-gram sample size, and for suspended-sediment samples collected on filters, in micrograms per liter, assuming 63 liters filtered.

[µg/kg, micrograms per kilogram; µg/L, micrograms per liter; mL, milliliter; ng/µL, nanograms per microliter]

Compound	Interim reporting level[1] (µg/kg)	Interim reporting level[2] (µg/L)
Aldrin	1.72	0.000273
cis-Chlordane	0.830	.000132
trans-Chlordane	0.414	.0000656
p,p'-DDD	2.06	.000327
p,p'-DDE	1.38	.000219
p,p'-DDT	0.884	.000140
Dieldrin	0.430	.0000681
Endosulfan I	0.468	.0000741
Endrin	0.672	.000107
HCB	2.86	.000453
alpha-HCH	1.10	.000174
beta-HCH	0.442	.0000700
gamma-HCH	0.400	.0000634
Heptachlor	0.618	.0000979
Heptachlor epoxide	1.20	.000190
p,p'-Methoxychlor	3.12	.000495
Mirex	1.18	.000187
trans-Nonachlor	0.770	.000122
PCB Aroclor 1016/1242	4.04	.000640
PCB Aroclor 1254	4.18	.000662
PCB Aroclor 1260	4.68	.000742
Toxaphene (technical)	200	.03

[1]The interim reporting level (IRL) for dry-weighted sediment samples was set at 2 times the estimated method detection limit (see table 8), except for toxaphene, which was arbitrarily set at about 3.5 times the estimated method detection limit to minimize false positive detection on the gas chromatography/electron capture detection instrument.

[2]The IRL for suspended-sediment samples collected on filters was determined from equations 17 and 18 given in the text, assuming a typical weight of extract before gel permeation chromatography (GPC) (W_1) of 6 g, assuming a typical weight of organochlorine extract processed through the GPC (W_2) of 1.5 g, and assuming a composite of 63 liters of water filtered based on a case study by Mahler and others (2001).

Table 10. Bias and precision data for method compounds in sodium sulfate reagent, Evergreen Lake sediment, and Clear Creek sediment from sets of eight replicates, each spiked at 1, 2, and 10 micrograms per kilogram (µg/kg) for individual organochlorine compounds; and 20, 40, and 5 µg/kg for each PCB Aroclor 1242, 1254, and 1260; toxaphene spiked separately.

[conc., concentration; µg/kg, micrograms per kilogram; g, gram; mL, milliliter; µL, microliter; ng/µL, nanogram per microliter; RSD, relative standard deviation; OC, organochlorine; PCB, polychlorinated biphenyl]

Compound	Spiked conc.[1] (µg/kg)	Sodium sulfate		Evergreen Lake		Clear Creek	
		Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)
Aldrin	1	57.4	8.09	64.7	6.89	70.4	11.86
	2	[2] 74.0	18.43	68.0	8.71	71.3	12.16
	10	[2] 64.8	5.80	64.3	15.98	[2] 69.4	4.44
cis-Chlordane	1	[2] 63.9	7.57	[3] 41.4	27.07	72.9	3.16
	2	[2] 62.5	10.51	29.6	43.94	60.9	9.02
	10	[2] 66.0	3.46	59.9	12.22	[2] 63.0	8.32
trans-Chlordane	1	[2] 70.1	9.42	[3] 47.9	24.44	71.8	4.50
	2	[2] 70.1	11.29	35.7	41.78	65.0	8.84
	10	[2] 65.1	7.51	65.4	13.82	[2] 69.5	9.51
p,p'-DDD	1	[2] 88.8	3.99	[3] 70.6	27.07	85.6	7.07
	2	[2] 82.0	19.95	66.7	44.34	82.3	9.54
	10	[3] 77.3	13.67	59.0	15.51	[2] 82.7	20.10
p,p'-DDE[7]	1	136.0	16.86	125.8	11.32	134.8	10.22
	2	[2] 136.7	12.37	137.2	7.79	129.1	11.45
	10	[2] 83.1	4.22	71.4	12.99	[2] 83.1	3.07
p,p'-DDT	1	[2] 71.1	19.78	[5,6] 48.7	14.48	91.6	13.57
	2	[2] 78.9	12.88	[6] 58.1	16.81	84.3	14.04
	10	[2] 87.4	4.72	64.1	15.51	[2] 98.5	7.60
Dieldrin	1	[2] 90.5	7.55	[3] 60.0	13.69	74.2	14.89
	2	[2] 88.7	11.47	71.5	27.43	74.7	16.14
	10	[4] 43.8	15.16	69.3	13.81	[4] 49.2	34.08
Endosulfan I	1	[2] 49.3	5.26	[3] 42.1	9.91	42.4	5.35
	2	[2] 47.6	78.81	45.1	23.36	44.9	7.58
	10	[4] 49.3	14.35	62.4	13.53	[4] 57.6	31.26
Endrin	1	[2] 114.7	9.32	[3] 109.8	9.03	126.1	8.54
	2	[2] 122.0	21.25	134.3	28.49	117.3	10.07
	10	[4] 65.1	26.15	75.0	14.09	[4] 96.8	33.57
HCB[8]	13	62.0	5.92	91.8	10.85	74.2	6.47
	26	[2] 62.0	10.93	103.9	11.12	62.3	8.12
	14.8	[2] 59.8	6.80	49.1	13.54	[2] 63.0	4.44
alpha-HCH	1	[2] 43.6	14.11	[3] 50.2	10.44	38.5	18.76
	2	[2] 58.0	15.08	61.3	34.56	45.1	9.45
	10	[2] 69.6	4.53	54.8	15.04	[2] 80.8	8.38
beta-HCH	1	[2] 72.7	9.68	[3] 61.9	7.89	72.5	5.03
	2	[2] 81.1	11.60	72.7	25.35	70.4	7.88
	10	[3] 72.5	16.84	60.6	14.56	[2] 75.0	26.33

Table 10. Bias and precision data for method compounds in sodium sulfate reagent, Evergreen Lake sediment, and Clear Creek sediment from sets of eight replicates, each spiked at 1, 2, and 10 micrograms per kilogram (µg/kg) for individual organochlorine compounds; and 20, 40, and 5 mg/kg for each PCB Aroclor 1242, 1254, and 1260; toxaphene spiked separately.—Continued

[conc., concentration; µg/kg, micrograms per kilogram; g, gram; mL, milliliter; µL, microliter; ng/µL, nanogram per microliter; RSD, relative standard deviation; OC, organochlorine; PCB, polychlorinated biphenyl]

Compound	Spiked conc.[1] (µg/kg)	Sodium sulfate		Evergreen Lake		Clear Creek	
		Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)
gamma-HCH	1	[2] 54.8	11.60	[3] 57.7	8.78	65.5	6.09
	2	[2] 68.6	15.95	70.3	28.6	63.9	7.62
	10	[2] 63.2	19.37	57.7	14.81	[2] 74.2	13.25
Heptachlor	1	66.2	15.54	87.3	10.51	79.8	10.48
	2	[2] 88.8	16.27	91.0	9.23	71.7	12.80
	10	[2] 69.3	5.80	58.6	15.42	[2] 72.9	3.76
Heptachlor epoxide	1	[2] 74.8	7.17	[3] 58.7	8.91	73.1	9.79
	2	[2] 76.5	12.44	67.4	27.02	72.1	8.91
	10	[4] 54.8	12.32	64.5	13.26	[4] 59.0	29.79
p,p'-Methoxychlor*	1	[2,13] 607.8	8.19	[3] 108.3	12.26	545.1	6.38
	2	[2,13] 506.6	57.69	538.2	24.94	451.0	6.61
	10	[4] 24.9	33.18	62.6	14.91	[4] 40.8	23.99
Mirex	1	70.6	6.32	64.4	11.59	72.9	9.65
	2	[2] 73.5	12.75	65.4	8.64	68.1	10.68
	10	[2] 62.8	4.27	49.5	12.08	[3] 59.1	3.14
trans-Nonachlor	1	[2] 56.9	21.58	[3] 70.9	10.01	75.6	14.72
	2	[2] 63.3	13.90	75.1	8.50	71.8	5.69
	10	[2] 71.1	1.73	64.1	14.74	[2] 75.1	7.56
PCB Aroclor 1016/1242[9]	20	[2] 75.9	10.32	112.1	12.80	83.4	8.07
	40	[2] 76.3	12.39	101.4	7.12	80.1	11.90
	5	[2] 87.0	14.82	65.6	21.33	[2] 103.6	9.24
PCB Aroclor 1254[10]	20	[2] 179.1	17.39	[6] 171.6	12.57	194.0	8.23
	40	[2] 198.6	12.26	[6] 172.6	7.24	201.9	14.73
	5	[2] 180.4	7.38	119.9	17.19	[2] 213.4	4.20
PCB Aroclor 1260[10]	20	[2] 120.5	10.32	146.4	9.95	125.8	8.66
	40	[2] 131.6	13.70	147.7	8.31	139.9	16.15
	5	[2] 138.6	10.77	82.5	18.74	[2] 157.4	4.17
Toxaphene (technical)[11*]	201	66.6	14.25	49.3	9.52	46.2	5.20

Table 10. Bias and precision data for method compounds in sodium sulfate reagent, Evergreen Lake sediment, and Clear Creek sediment from sets of eight replicates, each spiked at 1, 2, and 10 micrograms per kilogram (µg/kg) for individual organochlorine compounds; and 20, 40, and 5 mg/kg for each PCB Aroclor 1242, 1254, and 1260; toxaphene spiked separately.—Continued

[conc., concentration; µg/kg, micrograms per kilogram; g, gram; mL, milliliter; µL, microliter; ng/µL, nanogram per microliter; RSD, relative standard deviation; OC, organochlorine; PCB, polychlorinated biphenyl]

Compound	Spiked conc.[1] (µg/kg)	Sodium sulfate		Evergreen Lake		Clear Creek	
		Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)	Mean recovery (percent)	RSD (percent)
Surrogates							
alpha-HCH-d_6	2	[2] 85.9	11.10	[3] 102.4	9.09	82.4	6.50
	2	[2] 89.9	15.77	110.1	30.17	99.2	6.62
	2	[2] 75.1	5.72	64.6	16.27	[2] 88.0	9.56
	[12] 2	97.7	8.59	91.0	6.70	89.2	7.10
Isodrin	2	69.0	7.77	69.4	7.11	66.6	9.39
	2	[2] 99.6	16.29	71.4	7.43	72.9	11.51
	2	[2] 76.2	9.14	66.9	16.60	[2] 88.8	5.01
PCB-207	2	117.7	6.32	78.0	7.82	105.5	15.68
	2	[2] 118.0	12.89	75.3	7.94	77.5	10.00
	2	[2] 88.0	4.18	71.2	14.41	[2] 92.7	3.49

[1]One sample set for each sample matrix contained two subsets of replicates: one subset spiked at 1 µg/kg for individual OC pesticides and 20 µg/kg for each PCB Aroclor 1242, 1254, and 1260, and 2 µg/kg for surrogates, assuming a 25-g sample size; the other subset spiked at 2 µg/kg for individual OC pesticides and 40 µg/kg for each PCB Aroclor 1242, 1254, and 1260, and 2 µg/kg for surrogates, assuming a 25-g sample size. A second sample set for each sample matrix contained replicates spiked at 10 µg/kg for individual OC pesticides, and 5 µg/kg for each PCB Aroclor 1242, 1254, and 1260, and 2 µg/kg for surrogates, assuming a 25-g sample size. PCB Aroclor 1016 intentionally was not spiked in any of the replicates. A third sample set for each sample matrix contained replicates fortified with surrogates at 2 µg/kg, assuming a 25-g sample size, and 1-mL aliquots of a 5,028-ng/µL toxaphene solution, then diluted 1:1,000 to obtain a final expected concentration of 201 µg/kg for toxaphene.

[2]Number of observations was 7.

[3]Number of observations was 6.

[4]Number of observations was 4.

[5]Number of observations was 3.

[6]Recovery corrected for matrix blank contribution detected at or greater than the interim reporting level for the compound.

[7]Possible interference from PCB Aroclor 1254 or 1260.

[8]Hexachlorobenzene (HCB) is also a component of a polycyclic aromatic hydrocarbon (PAH) spike solution at 6 ng/µL that additionally was spiked into the replicates for the performance evaluation of PAHs in a separate sediment method not presented in this report. For the replicates spiked at the 1-µg/kg level of the individual OC-pesticide spike solution, HCB was spiked also at 12 µg/kg from the addition of PAH spike solution (50 µL), totaling 13 µg/kg HCB. For the replicates spiked at the 2-µg/kg level of the individual OC-pesticide spike solution, HCB also was spiked at 24 µg/kg from the addition of the PAH spike solution (100 µL), totaling 26 µg/kg HCB. For the replicates spiked at the 10-µL/kg level of the individual OC-pesticide spike solution, HCB also was spiked at 4.8 µg/kg from the addition of the PAH spike solution (20 µL), totaling 14.8 µg/kg HCB.

[9]PCB Aroclor 1242 is reported by the National Water Quality Laboratory as the combined Aroclor 1016/1242 (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum No. 99.10, 1999). PCB Aroclor 1016 was not spiked in this method-performance evaluation.

[10]Possible interference from *p,p'*-DDE.

[11]Replicates were neither fortified with individual OC pesticides nor PCBs.

[12]Spiked into the toxaphene replicates; only the fraction-2 surrogate was analyzed.

[13]The mean recovery from 18 laboratory reagent spikes in calendar year 2002 was 77.9 percent with a relative standard deviation of about 22 percent for *p,p'*-methoxychlor spiked at 2 µg/kg.

[*]Compound is permanently "E" coded (estimated) in this method.

trans-chlordane, *p,p'*-DDD, dieldrin, endrin, *alpha*- and *gamma*-HCH, heptachor epoxide, and *alpha*-HCH-d_6) in the Evergreen Lake matrix, and for all but five compounds (dieldrin, endosulfan I, endrin, *beta*-HCH, and heptachlor epoxide) in the Clear Creek matrix.

14.15 Compound *p,p'*-methoxychlor had high mean recoveries (451 to 608 percent) in all three matrices but not at all spiked concentrations. Interference from a nonmethod compound introduced upon fortifying the replicates is suspected for the high mean recoveries for *p,p'*-methoxychlor. Despite the high variable *p,p'*-methoxychlor recoveries, the compound is retained in this method because of customer request; however, data results for *p,p'*-methoxychlor will be reported permanently with the estimated (E-code) qualifier in samples.

14.16 Toxaphene also is retained in this method because of customer request. Though mean recoveries for toxaphene were 49 and 46 percent in the Evergreen Lake and Clear Creek sediments, respectively, mean recovery was 67 percent in the sodium sulfate reagent, and relative standard deviations were less than 15 percent in all three matrices. Because of pattern recognition problems (9.2.2), data results for toxaphene will be reported permanently with the estimated (E-code) qualifying in samples.

14.17 The mean recoveries listed in table 10 for *p,p'*-DDE reflect possible interferences from one or more coeluting congeners present in PCB Aroclor 1254 and 1260. Likewise, the mean recoveries listed in table 10 for PCB Aroclor 1254 and 1260 reflect possible interferences from *p,p'*-DDE. Qualifying the data results of these compounds in the presence of interference is discussed in section 12.4.

14.18 Hexachlorobenzene (HCB) is a component of a polycyclic aromatic hydrocarbon (PAH) spike solution that was spiked in addition to the individual OC-pesticide spike solution in the replicates for the purpose of evaluating PAH performance in a separate sediment method. Performance data for the PAHs are not presented in this report. The total amount of HCB in each set of replicates, however, is taken into account in table 10. See the footnote for HCB in table 10 for details.

14.19 Before 2004, the complex mixture technical chlordane was analyzed and identified by the detection of a few of its component compounds, namely, *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor as a trio. In the absence of performance data, technical chlordane has been dropped from the new method. Instead, performance data for the two octachlor and the nonachlor compounds characteristic of technical chlordane are presented in table 10, and the compounds will be reported individually in the new method.

Summary and Conclusions

A new method was developed to determine 19 organochlorine (OC) pesticides, including total toxaphene, and polychlorinated biphenyls quantified as Aroclor 1016/1242, 1254, and 1260 equivalents. The new method determines individual OC pesticide concentrations as low as 0.400 microgram per kilogram (µg/kg) and PCB Aroclors as low as 4.04 µg/kg in dry-weighted bed and suspended-sediment samples. The interim reporting level (IRL) for toxaphene is set at 200 µg/kg in this method. For wet-weighted suspended-sediment samples adhered to filters, the IRLs as determined by the new method are reported in micograms per liter. Reporting levels are subject to change following additional method-detection-limit determinations. The method provides effective preparatory separation of OCs using gel permeation chromatography, combined-column alumina/silica adsorption chromatography, and Florisil adsorption chromatography. The method also provides effective instrumental separation of selected OCs, using dual capillary-column gas chromatography with a time-efficient temperature ramp program, although superior PCB congener separations were obtained with the longer gas-chromatograph temperature ramp program in the U.S. Geological Survey (USGS) method O-5129-95. The new method modifies the earlier USGS method O-5129-95 (Foreman and others, 1995). Though the new method has fewer compounds than USGS method O-5129-95, there are fewer compound coelutions. Moreover, the additional Florisil adsorption chromatography step provides cleaner extracts which increases signal-to-noise ratios and improves method detection limits compared to the method by Foreman and others (1995).

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