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Determination of Wastewater Compounds in Sediment and Soil by Pressurized Solvent Extraction, Solid-Phase Extraction, and Capillary-Column Gas Chromatography/Mass Spectrometry

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Techniques and Methods 5–B2

U.S. Department of the Interior
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By Mark R. Burkhardt, Steven D. Zaugg, Steven G. Smith, and Rhiannon C. ReVello

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Conversion Factors

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
micrometer (µm)	0.00003937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	39.37	inch (in)
	Volume	
liter (L)	0.2642	gallon (gal)
microliter (µL)	0.000000264	gallon (gal)
milliliter (mL)	0.000264	gallon (gal)
milliliter per minute (mL/min)	0.0338	ounce per minute
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
microgram (µg)	0.00000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
	Pressure	
kilopascal (kPa)	0.1450	pound-force per inch (lbf/in)

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

$$°C = (°F-32)/1.8$$

Abbreviated water-quality units used in this report:

in.	inch
L/min	liters per minute
min	minute
mg/kg	milligram per kilogram
mg/mL	milligram per milliliter
µg/L	microgram per liter
ng/µL	nanogram per microliter
µg/kg	microgram per kilogram

Other abbreviations used in this report:

AHTN	acetyl-hexamethyl-tetrahydronaphthalene
AP	alkylphenol
APEC	alkylphenol ethoxycarboxylate
APEO	alkylphenol polyethoxylate
ASE	accelerated solvent extractor
CAS	Chemical Abstracts Service
CCV	continuing calibration verification solution
CLLE	continuous liquid–liquid extraction
DCM	dichloromethane
DEE	diethyl ether

ETFE	ethylenetetrafluoroethylene
GC	gas chromatograph or gas chromatography
GCC	glass bottle, amber
GC/MS	gas chromatography/mass spectrometry
HHCB	hexahydrohexamethyl-cyclopentabenzopyran
IPA	isopropyl alcohol
IDL	instrument detection level
LT–MDL	long-term method detection level
MDL	method detection limit
min	minute
MRL	minimum reporting level
MS	mass spectrograph or mass spectrometry
m/z	mass-to-charge ratio
NP	nonylphenol
NPEO	nonylphenol ethoxylate
NWQL	National Water Quality Laboratory
N/A	not applicable
OPEO	octylphenol ethoxylate
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PLE	pressurized liquid extraction
PLEHW	pressurized liquid extraction with subcritical heated water
PSDVB	polystyrene-divinylbenzene
PTFE	polytetrafluoroethylene
QA/QC	quality assurance and quality control
RSD	relative standard deviation
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Determination of Wastewater Compounds in Sediment and Soil by Pressurized Solvent Extraction, Solid-Phase Extraction, and Capillary-Column Gas Chromatography/ Mass Spectrometry

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Abstract

A method for the determination of 61 compounds in environmental sediment and soil samples is described. The method was developed in response to increasing concern over the effects of endocrine-disrupting chemicals in wastewater and wastewater-impacted sediment on aquatic organisms. This method also may be used to evaluate the effects of combined sanitary and storm-sewer overflow on the water and sediment quality of urban streams. Method development focused on the determination of compounds that were chosen on the basis of their endocrine-disrupting potential or toxicity. These compounds include the alkylphenol ethoxylate nonionic surfactants and their degradates, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, polycyclic aromatic hydrocarbons, and high-use domestic pesticides.

Sediment and soil samples are extracted using a pressurized solvent extraction system. The compounds of interest are extracted from interfering matrix components by high-pressure water/isopropyl alcohol extraction. The compounds were isolated using disposable solid-phase extraction (SPE) cartridges containing chemically modified polystyrene-divinylbenzene resin. The cartridges were dried with nitrogen gas, and then sorbed compounds were eluted with methylene chloride (80 percent)-diethyl ether (20 percent) through Florisil/sodium sulfate SPE cartridge, and then determined by capillary-column gas chromatography/mass spectrometry.

Recoveries in reagent-sand samples fortified at 4 to 72 micrograms averaged 76 percent ±13 percent relative standard deviation for all method compounds. Initial method reporting levels for single-component compounds ranged from 50 to 500 micrograms per kilogram. The concentrations of 20 out of 61 compounds initially will be reported as estimated with the "E" remark code for one of three reasons: (1) unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25 percent relative standard deviation), (2) reference standards prepared from technical mixtures, or (3) potential blank contamination.

Samples were preserved by freezing to –20 degrees Celsius. The U.S. Geological Survey National Water Quality Laboratory has established a 1-year sample-holding time limit (prior to sample extraction) from the date of sample collection (if the sample is kept at –20°C) until a statistically accepted method can be used to determine the effectiveness of the sample-freezing procedure.

Introduction

Industrial and domestic wastes need to be managed effectively to meet the challenges of increasing population, regulatory requirements, and aging wastewater-treatment facilities in the United States. Specific analytical methods are available for use in monitoring selected chemical compounds in wastewater to meet these challenges. The U.S. Environmental Protection Agency (USEPA) regulates many compounds, and appropriate analytical methods generally are available (U.S. Environmental Protection Agency, 1995) to monitor them in industrial wastes or in discharge from wastewater-treatment facilities. However, because of the complexity of the sample matrices for soils, sediments, and suspended sediments, specific analytical methods are required to determine polar and nonpolar organic compounds that might affect water quality. Other compounds known to be toxic to aquatic life currently (2005) are unregulated even though some, such as nonylphenol ethoxylates (NPEOs), are on the USEPA Toxic Substance Control Act Priority Testing List (U.S. Environmental Protection Agency, 1996). To meet some of the challenges of assessing the effect of wastewater discharge on water quality, the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) has developed an

analytical method to determine representative compounds from various chemical classes that reflect possible contamination from wastewater in environmental sediment samples.

Hydrophobic organic compounds, including the alkylphenol ethoxylate nonionic surfactants and their degradates (Geiger and others, 1984; Jobling and Sumpter, 1993; Blackburn and Waldock, 1995; Barber and others, 2000; Hale and others, 2000), food additives (Seiler and others, 1999), fragrances (Franke and others, 1999; Fromme and others, 1999; Simonich and others, 2000; Standley and others, 2000), flame retardants (de Boer and others, 1998; van Stee and others, 1999; Kuosmanen and others, 2001), plasticizers (Yang and others, 1997), industrial solvents (Yang and others, 1997), disinfectants (McMurry and others, 1998; van Stee and others, 1999), fecal sterols (Shigenaka and Price, 1988), polycyclic aromatic hydrocarbons (Hawthorne and others, 2000), and high-use domestic pesticides (Gan and others, 1999) may be associated with particulates or sediments, or both, in the environment (Yang and others, 1997; Field and Reed, 1999; Gan and others, 1999; Hawthorne and others, 2000; Wilkison and others, 2000; Kuosmanen and others, 2001; Dabrowski and others, 2002; Ying and others, 2002). Traditional methods for determining organic compounds in environmental sediment or soil samples generally are optimized for one or two classes of compounds and use liquid-solid extraction with an organic solvent followed by analysis with gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) detection (Furlong and others, 1996; Jha and Wydoski, 2003).

Pressurized liquid extraction (PLE) demonstrates advantages for automation, reduced extraction time, and requires less solvent than conventional Soxhlet extraction. Recently (2005), PLE with subcritical heated water (PLEHW) has been used for extracting polar to moderately polar organic compounds from sediments. At temperatures above 250ºC, extraction of nonpolar high molecular weight compounds, such as polycyclic aromatic hydrocarbon compounds (PAHs) (Hawthorne and others, 2000) and polychlorinated biphenyl compounds (PCBs) (Field and Reed, 1999) have been reported. The pressure required for PLEHW must be high enough to maintain water in the liquid state, but otherwise has little effect on solubility (U.S. Environmental Protection Agency, 2000). The PLEHW of sediments provides more selectivity for analytes than conventional Soxhlet extraction using organic solvents as evidenced by a dramatic reduction in the extraction of the bulk organic nonpolar matrix (Anderson and others, 2000). Although it is still possible to gain some degree of selectivity using modified PLEHW by varying the modifier concentration, the use of organic cosolvents produces dirtier extracts that often require cleanup prior to analysis. In a production laboratory, where stable reproducible instrument response with minimum maintenance is desirable, extract quality (low matrix background, greater than 60-percent analyte recovery) is important. PLEHW field extraction of petroleum-contaminated sediment samples with simultaneous absorption onto solid-phase extraction (SPE) disks has been reported to produce clean extracts (Hawthorne and others, 2000). However, in a laboratory setting, more options are possible for washing, adjusting the pH, and eluting SPE cartridges if the SPE is cleaned up offline.

The ASE™ 200 is a commercially available PLE instrument produced by Dionex (Sunnyvale, Calif., USA), and the process, which has been termed "accelerated solvent extraction" (ASE), generally uses conventional organic solvents at a temperature of about 100ºC. The upper operating temperature limit of 200ºC for the ASE™ 200 is too low to effectively extract nonpolar high molecular weight organic compounds, such as PAHs (about molecular weight 202 or higher) using subcritical water, without the addition of a cosolvent. Thus, substantially increasing the solvating power of PLEHW requires the addition of a few percent of cosolvent.

Environmental sediment samples require extensive extract clean-up procedures to provide the low matrix background extract that can be analyzed routinely in a production laboratory and yet retain most of the compounds of interest. Because most existing environmental sediment methods often use labor-intensive Soxhlet extraction and require extensive extract clean-up steps, it has become imperative to implement more efficient, environmental friendly methods. Analytical methods that use SPE as an alternative to liquid–liquid extraction have been implemented for the determination of pesticides in filtered water (Furlong and others, 2001; Sandstrom and others, 1992, 2001; Zaugg and others, 1995). These SPE methods are attractive because they are rapid, efficient, use much less solvent than liquid–liquid extraction, and, consequently, are more affordable and produce less toxic waste. Coupling SPE and PLE allows for extracting complex matrices, minimizing matrix interferences, and analyzing by full-scan GC/MS.

Purpose and Scope

This report describes a method (O-5433-05) for determining a broad range of wastewater compounds in environmental sediment and soil samples. It is rapid, efficient, and was developed potentially to replace Soxhlet sample-preparation techniques in use at the NWQL. The method supplements other methods of the USGS for the determination of organic substances in water that have been described previously by Wershaw and others (1987), Fishman (1993), and Zaugg and others (2002). Not all of the compounds in Schedule 1433 (Zaugg and others, 2002) appear in this new method; some were excluded because of high or low recovery, relative standard deviations greater than 30 percent, or low probability of the compounds partitioning into soil or sediment. This new method was approved for use by the USGS and is scheduled to be implemented at the NWQL in June 2006.

There are substantial advantages of using this method over previously used sediment methods. The pressurized solvent extraction, coupled with the solid-phase based clean-up step, provides a low matrix-background extract, which reduces chemical noise, resulting in low detection limits or use of full-scan ion monitoring, or both. The full-scan ion monitoring

allows for more specific compound identification along with the potential to tentatively identify unknown compounds in the sample extracts. The method also allows different compound classes to be monitored at the same time for use as a screening method in water-quality studies with several compound classes being determined from the sample extract.

This report provides a detailed description of all aspects of the method, including the apparatus and instrumentation, reagents, sample preparation and analysis (including pressurized solvent extraction characteristics and SPE procedure required for sample analysis), and instrument calibration. Method performance (bias and precision) and estimated method detection limits for 61 compounds are presented.

The scope of the study includes determination of method performance in reagent-sand, in river-sediment samples collected from Cherry Creek near Garland Park, Denver, Colorado, and in topsoil from a commercially available mixture. Method performance was determined at two appropriate concentrations for each compound (4- and 40-µg spikes for most compounds) in each sediment type. Method detection limits (MDL) were determined according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1997).

Analytical Method

Organic Compounds and Parameter Codes: Wastewater compounds, bottom sediment, soils, and solids, pressurized solvent extraction, solid-phase extraction, gas chromatography/mass spectrometry, O-5433-05, Lab Schedule 5433 (see table 1).

1. Scope and Application

This method is suitable for determining the compounds listed in table 1, in microgram-per-kilogram concentrations, in bed-sediment (stream and lake beds), aqueous suspended-sediment, and soil samples. The method includes many compounds that typically are associated with industrial and household wastewater (Paxéus and others, 1992), as well as some that are known or suspected endocrine-disrupting compounds. The method is applicable to compounds that are (1) efficiently extracted from sediment samples using high-pressure water/isopropyl alcohol, (2) partitioned from the resulting water/isopropyl alcohol extract onto polystyrene-divinylbenzene (PSDVB) in the organic phase, (3) volatile and thermally stable for gas chromatography (GC), and (4) sufficiently stable to chemical and thermal degradation to allow accurate quantification. Method compounds, endocrine-disrupting potential, Chemical Abstracts Service numbers, parameter and method codes, and possible compound uses or sources are listed in table 1.

2. Method Summary

2.1 Collect soil or sediment samples in the field by using the method outlined by Radtke and others (1998a).

2.2 Extract the sediment samples using water/isopropyl alcohol on a pressurized solvent extraction system.

2.3 Isolate the selected compounds from these extracts using a disposable, polypropylene SPE cartridge, which contains a PSDVB phase. Dry the SPE cartridges for 5 minutes. The SPE cartridges are not dried exhaustively.

2.4 Elute the compounds of interest with a mixture of dichloromethane (DCM) and diethyl ether (DEE) at an 80:20 ratio, respectively.

2.5 Also use the DCM–DEE to elute sorbed compounds from a Florisil/sodium sulfate SPE cartridge.

2.6 Evaporate the extract in a hood by using a gentle stream of nitrogen to a final volume of 1 mL.

2.7 Determine the compounds of interest in the concentrated extracts by capillary-column gas chromatography/mass spectrometry (GC/MS).

3. Safety Precautions and Waste Disposal

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

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

4. Interferences

Compounds that compete with or displace the compounds of interest from the SPE cartridge materials (PSDVB phase and Florisil) might cause interferences or low method recovery, or both. In addition, compound classes, such as humic and fulvic acids, might influence the extraction efficiency and because of the complex nature of sediment and soil samples, recoveries of compounds of interest might be reduced.

Table 1. Wastewater method compound names, endocrine-disrupting potential, parameter/method codes, and possible compound uses.

[EDP, endocrine-disrupting potential; S, suspected; K, known; CAS, Chemical Abstracts Service; F, fungicide; H, herbicide; I, insecticide; FR, flame retardant; GUP, general use pesticide; WW, wastewater; Manuf, manufacturing; >, greater than; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; UV, ultraviolet; NA, not applicable; --, no data]

Compound name	EDP[1]	CAS number	Parameter/ method codes[2]	Possible compound uses or sources[3]
1,4-Dichlorobenzene[4]	S	106-46-7	63163	Moth repellent, fumigant, deodorant
1-Methylnaphthalene	--	90-12-0	63165	2-5 percent of gasoline, diesel fuel, or crude oil
2,6-Dimethylnaphthalene[4]	--	581-42-0	63167	Present in diesel/kerosene (trace in gasoline)
2-Methylnaphthalene	--	91-57-6	63168	2-5 percent of gasoline, diesel fuel, or crude oil
3,4-Dichlorophenyl isocyanate	--	102-36-3	63169	Degradate of diuron, a noncrop herbicide
3-*beta*-Coprostanol	--	360-68-9	63170	Carnivore fecal indicator
3-Methyl-1H-indole (skatol)	--	83-34-1	63171	Fragrance, stench in feces and coal tar
3-*tert*-Butyl-4-hydroxyanisole (BHA)	K	25013-16-5	63172	Antioxidant, general preservative
4-Cumylphenol	K	599-64-4	63173	Nonionic detergent metabolite
4-*n*-Octylphenol	K	1806-26-4	63174	Nonionic detergent metabolite
4-*tert*-Octylphenol	K	140-66-9	63176	Nonionic detergent metabolite
Acetophenone	--	98-86-2	63178	Fragrance in detergent and tobacco, flavor in beverages
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	--	21145-77-7	63179	Musk fragrance (widespread use) persistent in ground water
Anthracene[4]	--	120-12-7	63180	Wood preservative, component of tar, diesel, or crude oil, CP
Anthraquinone[4]	--	84-65-1	63181	Manuf dye/textiles, seed treatment, bird repellent
Atrazine	--	1912-24-9	63182	Selective triazine herbicide
Benzo[*a*]pyrene[4]	K	50-32-8	63183	Regulated PAH, used in cancer research, CP
Benzophenone	S	119-61-9	63184	Fixative for perfumes and soaps
beta-Sitosterol	--	83-46-5	63185	Plant sterol
beta-Stigmastanol	--	19466-47-8	63186	Plant sterol
Bisphenol A	K	80-05-7	63188	Manuf polycarbonate resins, antioxidant, FR
Bromacil[4]	--	314-40-9	63189	H (GUP), >80 percent noncrop usage on grass/brush
Camphor	--	76-22-2	63192	Flavor, odorant, ointments
Carbazole	--	86-74-8	63194	I, Manuf dyes, explosives, and lubricants
Chlorpyrifos[4]	K	2921-88-2	63195	I, domestic pest and termite control (domestic use restricted as of 2001)
Cholesterol	--	57-88-5	63196	Often a fecal indicator
Diazinon[4]	K	333-41-5	63198	I, > 40 percent nonagricultural usage, ants, flies
Diethyl phthalate	--	84-66-2	63202	Plasticizer for polymers and resins
Diethylhexyl phthalate	--	117-81-7	63187	Plasticizer for polymers and resins, pesticides
d-Limonene	--	5989-27-5	63203	F, antimicrobial, antiviral, fragrance in aerosols
Fluoranthene[4]	--	206-44-0	63208	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Hexahydrohexamethyl-cyclopenta-benzopyran (HHCB)	--	1222-05-5	63209	Musk fragrance (widespread use) persistent in ground water
Indole	--	120-72-9	63210	Pesticide inert ingredient, fragrance in coffee
Isoborneol	--	124-76-5	63211	Fragrance in perfumery, in disinfectants
Isophorone[4]	--	78-59-1	63212	Solvent for lacquer, plastic, oil, silicon, resin

Table 1. Wastewater method compound names, endocrine-disrupting potential, parameter/method codes, and possible compound uses.—Continued

[EDP, endocrine-disrupting potential; S, suspected; K, known; CAS, Chemical Abstracts Service; F, fungicide; H, herbicide; I, insecticide; FR, flame retardant; GUP, general use pesticide; WW, wastewater; Manuf, manufacturing; >, greater than; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; UV, ultraviolet; NA, not applicable; --, no data]

Compound name	EDP[1]	CAS number	Parameter/ method codes[2]	Possible compound uses or sources[3]
Isopropylbenzene (cumene)	--	98-82-8	63213	Manuf phenol/acetone, fuels and paint thinner
Isoquinoline[4]	--	119-65-3	63214	Flavors and fragrances
Menthol	--	89-78-1	63215	Cigarettes, cough drops, liniment, mouthwash
Metalaxyl[4]	--	57837-19-1	63216	H, F (GUP), mildew, blight, pathogens, golf/turf
Methyl salicylate	--	119-36-8	63217	Liniment, food, beverage, UV-absorbing lotion
Metolachlor[4]	--	51218-45-2	63218	H (GUP), indicator of agricultural drainage
N,N-Diethyl-*meta*-toluamide (Deet)	--	134-62-3	63219	I, urban uses, mosquito repellent
Naphthalene[4]	--	91-20-3	63220	Fumigant, moth repellent, major component (about 10 percent) of gasoline
Nonylphenol, diethoxy- (total, NPEO2)	K	26027-38-3	63200	Nonionic detergent metabolite
Nonylphenol, monoethoxy- (total, NPOE1)	--	NA	63221	Nonionic detergent metabolite
Octylphenol, diethoxy- (OPEO2)	K	26636-32-8	63201	Nonionic detergent metabolite
Octylphenol, monoethoxy- (OPEO1)	K	26636-32-8	63206	Nonionic detergent metabolite
para-Cresol[4]	S	106-44-5	63222	Wood preservative
para-Nonylphenol (total)	K	84852-15-3	63175	Nonionic detergent metabolite
Pentachlorophenol[4]	S	87-86-5	63223	H, F, wood preservative, termite control
Phenanthrene[4]	--	85-01-8	63224	Manuf explosives, component of tar, diesel fuel, or crude oil, CP
Phenol[4]	--	108-95-2	63225	Disinfectant, manuf several products, leachate
Prometon[4]	--	1610-18-0	63226	H (noncrop only), applied prior to blacktop
Pyrene[4]	--	129-00-0	63227	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Tetrabromodiphenyl ether	--	40088-47-9	63166	Fire retardant
Tri(2-butoxyethyl) phosphate	--	78-51-3	63229	Flame retardant
Tri(2-chloroethyl) phosphate	S	115-96-8	63230	Plasticizer, flame retardant
Tri(dichloroisopropyl) phosphate	S	13674-87-8	63235	Flame retardant
Tributyl phosphate	--	126-73-8	63231	Antifoaming agent, flame retardant
Triclosan	S	3380-34-5	63232	Disinfectant, antimicrobial (concern for acquired microbial resistance)
Triphenyl phosphate	--	115-86-6	63234	Plasticizer, resin, wax, finish, roofing paper, FR

[1]World Wildlife Fund Canada (1999).

[2]Parameter codes define sample constituent variables linked to compound analytical results stored in the National Water Information System data base (U.S. Geological Survey, 2003).

[3]ChemFinder Webserver (2001); National Toxicology Program (2001); National Institute of Standards and Technology (2001); Spectrum Laboratories, Inc. (2001); HealthCentral.com (2001); EXtension TOXicology NETwork (2001).

[4]Compound determined by at least one other method at the National Water Quality Laboratory.

Compounds that have gas-chromatographic retention times and characteristic ions with a mass-to-charge ratio identical to or similar to the compounds of interest might interfere, and again because of the complex nature of sediment and soil samples, often there are unknown compounds that might interfere.

Phthalates, antioxidants, and preservatives in the SPE cartridge housing often contribute to low-concentration contamination. Samples, collection equipment, or SPE cartridges that are handled improperly also might become contaminated with soaps, caffeine, and fragrances. Precautions are necessary to avoid contamination during sample collection (see section 11.1, Field Sampling) because some method compounds are contained in commonly used commercial consumer products. Sample-collection protocols and cleaning procedures for field equipment (Radtke and others, 1998a, p. 57; 1998b, p. 11–13) need to be followed to reduce interferences.

5. Apparatus and Instrumentation

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

5.2 *Pressurized extraction system*—Dionex ASE 200 Accelerated Solvent Extractor or equivalent.

5.2.1 *Operating conditions*—Pressure 13,800 kPa (2,000 lb/in^2), temperatures 120° and 200°C, preheat time 0, heat time 0, static time 10 minutes, flush volume 25 mL, purge time 20 seconds, static cycles 3, solvent concentrations 50 percent water/50 percent isopropyl alcohol, solvent concentrations 20 percent water/80 percent isopropyl alcohol.

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

5.4 *Extraction cells*—Dionex ASE 200 stainless steel 22-mL extraction cells and end caps or equivalent.

5.5 *Carboy*—Nalgene™, thick-walled, capable of maintaining a vacuum of 200 kPa (29 in.) of mercury, 10-L volume, Van Waters & Rogers Scientific, Inc. (VWR) or equivalent.

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

5.7 *25-mL graduated Kuderna-Danish receivers (concentrator tubes)*—Kontes part number 570081-2526 or equivalent.

5.8 S*olvent reservoirs*—Amber glass, 1,000-mL.

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

5.10 *Analytical balances*—Balance for accurately weighing samples, 1,400 ± 1 g. Balance for standard preparation accurately weighs 10 ± 0.01 mg.

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

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

5.13 *Glass and stepper syringes*—10 to 500-µL volumes.

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

5.15 *Positive pressure nitrogen manifold or equivalent*.

5.16 *Fused-silica capillary column*—Any column that provides adequate resolution, capacity, accuracy, and precision. A 30-m by 0.25-mm inside diameter fused-silica capillary column coated with a 0.50-µm bonded film of 5-percent polyphenylmethylsilicone; Hewlett-Packard HP-trace analysis column or equivalent.

5.17 *GC/MS bench-top system*—Agilent Technologies, Model 5973 or equivalent.

5.17.1 *GC condition*—Oven, 40°C (hold 3 minutes), then ramp at 4°C/min to 100°C, and 9°C/min to 320°C; injection port, 290°C with electronic pressure control set for a constant flow of helium carrier gas of 0.9 mL/min; injection volume, 2 µL, splitless injection.

5.17.2 *MS conditions*—Source, 200°C; analyzer, 100°C; interface, held at 250°C and programmed at 9°C/min to 290°C when the oven temperature surpasses 250°C; electron-impact ionization mode (70 electron volts). Full-scan mode from 45 to 450 atomic mass units in 0.5 second.

6. Reagents and Consumable Materials

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

6.2 *Glass fiber thimbl*e—Whatman glass fiber thimble-shaped filters, item number 2814199 or equivalent.

6.3 *Nitrogen gas*—For evaporation, 99.999 percent pure.

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

6.5 *Florisil SPE cartridges*—6-mL barrel, packed with 1 g of Florisil, IST Inc., catalog number 712-0100-C or equivalent.

6.6 *Column reservoir*—Polypropylene 150 mL, empty column, Macherey-Nagel GMBH and Co., KG, custom made or equivalent.

6.7 *Isolation SPE cartridges*—20-mL barrel, packed with 1 g of PSDVB; OASIS PSDVB packing material, Waters Inc., catalog number 186000117 or equivalent.

6.8 *Glass bottles*—Amber, 1,000 mL, wide mouth, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps or equivalent.

6.9 *Solvents*—Dichloromethane (DCM), pentane, acetone, isopropyl alcohol (IPA), and diethyl ether (DEE); B&J Brand pesticide grade or equivalent.

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

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

6.12 *Dichloromethane:diethyl ether mixture*—80:20 volume per volume.

6.13 *Water/isopropyl alcohol mixtures*—50:50 volume per volume, and 20:80 volume per volume.

6.14 *Sodium sulfate*—Aldrich Chemical Co. reagent grade or equivalent, baked at 450°C for at least 1 hour.

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

7. Standards

7.1 *Stock standard solutions at 10,000 ng/µL*—Obtain method compounds and surrogate compounds at greater than 99-percent purity, if available, from commercial vendors. Prepare stock standard solutions of each individual compound at about 10,000 ng/µL (10 mg/mL) by accurately weighing, to the nearest 0.002 mg, 20 mg of the neat material in a 2-mL volumetric flask and dilute to volume with DCM. Three of the method compounds (para-nonylphenol, OPEO1, and OPEO2) are only available in technical mixtures. For the technical grade nonylphenol (NP) mixture (NPOE1 and NPOE2) and the OPEO1 and OPEO2 mixtures, the final concentration of each component in the stock standard solutions is calculated on the basis of the percentage contribution of each compound to the total ion chromatograms of the technical mixtures. These compounds are identified in the total ion chromatogram by referring to their characteristic ions and relative retention times (see table 2 in Section 10, Instrument Calibration).

The total contribution of the *para*-nonylphenols (total) in the NP technical mixture is determined by manually integrating the sum of the peaks within the expected retention time window (fig. 1) for the quantitation ion (m/z 135, see table 2, Section 10). Also, the qualification ion profile patterns (m/z 220 and 107) are compared to the m/z to verify the elution range of the ions used. The *ortho*-NPs elute prior to the *para*-NPs and are not determined in this method because their contribution to the total ion chromatogram is minimal (less than 7 percent). In general, it is desirable for the purposes of making dilutions of the mixed standard solution, to prepare a stock standard solution of the *para*-NP isomers (total), which is 16 times the concentration of the stock standard solutions of the single-component compounds in the method. To prepare this stock standard solution, calculate the necessary amount of the technical mixture needed (about 180 mg/mL).

The Igepal 210 technical mixture is mainly composed of single components of OPEO1 and OPEO2 in a ratio of about 10 to 1, respectively. A convenient concentration of a stock standard solution for OPEO1 is prepared at 4 times the concentration of the single-component compounds, or 40 mg/mL. This concentration also provides enough material for calibrating OPEO2 (about 4 mg/mL) from the same stock standard solution. The preparation of the OPEO1 and OPEO2 stock standard solution, thus, generally requires about 45 mg/mL (as calculated) of the Igepal 210 technical mixture.

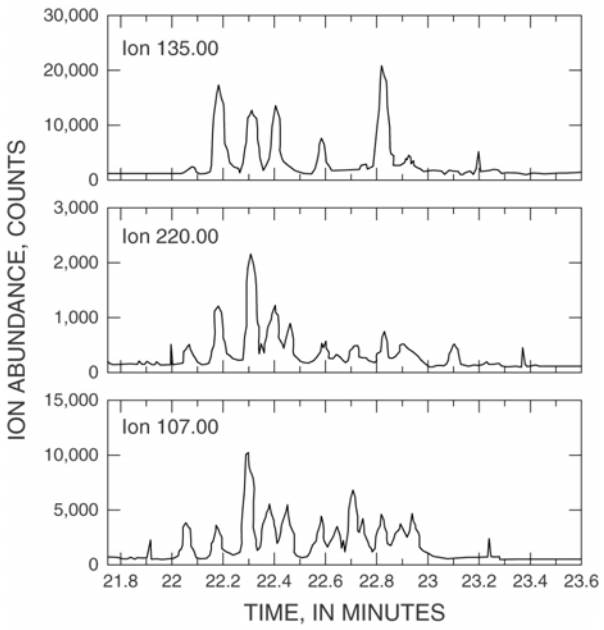

Figure 1. Manual integration of the extracted ion profile for the quantitation ion (mass-to-charge ratio 135) of *para*-nonylphenol from the 2 nanogram-per-microliter calibration solution for the wastewater method (from Zaugg and others, 2002, p. 10).

During development of the custom wastewater method (Zaugg and others, 2002) that this method is based on, NPEO1 and NPEO2 only were available in a technical mixture. Since 2002, a source of NPEO2 standard has been identified and evaluated for purity, so it was included in this method. Standards of the NPEO1 compounds also became available and currently (2005) are being evaluated for composition and purity for possible inclusion in the method.

7.2 *Intermediate method compound standard solution at 100 ng/µL*—Prepare a mixed stock standard solution that contains each method compound at 100 ng/µL. Use an adjustable 100-µL dispenser and a 10-mL volumetric flask to prepare this intermediate method compound standard solution and dilute with DCM.

7.3 *Surrogate spiking solution at 80 ng/µL*—Combine 400 µL of stock standard solution at 10,000 ng/µL for each surrogate compound listed in table 2 (see Section 10, Instrument Calibration) in a 50-mL volumetric flask and dilute with isopropyl alcohol.

Add 100 µL of the surrogate 80-ng/µL spiking solution to a 25-g environmental sample to obtain a surrogate spiking concentration of 400 µg/kg. A surrogate concentration of 8 ng/µL is expected in a 1.0-mL extract if 100 percent of the surrogate is recovered through the sample preparation procedure.

7.4 *Method compound solution at 50 ng/µL*—Add 5.0 mL of the 100-ng/µL intermediate method compound standard solution (see section 7.2) to a 10-mL flask. Add 50 µL of each of the stock standard solutions at 10,000 ng/µL (see section 7.1) and dilute with DCM. This mixture is used to prepare the calibration solutions (section 7.7).

7.5 *Spiking solution at 20 ng/µL*—Dilute 2.0 mL of the intermediate method compound standard solution at 100 ng/µL in a 10-mL volumetric flask with isopropyl alcohol. Add 200 µL to a 15-g sand sample to obtain a compound concentration of 267 µg/kg. A concentration of 4.0 ng/µL is expected in a 1.0-mL extract if 100 percent of the spike is recovered.

7.6 *Polycyclic aromatic hydrocarbon (PAH) procedural internal standard solution at 100 ng/µL*—The internal standards (see table 2, Section 10, Instrument Calibration) are obtained from Supelco in a mixture at 2,000 ng/µL. Add 2.5 mL of this mixture to a 50-mL flask and dilute with DCM. Note that 20 µL of PAH procedural internal standard solution at 100 ng/µL in a 1.0-mL extract is equivalent to a concentration of 2 ng/µL.

7.7 *Calibration solutions*—Prepare a series of calibration solutions in DCM that contain all of the method and surrogate compounds at concentrations for most compounds ranging from 0.05 to 40.0 ng/µL (0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 40 ng/µL). The concentration of single-component solutions in the calibration mixture that responds poorly by GC/MS (cholesterol, 3-*beta*-coprostanol, *beta*-stigmastanol, *beta*-sitosterol, OPEO1, and 5-methyl-1H-benzotriazole) needs to be 4 times that of the other single-component compounds. The concentration of the multicomponent compounds in the calibration solution, NP (total) and NPEO2 (total), needs to be 20 and 16 times, respectively, that of the single-component compounds in the calibration solution. The concentration of the PAH procedural internal standard compounds in the calibration solutions is kept constant at 5.0 ng/µL. Prepare these calibration solutions by adding the appropriate volumes of the mixed surrogate and method compound solution at 50 ng/µL and the PAH procedural internal standard solution at 100 ng/µL into volumetric flasks and diluting to volume with DCM.

8. Sample Preparation

8.1 *Collection, shipment, and storage of sediment samples*—Collect bed-sediment (stream and lakebeds), aqueous suspended-sediment, and soil samples using sampling methods that accurately represent the organic contamination and concentrations at a given location. Use sampling equipment that is free of plastic tubing, gaskets, and other parts that might leach interferences, absorb compounds of interest, or potentially contaminate or degrade the sediment samples. Collect the sediment samples using the process described by Radtke and others (1998a). Field-sampling procedures need to follow those typically used to collect samples for trace organic compound analyses (Hardy and others, 1989; Ward and Harr, 1990; Radtke and others, 1998a, 1998b).

CAUTION: Some of the compounds that are determined by this method are found in commonly used products, such as coffee, tea, cola, soap, and insecticide repellent. Project personnel need to be careful to avoid potential contamination of samples from such sources by avoiding consumption or contact with these materials immediately prior to and during sampling procedures. Limit or avoid contact with any fragranced materials. The probability of sample contamination with compounds determined by this method is higher than for other NWQL methods. For this reason, sample duplicates or field blank samples, or both, need to be analyzed routinely to monitor for potential sample contamination.

All sampling equipment needs to be cleaned according to procedures outlined by Wilde and others (1998) to remove all traces of possible contamination. The sampling equipment has to be cleaned before each sample is collected to prevent cross-contamination between samples.

Ship all sediment samples on ice to the NWQL in 500- or 1,000-mL wide-mouth glass jars with lids lined with polytetrafluoroethylene (PTFE) via overnight service as soon as possible after collection. The amount of water in the container should be minimized. Allow adequate space for the water present in the sample to expand during freezing. If adequate space is not allowed, the glass container will break and the sample is susceptible to contamination or loss.

Sediment samples are stored at the NWQL after login at –20°C or less until the sample is extracted. The NWQL has established a 1-year sample-holding time limit (Maloney, 2005; U.S. Environmental Protection Agency, 1998, table 8-2) from the date of sample collection to the date of sample extraction. This holding time will be used until an accepted statistical procedure determines its effectiveness.

8.2 *ASE extraction*—Retrieve samples from sample freezer and allow to thaw completely. Thoroughly homogenize each sample with a clean spatula or scoopula. Place a glass fiber filter thimble into the 22-mL ASE extraction cells and weigh. Remove any excess glass fiber thimble with a razor blade. Fill the thimbles with sample. Typical wet sample weights used range from 0.5 g (high organic content samples) to 40 g (typical sandy river sediment). Place the extraction cells into the ASE system. Extract the samples twice using the conditions outlined in section 5.2. Two collection vessels are required for each sample; a collection vessel is required for the 120°C and the 200°C extraction of each sample. Add 3 mL of pentane to the 200°C collection vessel to reduce analyte loss. Extraction volumes range from 20 to 50 mL. After extraction, weigh the extraction vessel with the thimble and sample. Remove the thimble and sample. The difference between the weight of the extraction vessel after extraction (includes thimble and sample) and the weight of the extraction vessel and thimble pre-extraction equals the dry weight of the sample processed. This measurement is required for calculating the final concentrations of the compounds of interest in a known amount of environmental sample.

Prepare laboratory reagent-sand set blank and set spike samples with each set (10 environmental samples). Add 50 µL of the surrogate solution (80 ng/µL; see section 7.3) to each sample, set spike, and set blank by using a stepper syringe to make the 100-µL additions. Fortify the spike sample with 200 µL of the spiking solution (20 ng/µL; see section 7.5) by using a micropipette dispenser and 200-µL disposable glass bore.

Note: Allow the spike and surrogate solutions to come to room temperature, and then shake well before adding them to samples.

8.3 *SPE cartridge cleaning*—Add 20 mL (the OASIS SPE barrel volume) of the elution solvent (DCM–DEE, 80:20 volume per volume) to rinse the OASIS SPE cartridges and polypropylene reservoirs. Allow the solvent to drain by gravity until the phase is completely saturated before applying vacuum. Then open the Luer-Lok fittings on the vacuum manifold by turning them counterclockwise to allow the solvent to be removed from the cartridges by vacuum. Rinse the cartridges with an additional 10 mL of DCM–DEE and allow at least 10 minutes for the vacuum to remove any residual solvent. Dispose of solvent following current local guidelines.

Add 10 mL (the Florisil SPE barrel volume) of acetone to rinse the Florisil SPE cartridges. Allow the solvent to drain by gravity until the phase is completely saturated before applying vacuum. Then open the Luer-Lok fittings on the vacuum manifold by turning them counterclockwise to allow the solvent to be removed from the cartridges by vacuum. Rinse the cartridges with an additional 10 mL of acetone and allow at least 10 minutes for the vacuum to remove any residual solvent. Dispose of solvent following current NWQL guidelines.

Note: Unlike most other SPE phases, it is permissible for PSDVB to dry prior to sample extraction.

8.4 *Sample isolation*—Immediately prior to using the SPE cartridges, visually inspect by rotating them to ensure that there is no substantial void-volume between the polyethylene frits and the PSDVB phase. Attach the SPE cartridges to the vacuum lines from the vacuum manifold assembly.

CAUTION: Loosely packed PSDVB phase can cause uneven flow or channeling during the SPE process and result in reduced compound recoveries. Therefore, it is essential to ensure that the PSDVB phase is packed firmly before using SPE cartridges. If the PSDVB phase is loosely packed, dispose of the SPE cartridge and prepare another SPE cartridge for use.

CAUTION: Ensure that the 10-L waste carboys have enough headspace (empty volume) remaining to accommodate the total water/isopropyl alcohol volume from all samples before a new sample set is extracted, otherwise it may be difficult to exchange carboys during the extraction.

Attach a polypropylene 150-mL empty sample reservoir to each cleaned OASIS SPE cartridge using a Teflon valved Luer-Lok adapter in the closed position. Next, add the 200°C ASE extracts to each corresponding reservoir. Add 50 mL of the phosphate buffer solution to each ASE collection vial. Cap and shake collection vial for 10 seconds. Add this buffer solution to each corresponding reservoir. Repeat the phosphate buffer cleaning step one additional time. Open the Teflon valve between the OASIS cartridge and the reservoir to allow gravity to pull the ASE extract and buffer washes through the OASIS SPE cartridges. A small vacuum may have to be applied to start the extraction. Obtain the desired extraction flow-rate range (between 5 to 10 mL/min) by loosening the vacuum manifold system frits, which might need to be done once or twice during sample extraction. Repeat this entire process by extracting the 120°C ASE extract into the same SPE cartridge used for the 200°C ASE extracts.

Note: Reasonable extraction times range from 15 to 30 minutes for 150-mL samples and correspond to flow rates between 5 and 10 mL/min. No adverse effects on compound recoveries have been observed when flow rates are maintained in this operating range.

8.5 *Cartridge drying*—Dry the OASIS SPE cartridges at 2 L/min of nitrogen for 15 minutes by using a positive pressure nitrogen manifold.

Note: The color of the PSDVB phase becomes lighter as it dries, and the wet/dry boundary layer is noticeable if carefully observed. It is important to ensure that the cartridge does not completely dry.

Note: Recoveries of compounds more volatile than naphthalene have been observed to decrease by about 10 to 20 percent if cartridges are allowed to remain under vacuum beyond 15 minutes.

8.6 *Compound elution*—Attach the corresponding 150-mL polyethylene reservoir to the corresponding OASIS SPE cartridges with a Teflon adapter. Add ~2.5 g baked sodium sulfate to the top of each Florisil cartridge. Attach a Florisil/sodium sulfate SPE cartridge to the bottom of the dried OASIS SPE cartridge. Place the end of these three stacked components (reservoir, OASIS SPE cartridge, and Florisil/sodium/sulfate SPE cartridge) in 30-mL glass receivers.

Note: Thoroughly rinsing the sample reservoirs is important because as much as 30 to 40 percent of some hydrophobic compounds (particularly PAHs, sterols, and organochlorine compounds) might adhere to the polypropylene walls.

Add 10 mL of DCM–DEE to the 150-mL polyethylene reservoir to elute the OASIS SPE cartridge. The first 10 mL will only wet the OASIS and Florisil SPE beds. Add another 10 mL of the DCM–DEE and allow gravity to pull the elution solvent into the 30-mL glass receivers. Allow the DCM–DEE level to merge with the top of the OASIS bed before adding the next aliquot. Repeat this process a third time, using a large syringe or small vacuum to force all residual DCM–DEE from the two stacked SPE cartridges. The addition of 30 mL of DCM–DEE to the two SPE cartridges will result in about 25 mL of elution solvent to be collected. Five milliliters of the DCM–DEE will be retained on the SPE beds.

Note: During the developmental stages of this method, it was observed that most problems with compound recovery were associated with difficulties in the elution step, usually related to complete removal of water from the SPE cartridges prior to elution.

8.7 *Sample concentration*—Prepare the 24-position N-Evap nitrogen evaporator by attaching cleaned and baked stainless-steel needles in each position. Set the nitrogen flow rate to about 3.5 L/min and adjust this flow visually so that a slightly detectable ripple can be seen on the surface of the extracts. When the extract volume is between 2 and 5 mL, add 20 µL of the internal standard solution (100 ng/µL) by using a 1.0-mL stepper syringe. Remove each extract when the final

volume is about 1 mL, but to maintain a more consistent flow rate for the remaining samples, leave the needles attached to the N-Evap with the flow of nitrogen remaining unaltered. Concentrate the DCM–DEE extract at ambient temperature and periodically check the extract; do not allow the extract to evaporate completely. Allow about 60 to 120 minutes for evaporation of nearly 25 mL of DCM–DEE to 1 mL.

8.8 *Vial sample extracts*—Vortex the extract so that the solvent rinses the glass walls of the receiver. Then use a baked, disposable glass Pasteur pipette to transfer concentrated extracts to appropriately labeled GC vials. Store extracts in a freezer (–10°C) prior to GC/MS analysis.

9. Sample Analysis Procedure

The performance of the analytical instrumentation is checked at least every 24 hours to ensure that it meets quality-control guidelines of sensitivity and accuracy necessary to obtain reproducible sample results.

9.1 Gas Chromatograph (GC) Performance Evaluation

9.1.1 GC performance normally is indicated by peak shape, compound resolution, and variation of selected-compound response factors relative to response factors obtained by using a new capillary column and freshly prepared calibration solutions. An example of the separation and peak shape for the complex mixture of nonylphenol compounds is shown in the selected ion chromatogram (fig. 1) of a 2.0-ng/µL calibration solution. Change the injection port liner or perform maintenance on the capillary column to bring the GC into compliance if peak shape and resolution deteriorate (indicated by a loss in the number of resolved NP isomers) or if compounds fail to meet the calibration criteria (see section 10, Instrument Calibration). About 0.6 m (one column loop) of the capillary-column inlet end often can be removed to restore GC performance. Specifically, a loss in response greater than 30 percent for cholesterol indicates the need for replacement of the GC inlet liner or maintenance of the column, or both. Sediment samples generally require capillary column maintenance (including removing one column loop) after every set of 12 environmental samples to maintain method performance. Instrument maintenance requires recalibrating the method compounds.

9.2 Mass Spectrometer Performance Evaluation

9.2.1 Check for air (m/z 28 and 32) and water (m/z 18) leaks in the GC/MS prior to analysis. If air leaks are detected, as indicated by the presence of nitrogen (m/z 28) greater than 10 percent of the m/z 69 peak area of the perflurotributylamine (PFTBA) tuning compound, locate and fix the leaks. Also, check the instrument before every analytical set to ensure that MS performance is in accordance with the PFTBA tuning criteria outlined in section 9.2.2. In addition, initially adjust the MS response (also outlined in section 9.2.2) to ensure that the established minimum reporting level (MRL) for each selected compound can be achieved.

9.2.2 Check the mass spectrometer tune before every analytical set.

Note: The following guidance applies to the Agilent Technologies model 5973 GC/MS system. Other GC/MS systems might require different adjustments to achieve the method performance criteria.

PFTBA is introduced into the MS vacuum manifold through a factory-set calibrated leak. Set mass axis and MS peak-width adjustment characteristics to give ±0.15-atomic mass unit accuracy at m/z 69, 219, and 502 in the spectrum of PFTBA. Adjust the electron multiplier voltage to achieve about 1,000,000 counts for the m/z 69. This setting generally provides sufficient signal to meet detection requirements for method compounds at method detection limit (MDL) concentrations in samples, provided that the GC is performing properly. Manually adjust the MS characteristics so that m/z ion 69 has 100-percent abundance, m/z 219 is 40 ±20 percent, and m/z 502 is 3 ±2 percent relative abundance. Check mass assignments to ensure accuracy to ±0.15 atomic mass unit. Adjust peak widths measured at half height for m/z 69, 219, and 502 so that they range from about 0.5 to 0.65 atomic mass unit. Adjustment of tune settings requires subsequent recalibration of the method compounds.

10. Instrument Calibration

10.1 Acquire initial calibration data by using a new capillary column and freshly prepared calibration solutions (section 7.7). Use these data in subsequent evaluation of the GC/MS performance.

10.2 Prior to the analysis of each sample set and every 10 samples thereafter during a series of analyses, analyze and evaluate a calibration check solution (or solutions) that contains all of the method compounds to ensure that GC/MS performance is in compliance. The observed concentration of method compounds in the continuing calibration verification solutions (CCVs), using the initial calibration curve, generally should be within ±20 percent of the expected concentration. Specific acceptance criteria for each compound may be established as subsequent data are acquired.

10.3 Inject 2 µL of each calibration solution into the GC/MS and acquire data by using the previously described GC/MS conditions. Enter the compound names, mass spectral ions, approximate retention times (table 2), and calibration concentration levels into the data system. The GC/MS data-processing software then calculates the relative retention time and response factors for each compound and surrogate in relation to their designated internal standards in the calibration solution. The data-processing software also uses linear regression (or other) routines to calculate and plot calibration curves for each compound. Typical equations used to calculate calibration curves for this method are similar to other NWQL methods (Sandstrom and others, 2001). Compound quantitation ions and their respective PAH internal-standard reference compounds used for these calculations are listed in table 2.

10.4 In the course of performing sample analyses, it is not necessary to perform a full calibration with each analytical batch, as long as performance criteria are met for CCVs and other QC samples (section 11).

10.5 *Calibration of multicomponent compounds*—The *para*-NPs, NPEO1, and NPEO2 mixtures are each composed of 10 to 20 discernible isomers. They are calibrated manually by integrating the area of their respective quantitation ion peaks that are present in the expected range of the retention time window (table 2). This range is 1 to 1.5 minutes wide. This approach also was used for determining the concentration of compounds in the preparation of stock standard solutions (section 7.1) and also has been used in other studies (Blackburn and Waldock, 1995).

10.6 *Qualitative determination*—A compound is identified based on retention time relative to the internal standard. It is also identified by comparing the background-subtracted mass spectrum with the confirmation ions (table 2) of a reference mass spectrum obtained from calibration standards. Three or four confirmation ions are defined as the ions that have the greatest relative intensity, or are desirable for their unique mass, in the reference spectrum. Compounds are identified as present when the following criteria are met (or as reason allows):

10.6.1 *Retention time*—The intensities of the characteristic ions of a compound are at a maximum that coincides within ±0.05 minute of the selected compound's relative retention time. For this schedule, the method is set (under Global to Compound ID) to choose the peak in a sample that is closest to the specified peak retention time derived from the calibration standards. In addition, the quantification ion and associated confirmation ions should have their maxima within 0.01 minute of each other. However, matrix effects can have a substantial influence on GC retention times, and retention time reproducibility can be highly compound dependent.

10.6.2 *Spectra*—The identity of each selected compound is verified by comparing the mass spectrum at the apex of the extracted ion profile of the quantitation ion with a reference spectrum obtained from the standard for that compound. In particular, the relative ratios of the extracted ion profiles need to be within 20 percent of the relative ratios obtained on injection of a calibration standard solution produced using the conditions of this method. It is difficult to define explicitly which features of a sample mass spectrum must be present to consider the identification to be positive. In general, the sample spectrum should have the same base peaks, major fragmentation ions, significant isotope clusters, and molecular ion (where appropriate) as a standard. The analyst determines if the ratios of Target® ion profiles are appropriate and have relative intensities that are consistent with the reference mass spectrum, or if differences are caused by interference ions, or are a result of contributions of Target® and interference ions. Experience and training are necessary for the analyst to recognize the salient features of individual mass spectra as well as potential interferences.

11. Quality Assurance and Quality Control

The NWQL has prepared a Quality Management System guidance document (Maloney, 2005) for Analytical Services that is followed for this wastewater sediment method to ensure that QC standards are correctly established and consistently met. The sample matrix, sample-preparation, and sample-analysis steps are evaluated to determine data quality for each sample individually, and for all samples as part of a sample-preparation set and a sample-analysis set.

Quality-control information needs to be evaluated in aggregate to determine whether analytical data are acceptable for reporting or if corrective actions are needed. Minimum quality-control requirements include the following: (1) determination of potential field-sampling errors; (2) determination of potential matrix effects; (3) analysis of third-party check solutions; (4) determination of potential blank contamination in the set blank; (5) determination of method performance by analysis of the set spike and CCV samples; (6) determination of the surrogate recovery for the individual sample; (7) determination of internal standard volume correction; and (8) corrections for instances of out-of-acceptance criteria.

11.1 *Field sampling*—Accuracy of the sampling process and possible contamination from handling samples in the field (proper sample containers, proper sample storage) is monitored when the appropriate field blanks and field duplicates are submitted to the laboratory for analysis. Even then, only limited information can be inferred because each individual sample is handled separately.

Before sample-hold time expiration, each environmental sample is prepared for analysis as part of a sample-preparation set that contains a laboratory reagent set spike and set blank to monitor method performance and contamination. There is no guarantee, however, that each unique sample matrix will perform similarly to the recoveries of compounds and surrogates obtained from the reagent set spike and set blank. Consequently, spiking of field duplicate samples at the laboratory is encouraged, as part of a project quality assurance/quality control (QA/QC) plan, to gain some indication of how method compounds perform in a particular sample matrix. Laboratory set spikes do not reflect matrix effects, either positively or negatively, because they are prepared in reagent sand, which usually is not indicative of the sample matrix. Furthermore, surrogate compounds added to monitor gross sample preparation might perform well in a given matrix, but this does not mean that all method compounds will perform equally well. Historically, statistical data for set spikes may be used to anticipate method compound recovery, but they are no substitute for field sample spikes to determine specific matrix effects.

11.2 *Sample matrix compatibility*—The sample matrix needs to be consistent with the requirements of the method (bed sediment, suspended sediment, soil samples). Problematic sample matrices will affect the performance of the method during sample preparation and analysis. Extremely complex sample matrices, such as raw sewage, are discouraged for this method because they contaminate sample-preparation

Table 2. Wastewater method compound retention time, quantitation ion, confirmation ions, surrogate compounds, and internal standard reference compounds.

[Compounds are listed in order of retention time. min, minutes; m/z, mass-to-charge ratio; IS, internal standard; --, not used]

Compound name	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Confirmation ion (m/z)	Internal standard reference
Isopropylbenzene (cumene)	11.507	105	120	--	IS1
Phenol	13.651	94	66	65	IS1
1,4-Dichlorobenzene	15.212	146	148	111	IS1
d-Limonene	15.819	93	136	121	IS1
Acetophenone	17.234	105	120	77	IS1
para-Cresol	17.460	107	108	77	IS1
Isophorone	19.298	82	138	--	IS2
Camphor	20.135	90	105	152	IS2
Isoborneol	20.582	95	136	140	IS2
Menthol	20.921	95	123	138	IS2
Naphthalene	21.123	128	127	102	IS2
Methyl salicylate	21.269	120	152	92	IS2
Isoquinoline	22.834	129	102	--	IS2
Indole	23.418	117	89	--	IS2
Diethyl phthalate	23.500	149	177	--	IS3
2-Methylnaphthalene	23.568	142	141	115	IS3
3,4-Dichlorophenyl isocyanate	23.639	187	189	124	IS3
1-Methylnaphthalene	23.869	142	141	115	IS3
3-Methyl-1H-indole (skatol)	25.120	130	131	--	IS3
2,6-Dimethylnaphthalene	25.519	156	141	--	IS3
Atrazine	26.550	200	215	202	IS3
3-*tert*-Butyl-4-hydroxyanisole (BHA)	26.606	180	165	137	IS3
N,N-Diethyl-*meta*-toluamide (Deet)	27.983	119	190	91	IS3
4-*tert*-Octylphenol	28.320	135	206	107	IS3
Nonylphenol, monoethoxy- (total, NPEO1)	28.5–29.5	179	193	207	IS4
Benzophenone	28.806	182	105	77	IS3
Tributyl phosphate	28.830	99	155	211	IS3
para-Nonylphenol (total)	29.7–30.6	135	220	107	IS4
Prometon	30.099	210	225	168	IS4
Tri(2-chloroethyl) phosphate	30.311	249	251	205	IS4
Pentachlorophenol	30.394	266	264	268	IS4
4-*n*-Octylphenol	30.448	107	206	--	IS4
Diazinon	30.673	304	179	199	IS4
Phenanthrene	30.903	178	176	89	IS4
Octylphenol, monoethoxy-(OPEO1)	30.903	135	107	179	IS4
Anthracene	31.044	178	176	89	IS4
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	31.538	243	258	197	IS4

Table 2. Wastewater method compound retention time, quantitation ion, confirmation ions, surrogate compounds, and internal standard reference compounds.—Continued

[Compounds are listed in order of retention time. min, minutes; m/z, mass-to-charge ratio; IS, internal standard; --, not used]

Compound name	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Confirmation ion (m/z)	Internal standard reference
Carbazole	31.524	167	139	166	IS4
Hexahydrohexamethyl cyclopentabenzo-pyran (HHCB)	31.468	243	258	213	IS4
4-Cumylphenol	31.576	197	212	--	IS4
Metalaxyl	32.135	206	220	249	IS4
Bromacil	32.587	205	207	--	IS4
Metolachlor	32.850	162	138	240	IS4
Chlorpyrifos	32.878	314	316	197	IS4
Anthraquinone	33.095	208	180	152	IS4
Fluoranthene	34.134	202	101	203	IS4
Triclosan	34.378	288	290	218	IS4
Diethylhexyl phthalate	34.700	149	167	279	IS5
Pyrene	34.731	202	101	203	IS5
Bisphenol A	34.994	213	228	119	IS5
Octylphenol, diethoxy- (OPEO2)	35.168	223	135	294	IS5
Nonylphenol, diethoxy- (total, NPEO2)	335.7–36.5	237	223	279	IS5
Tetrabromodiphenyl ether	35.7	328	326	324	IS5
Tri(dichloroisopropyl) phosphate	36.400	379	383	381	IS5
Tri(2-butoxyethyl) phosphate	37.054	299	199	125	IS5
Triphenyl phosphate	37.176	326	325	215	IS5
Benzo[a]pyrene	41.431	252	250	126	IS6
3-*beta*-Coprostanol	42.927	373	355	388	IS6
Cholesterol	43.209	386	301	275	IS6
beta-Sitosterol	45.038	414	396	381	IS6
beta-Stigmastanol	45.193	416	401	233	IS6
Surrogates					
Decafluorobiphenyl	18.786	334	265	--	IS2
Fluoranthene-d_{10}	34.087	212	106	--	IS4
Bisphenol A-d_3	34.947	216	234	--	IS4
Internal Standards					
1,4-Dichlorobenzene-d_4 (IS1)	15.132	150	152	--	--
Naphthalene-d_8 (IS2)	21.048	136	--	--	--
Acenapthene-d_{10} (IS3)	26.700	164	162	160	--
Phenanthrene-d_{10} (IS4)	30.842	188	--	--	--
Chrysene-d_{12} (IS5)	38.010	240	--	--	--
Perylene-d_{12} (IS6)	41.558	264	132	--	--

equipment and instrumentation, thus affecting the results of subsequent samples. In contrast, the reagent sand used for set spikes and blanks is not representative (lacking dissolved organic carbon) of an environmental sample matrix. Consequently, recoveries of surrogate and method compounds from reagent sand often are less than or greater than spike recoveries obtained from environmental sample matrices. This result demonstrates some of the limitations of comparing different sample matrices; however, laboratory spike recovery control limits need to be used as a basis to assess matrix spike recoveries.

11.3 *Third-party check*—The third-party check is either a commercially available mixture of the compounds of interest or separate lot of a mixture. The third-party check is analyzed in each sequence after the calibration standards to independently verify the calibration curve. The third-party calculated check concentrations need to be within ±30 percent of the expected concentration. If the third-party check sample concentrations do not fall within the ±30-percent window, the source of the error needs to be determined before any environmental samples are analyzed.

11.4 *Set blank*—Some compounds in the wastewater method are common in personal-care products and might be detected occasionally in laboratory or field blanks. If compounds are detected in more than 10 percent of the historical laboratory set blanks, they are treated as though they always are potentially present in sample background. If this is the case, use the 95th percentile of historical laboratory blank concentrations to establish a higher MRL for the specific compound than might otherwise be derived from the standard MDL calculation (U.S. Environmental Protection Agency, 1995).

Set blanks provide information regarding possible contamination introduced to the sample at the laboratory. Each time a set of samples is extracted, a set blank is extracted using a sand matrix. The set blank monitors all reagents, glassware, equipment, and the entire extraction process for potential contamination. If contamination interferes with the identification or quantification of the compounds of interest, the source of contamination needs to be identified and eliminated before additional environmental samples are processed. If the contamination cannot be eliminated, the data associated with the contamination are qualified with a remark code (per NWQL QA/QC policy; Maloney, 2005), or the minimum reporting level is adjusted to a higher concentration to reflect the level of contamination.

11.5 *Set spike and continuing calibration verifications*—Set spikes provide information regarding method performance for each compound. Each time a set of samples is extracted, a set spike is extracted using a sand matrix. The set spike monitors the recovery of the compounds of interest through the entire process (includes reagents, glassware, sample extraction process, and sample analysis). If there appears to be a process error that interferes with the identification or quantification of the compounds of interest, the source of the error needs to be identified and corrected before additional environmental samples are processed. If the error cannot be corrected, the data associated with the error must be qualified with an appropriate remark code according to NWQL QA/QC policy (Maloney, 2005).

Laboratory set spike data are acquired and statistically evaluated to develop acceptance criteria on an on-going basis. These control limit criteria are entered into the Target spike and CCV sublists. If a sample set contains a spike with unacceptable recovery results (as judged by the spike sublist), then surrogate recovery in the associated samples and blank need to be evaluated along with any observations recorded during sample preparation. If it is apparent that the unacceptable recovery is caused by laboratory process error, then the possibility of the error adversely affecting the other samples associated with that set needs to be considered.

Concentrations determined by this method for compounds and surrogates in environmental samples are reported without correction for spike recoveries.

11.6 *Surrogate recovery*—Surrogate compounds, which are chemically similar to method compounds, are added to each sample prior to preparation. Surrogate standard recoveries are used to measure gross sample-processing problems and matrix effects. Control limits for surrogates generally are set at the mean percent recovery ±3 standard deviations as compiled from laboratory set spike and blank samples. The recoveries of bisphenol A-d_3 and fluoranthene-d_{10} may be used to monitor sample preparation and potential matrix effects for their respective nonisotopically labeled analogs, as well as other chemically similar (by functionality, reactivity, or volatility) compounds. Surrogate recoveries generally are used to evaluate specific sample-preparation steps and are of limited use for assessing compound recoveries.

Concentrations reported by this method for compounds in environmental samples are not corrected for surrogate recoveries.

11.7 *Internal standard*—Each environmental sediment sample and all method QC samples have internal standard compounds added, just prior to final extract vialing, to correct automatically for any differences (generally less than ±10 percent) in extract volume, as well as automatically adjust for slight variations in instrumental performance. The internal standards are used to monitor instrument conditions, such as extract injection errors, GC retention time shifts, or instrument abnormalities caused by power interruptions or component malfunctions.

11.8 *Out-of-acceptance criteria*—It is difficult to troubleshoot QA/QC problems that may represent a combination of a dirty sample matrix, sample preparation errors, or a marginally acceptable analysis. Certain process failures require sample preparation to be repeated if sufficient sample has been received. Other failures might be identified as "matrix-induced" and be impossible to correct, thus requiring associated data qualifiers for reporting results. In rare cases, certain failures, such as unacceptable surrogate recoveries, might indicate that sample results are unreliable and should not be reported.

If the instrument performance does not meet acceptance criteria, then follow suggested procedures of cleaning and maintenance (see section 9.1) to bring the instrument back into compliance. It might be possible to reanalyze only that portion of the sequence corresponding to the instrumental failure between bracketing CCVs because samples are analyzed in a specific sequence. In some cases, identifying and removing problematic sample extracts from sequences, or reorganizing sequences, might be required to meet performance criteria for other sample results.

11.9 *Instrumental analysis quality control*—A typical analytical sequence used for this method is listed in table 3. Sample extract(s) are analyzed in an instrument batch or sequence to provide additional information for quality assurance and to facilitate corrective actions that might be required if performance criteria are not met. The analytical sequence includes continuing calibration verification solutions (CCVs) to check periodically at designated intervals (10 environmental samples or less) that the instrument is in compliance with initial calibration criteria. For those compounds that are quantitatively reported (not permanently assigned an estimated concentration) by using this method, a calculated concentration within ±20 percent of the expected CCV concentration is required. Finally, a low-concentration standard equivalent [instrument detection level (IDL)] to 1 µg per sample (or less) is analyzed in each sequence after the environmental samples to ensure that instrument sensitivity is maintained throughout the sample set.

Table 3. Gas chromatography/mass spectrometry analytical sequence suggested for use in determining wastewater compounds in sediment and soil.

Analytical sequence	Sample type
1	Decafluorotriphenylphosphine mass spectrometer calibration solution
2	Instrument blank (injection of pure solvent)
3	Instrument detection level (IDL) solution
4	Third-party check (if available, only during full calibration, section 11.3)
5	Continuing calibration verification (CCV) solution
6	Set A spike
7	Set A blank
8	Sample 1 Set A
9	Sample 2 Set A
10	Sample 3 Set A
11	Sample 4 Set A
12	Sample 5 Set A
13	Sample 6 Set A
14	Sample 7 Set A
15	Sample 8 Set A
16	CCV solution
17	Sample 9 Set A
18	Sample 10 Set A
19	Set B spike
20	Set B blank
21	Sample 1 Set B
22	Sample 2 Set B
23	Sample 3 Set B
24	Sample 4 Set B
25	Sample 5 Set B
26	Sample 6 Set B
27	CCV solution
28	IDL solution

12. Calculation of Results

Before quantitative results are reported, each compound first needs to meet qualitative criteria.

12.1 *Qualitative Identification*—The retention time of the quantitation ion for the compound of interest should be within 0.1 minute (±6 seconds) of the expected retention time (as calculated from the relative retention time of calibration standards and the retention time of the internal standard in the sample) in the absence of any obvious matrix effects. Furthermore, the profiles of the two qualification and the quantification ion peaks must maximize within two scans of each other (in the absence of any obvious interference). Visually compare the sample compound spectra to the reference standard spectra and confirm a reasonable match.

Note: Occasionally, ion(s) can appear to be missing or ion abundance ratios can appear to be distorted in the spectrum of a compound in a sample when compared to the reference spectrum, especially at concentrations near the MDL if there is interfering spectral contamination. A distorted sample spectrum often results from automatic data-processing routines that subtract the average of the two spectra before and after the spectrum at the apex of the peak. Subtracting the spectral background of a well-defined sample peak usually enhances the spectrum, whereas subtracting interfering ions with substantial ion abundances from a poorly defined sample peak can result in a nonsensical spectrum. In this situation, the main consideration for positive identification of a compound is the requirement for the ion profiles to maximize within two scans of each other (after accounting for interfering ion profiles, if necessary). If the compound is present, an improved spectrum also needs to be obtained after manually subtracting appropriate background scan(s) that are free from the ions of the interfering peak.

12.2 Quantitation

12.2.1 *Determination of single-component compounds*—The concentration of a compound is calculated according to the calibration curve used to establish the best fit between the calibration points after a compound has passed qualitative criteria. Curve-fitting routines provided by the instrument manufacturer, and summarized in similar NWQL method reports (Furlong and others, 1996; Jha and Wydoski, 2003), are used to obtain a calibration curve for each compound. If the calculated concentration of a compound exceeds the highest concentration point of the calibration curve by 20 percent or more, add higher concentration calibration standards to the curve or dilute the extract to bring the compound response within the range of the calibration curve. Concentration results need to be reported as estimated with the "E" qualifier code if compound response is less than the lowest point on the calibration curve or the minimum reporting level (MRL). If curve-fitting routines (quadratic curves and power curves) are used for calibration, verify that the sample compound response is not outside the working range of the calibration curve (or in a region of unexpected deviations in the calibration curve); or recalculate the concentration by using another type of calibration curve.

12.2.2 *Determination of multicomponent compounds*—The *para*-NPs, NPEO1, and NPEO2 mixtures each consist of 10 to 20 discernable isomers. Manually integrate the isomeric peak areas of their respective quantitation ions present in the expected retention time window range (table 2), similar to the calibration process described earlier (section 10, Instrument Calibration) for these compounds. If interferences cause the ratios of the quantitation ions to the confirmation ions to be unreasonable, then integrate that portion of the ion chromatogram that is caused by the contamination or interference (peaks in the sample chromatogram that are not in the calibration standard chromatogram) and subtract the interference from the total.

Note: This procedure seldom is necessary because the quantitation and confirmation ions for *para*-NP, NPEO1, and NPEO2 compounds normally are unique from coeluting interference.

12.2.3 *Calculations*—The calculation of a final concentration of the compounds of interest in a sediment sample requires multiple calculations, as follows:

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

$$W_s = (W_{cell} + W_{thimble} + W_w)_{postextraction} - (W_{cell} + W_{thimble})_{preextraction} \quad (1)$$

where

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

12.2.3.2 Calculate sample concentrations.

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

$$C = C_o / W_s \quad (2)$$

where

C = the concentration of the compound of interest in the sample, in micrograms per kilogram;
C_o = raw amount of analyte calculated from the calibration curve, in micrograms; and
W_s = the dry weight of sample extracted, in kilograms, calculated above.

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

$$R_a = [(C_s \times V_f)/(C_a \times V_a)] \times 100 \quad (3)$$

where

R_a = recovery of surrogate in sample, in percent;
C_s = concentration of surrogate in sample, in micrograms per kilogram, calculated using equations 3 and 4;
V_f = final extract volume, in microliters;
C_a = concentration of compound in the surrogate solution added to the sample, in micrograms per kilogram; and
V_a = volume of surrogate solution added to the sample, in microliters.

12.2.3.4 Calculate the percent recovery of compounds in set spike sample using

$$R_b = [(C_{sp} \times V_f)/(C_b \times V_b)] \times 100 \quad (4)$$

where

R_b = recovery of fortified compound in the set spike sample, in percent;
C_{sp} = concentration of compound in set spike sample, in micrograms per kilogram, calculated using equations 3 and 4;
V_f = final extract volume, in microliters;
C_b = concentration of compound in individual spike solution added to sample, in micrograms per kilogram; and
V_b = volume of individual spike solution added to the sample, in microliters.

12.3 *Reporting of Results*—The wastewater method requires that results be transmitted to project investigators and data interpreters because it is used in calculating the presence, fate, and transport of compounds in the environment. Therefore, data are reported according to the latest laboratory quality-assurance information (Maloney, 2005; Childress and others, 1999). Alphanumeric data-qualifier codes are used to report information about the presence and concentration of a compound when concentrations are less certain because of matrix effects, interferences, and other unexpected circumstances.

The wastewater sediment method is considered to be "information-rich" (Childress and others, 1999) because compound identifications are determined by mass spectrometry; consequently, results are not censored at the MRL. Compound concentrations, therefore, are reported as follows.

If the concentration is equal to or greater than the MRL, the concentration is reported to three significant figures. If the concentration is less than either the MRL or the lowest calibration standard (usually equivalent to 8.0 µg/kg), results are reported by using the "E" code to indicate that it has been estimated. Other instances where it is appropriate to use the "E" code have been documented (Maloney, 2005; Childress and others, 1999). They include, for example, matrix interferences, method compounds that have been permanently assigned an "E" code, and those compounds that do not meet quality-control criteria, such as being out of calibration by more than ±20 percent. If the result is greater than the highest concentration standard in the calibration curve, then the sample is diluted into the range of the calibration curve and reanalyzed.

Note: MRL data are subject to annual change in conjunction with the NWQL long-term method detection level (LT–MDL) program (Childress and others, 1999).

The attempt to report consistent data near the method detection limit (MDL) is difficult, especially with the intention to transmit as much information as possible in complex samples and also avoid data censoring. Reporting compound results as estimated because their concentrations are less than the MRL need not decrease confidence in qualitative identification. However, there is more uncertainty for concentrations reported near or less than the MDL. If compounds are barely discernible in mass spectra and responses are near or less than the MDL, then the potential for reporting false detections (false positives) or mistakenly reporting compounds as not present (false negatives) increases. In most of these instances, when there is considerable doubt about qualitative identification, reporting conservative results (less than the MRL, analyte undetected) is appropriate.

12.4 *Reporting Units*—Report compound concentrations for field samples in microgram per kilogram dry sediment (µg/kg) using three significant figures. Report surrogate data for each sample as percent recovery. Report data for the set spike as percent recovery. Compounds identified and quantified in the set blank are reported in microgram per kilogram, assuming a 25-g dry-weight sample.

Results and Discussion of Method Validation

Reagent-sand samples and surface-water sediment samples collected from Cherry Creek near Garland Park, Denver, Colo., and soil samples collected from a commercially available topsoil mix, were used to test method performance. One set of the subsamples was fortified at a lower concentration (4 to 72 µg) of each compound, and the other set was fortified at a higher concentration (40 to 720 µg) of each compound. In addition, the three sample matrices were extracted and analyzed (unfortified) to determine the ambient concentrations of any method compounds (table 4). The average concentration of selected compounds found in the reagent-sand blank samples processed with each sample set is listed in table 4. The presence of 16 compounds in the reagent-sand sample blank at or near detectable concentrations reemphasizes the ubiquitous presence of about half of the method compounds, as well as the importance of avoiding contamination throughout sample collection, preparation, and analysis.

Fortified samples were extracted and analyzed on different days, so comparisons of different matrices and concentrations include day-to-day variation. Mean bias and precision data from the analyses are listed in table 5. Recovery was corrected for concentration of compounds found in the unfortified matrices. The matrix samples were fortified (after loading into ASE extraction cells) with a known concentration (in micrograms), and percent recoveries were calculated. Average recovery of all method compounds for short-term single-operator results in reagent-sand samples fortified at 4 to72 µg was 76 ± 13 percent relative standard deviation. Initial method detection limits for single-component compounds ranged from 12.5 to 852 µg/kg. Because environmental sediment and soil samples contained rock, twigs, plant and animal materials, even with sample mixing, exact matrix duplicates (by weight) were difficult to obtain. The sample concentrations were not converted to micrograms per kilogram because of the potential variability in loading these variable samples into the ASE extraction cells.

The concentration of 20 compounds will be reported as estimated with the "E" remark code for one of three reasons: (1) unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25 percent RSD), (2) reference standards prepared from technical mixtures, or (3) potential blank contamination. Initial MDLs were calculated for compounds in reagent sand by using the corresponding spike concentration as listed in table 5.

Table 6 lists the compounds (Zaugg and others, 2002) that were investigated in the development of this method but were excluded because of high (>120 percent) or low (<30 percent) recovery, or relative standard deviations greater than 30 percent.

Table 4. Wastewater method compounds detected in unfortified reagent-sand, river-sediment, and topsoil samples.

[µg/kg, micrograms per kilogram; < MRL, less than minimum reporting level; *n*, number of samples; *, detected but average less than 1.0 µg/kg]

Compound name	Average concentration (µg/kg)		
	Sand *n* = 14	River sediment *n* = 3	Topsoil *n* = 3
1,4-Dichlorobenzene	< MRL	< MRL	< MRL
1-Methylnaphthalene	< MRL	< MRL	< MRL
2,6-Dimethylnaphthalene	<1*	< MRL	< MRL
2-Methylnaphthalene	< MRL	< MRL	< MRL
3-*beta*-Coprostanol	< MRL	< MRL	< MRL
3-Methyl-1H-indole (skatol)	< MRL	40.0	< MRL
3-*tert*-Butyl-4-hydroxyanisole (BHA)	< MRL	< MRL	< MRL
3,4-Dichlorophenyl isocyanate	< MRL	< MRL	< MRL
4-Cumylphenol	< MRL	< MRL	< MRL
4-*n*-Octylphenol	< MRL	< MRL	< MRL
4-*tert*-Octylphenol	< MRL	< MRL	< MRL
Acetophenone	< MRL	24.8	< MRL
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	< MRL	< MRL	< MRL
Anthracene	<1*	< MRL	< MRL
Anthraquinone	< MRL	< MRL	< MRL
Atrazine	< MRL	< MRL	< MRL
Benzo[*a*]pyrene	< MRL	31.7	< MRL
Benzophenone	2.1	< MRL	100
beta-Sitosterol	< MRL	367	4,440
beta-Stigmastanol	< MRL	224	1,380
Bisphenol A	< MRL	< MRL	< MRL
Bromacil	< MRL	< MRL	< MRL
Camphor	< MRL	< MRL	< MRL
Carbazole	< MRL	< MRL	< MRL
Chlorpyrifos	< MRL	< MRL	< MRL
Cholesterol	35	384	800
Diazinon	< MRL	< MRL	< MRL
Diethyl phthalate	8.4	< MRL	< MRL
Diethylhexyl phthalate	160	102	410
d-Limonene	< MRL	< MRL	< MRL
Fluoranthene	<1*	122	< MRL
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	< MRL	< MRL	< MRL
Indole	<1*	35.2	< MRL
Isoborneol	< MRL	< MRL	< MRL
Isophorone	1.7	< MRL	< MRL
Isopropylbenzene (cumene)	< MRL	< MRL	< MRL
Isoquinoline	< MRL	< MRL	< MRL
Menthol	1.4	< MRL	< MRL
Metalaxyl	< MRL	< MRL	< MRL

Table 4. Wastewater method compounds detected in unfortified reagent-sand, river-sediment, and topsoil samples.—Continued

[µg/kg, micrograms per kilogram; < MRL, less than minimum reporting level; *n*, number of samples; *, detected but average less than 1.0 µg/kg]

Compound name	Average concentration (µg/kg)		
	Sand *n* = 14	River sediment *n* = 3	Topsoil *n* = 3
Menthol	1.4	< MRL	< MRL
Metalaxyl	< MRL	< MRL	< MRL
Methyl salicylate	< MRL	< MRL	< MRL
Metolachlor	< MRL	< MRL	< MRL
N,N-Diethyl-*meta*-toluamide (Deet)	< MRL	< MRL	< MRL
Naphthalene	<1*	< MRL	< MRL
Nonylphenol, diethoxy- (total, NPEO2)	< MRL	225	< MRL
Nonylphenol, monoethoxy-(total, NPEO1)	< MRL	< MRL	200
Octylphenol, diethoxy- (OPEO2)	< MRL	< MRL	< MRL
Octylphenol, monoethoxy- (OPEO1)	9.0	< MRL	< MRL
para-Cresol	<1*	59.4	100
para-Nonylphenol (total)	< MRL	< MRL	< MRL
Pentachlorophenol	< MRL	< MRL	< MRL
Phenanthrene	<1*	74.7	< MRL
Phenol	8.2	40.6	270
Prometon	< MRL	< MRL	< MRL
Pyrene	< MRL	76.6	< MRL
Tetrabromodiphenyl ether	< MRL	< MRL	< MRL
Tri(2-butoxyethyl) phosphate	< MRL	< MRL	< MRL
Tri(2-chloroethyl) phosphate	<1*	< MRL	< MRL
Tri(dichloroisopropyl) phosphate	< MRL	< MRL	< MRL
Tributyl phosphate	< MRL	< MRL	< MRL
Triclosan	< MRL	< MRL	< MRL
Triphenyl phosphate	< MRL	< MRL	< MRL

Table 5. Wastewater method mean bias and precision of spike recovery data for seven or eight replicates with compounds spiked at two concentrations ranging from 4 to 720 micrograms per sample in reagent-sand (including calculated method detection limits), river-sediment, and topsoil samples.

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

Compound name	Spike amount (µg)	Mean recovery (percent)			RSD (percent)			Initial MDL (µg/kg)
		Sand	River sediment	Topsoil	Sand	River sediment	Topsoil	
1,4-Dichlorobenzene	4.0	70.1	45.4	67.2	7.02	14.0	4.97	27.6
	40	64.6	51.6	64.4	8.60	16.9	10.8	
1-Methylnaphthalene	4.0	76.7	77.5	77.2	6.48	13.5	3.78	27.8
	40	78.5	78.1	82.6	5.18	8.26	1.04	
2,6-Dimethylnaphthalene	4.0	75.7	77.0	75.6	5.86	12.1	4.82	24.8
	40	78.5	77.4	82.3	4.55	7.87	1.70	
2-Methylnaphthalene	4.0	76.7	77.5	77.2	6.48	13.5	3.78	27.8
	40	78.5	78.1	82.6	5.18	8.26	1.04	
3,4-Dichlorophenyl isocyanate[1]	4.0	43.3	36.3	36.4	24.9	18.0	28.0	60.4
	40	24.9	26.1	31.8	74.3	26.7	28.8	
3 *beta*-Coprostanol	16	105.7	73.18	93.1	15.2	31.7	23.4	359.7
	160	92.6	77.3	70.2	14.6	12.8	8.27	
3-Methyl-1H-indole (skatol)	4.0	83.1	99.9	78.9	6.65	11.9	8.41	30.9
	40	84.7	106.6	80.2	2.54	10.6	4.01	
3-*tert*-Butyl-4-hydroxyanisole (BHA)1	4.0	79.0	40.6	93.6	22.9	26.9	8.52	101
	40	66.0	38.1	80.5	17.7	45.5	9.54	
4-Cumylphenol	4.0	85.9	79.6	84.0	7.01	10.6	4.80	33.7
	40	92.9	96.5	92.0	4.80	4.69	6.81	
4-*n*-Octylphenol	4.0	82.3	77.1	82.5	7.97	10.1	5.24	36.8
	40	89.3	90.5	88.5	5.22	6.34	9.79	
4-*tert*-Octylphenol	4.0	85.3	82.9	86.7	4.79	10.5	5.08	22.9
	40	87.4	88.5	89.0	3.06	4.73	2.59	
Acetophenone[1]	4.0	45.0	26.7	28.9	40.0	49.5	67.5	101
	40	53.6	42.2	39.6	13.7	9.35	7.79	
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	4.0	76.8	76.6	78.4	3.84	14.2	6.30	16.5
	40	82.7	78.2	82.2	4.02	6.32	7.75	
Anthracene	4.0	78.1	80.3	75.7	4.54	10.9	7.06	19.8
	40	84.2	83.1	79.4	2.88	5.16	2.18	
Anthraquinone	4.0	84.3	87.0	84.3	5.15	6.22	4.73	24.3
	40	84.4	74.7	85.6	2.72	39.5	2.45	
Atrazine	4.0	78.7	70.0	66.0	13.4	16.9	15.4	58.9
	40	99.7	92.1	86.6	4.97	7.10	6.93	
Benzo[*a*]pyrene	4.0	77.8	84.7	75.8	5.64	22.2	7.05	24.6
	40	81.7	79.2	76.9	3.82	5.22	9.47	
Benzophenone	4.0	88.8	87.9	96.1*	6.4	7.75	5.51	31.8
	40	87.5	86.4	95.8*	0.92	3.83	2.98	

Table 5. Wastewater method mean bias and precision of spike recovery data for seven or eight replicates with compounds spiked at two concentrations ranging from 4 to 720 micrograms per sample in reagent-sand (including calculated method detection limits), river-sediment, and topsoil samples.—Continued

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

Compound name	Spike amount (µg)	Mean recovery (percent)			RSD (percent)			Initial MDL (µg/kg)
		Sand	River sediment	Topsoil	Sand	River sediment	Topsoil	
beta-Sitosterol	16.0	97.4	123	101*	16.7	25.7	28.6	363
	160	82.1	66.8	83.8	10.9	12.9	12.1	
beta-Stigmastanol	16.0	96.1	73.2	92.8	17.1	27.2	31.4	367
	160	79.8	63.8	72.2	9.73	9.41	9.10	
Bisphenol A[1]	4.0	64.5	53.2	58.0	8.75	18.1	15.6	31.6
	40	53.5	44.4	59.6	13.5	5.64	7.99	
Bromacil[1]	14.0	62.8	43.9	48.9	20.7	36.0	39.8	254
	140	78.3	63.6	52.7	5.13	8.07	11.1	
Camphor	4.0	79.1	70.6	67.6	6.09	12.8	17.1	27.0
	40	87.3	84.6	84.4	1.90	5.87	6.47	
Carbazole	4.0	82.9	82.0	79.7	4.83	7.51	4.79	22.4
	40	93.2	91.5	91.4	1.34	4.02	4.12	
Chlorpyrifos	4.0	60.4	62.2	68.3	9.92	29.1	18.9	33.6
	40	92.0	92.3	86.4	7.58	5.67	5.42	
Cholesterol	16.0	99.3	125	92.4	7.57	19.2	16.9	168
	160	92.3	77.3	70.2	14.6	19.1	12.1	
Diazinon	4.0	75.8	75.5	76.0	11.5	28.2	13.1	48.7
	40	76.9	70.8	80.2	5.02	10.4	4.47	
Diethyl phthalate[3]	4.0	58.2	58.3	61.0	14.3	5.73	7.86	46.7
	40	70.3	74.8	82.6	5.58	9.13	9.8	
Diethylhexyl phthalate[3]	4.0	153	147	129	16.1	25.2	20.6	138
	40	82.9	75.4	58.2	11.2	13.0	5.52	
d-Limonene[1]	4.0	65.7	29.0	64.2	6.45	20.6	5.09	23.7
	40	65.1	48.0	64.8	10.5	21.3	12.1	
Fluoranthene	4.0	81.0	102	82.0	5.11	38.0	4.23	23.2
	40	84.7	85.1	85.6	2.80	5.33	3.23	
Hexahydrohexamethyl-cyclo-pentabenzopyran (HHCB)	4.0	78.0	79.0	80.4	2.86	10.0	6.14	12.5
	40	83.7	77.4	83.6	3.85	6.11	5.3	
Indole	4.0	82.0	89.4	74.6	11.7	18.0	19.5	
	40	83.3	71.8	65.0	3.35	6.94	19.4	
Isoborneol	4.0	86.5	78.8	85.0	8.11	20.3	9.02	39.3
	40	86.9	76.2	87.6	5.14	8.80	2.74	
Isophorone[1]	4.0	12.1	4.53	5.47	64.1	45.9	56.8	43.4
	40	46.3	33.0	32.8	12.3	11.9	20.2	
Isopropylbenzene (cumene)[1]	4.0	54.4	15.1	52.8	28.4	41.0	10.5	86.6
	40	61.0	37.1	59.1	9.56	28.8	15.0	

Table 5. Wastewater method mean bias and precision of spike recovery data for seven or eight replicates with compounds spiked at two concentrations ranging from 4 to 720 micrograms per sample in reagent-sand (including calculated method detection limits), river-sediment, and topsoil samples.—Continued

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

Compound name	Spike amount (µg)	Mean recovery (percent)			RSD (percent)			Initial MDL (µg/kg)
		Sand	River sediment	Topsoil	Sand	River sediment	Topsoil	
Isoquinoline[1]	4.0	59.5	46.3	37.3	25.0	31.8	50.0	83.1
	40	65.6	49.7	42.8	11.2	15.1	4.59	
Menthol	4.0	88.4	84.2	82.9	8.50	12.8	18.0	42.0
	40	86.9	70.8	94.2	16.3	9.83	12.9	
Metalaxy[1]	4.0	57.7	37.6	41.3	20.7	43.4	61.8	53.4
	40	79.7	53.2	53.6	5.85	24.0	16.1	
Methyl salicylate[1]	4.0	13.4	12.3	35.4	47.7	156	77.9	35.8
	40	22.7	14.4	46.4	42.7	51.9	36.9	
Metolachlor	4.0	83.9	85.7	81.2	7.91	10.5	4.84	37.2
	40	92.0	92.3	86.4	7.58	5.67	5.42	
N,N-Diethyl-*meta*-toluamide (Deet)[1]	4.0	76.3	58.7	56.7	13.2	27.5	35.8	56.2
	40	75.5	62.4	58.0	10.2	14.1	7.54	
Naphthalene	4.0	75.7	71.2	76.6	5.55	8.35	3.36	23.5
	40	78.9	73.6	81.6	3.66	11.2	3.28	
Nonylphenol, diethoxy- (total, NPEO2)[2]	64	106	106	113	8.93	20.6	6.83	852
	640	98.6	93.6	99.4	2.90	4.04	6.37	
Nonylphenol, monoethoxy- (total,NPEO1)[2]	32	93.7	90.6	96.2	8.01	20.8	4.79	336
	320	93.1	89.2	93.8	3.47	6.64	7.15	
Octylphenol, diethoxy- (OPEO2)[2]	2.8	103	98.3	109	9.55	24.3	8.58	38.5
	28	99.1	94.2	98.4	1.36	3.22	1.90	
Octylphenol, monoethoxy- (OPEO1)[2]	28	86.6	83.9	85.3	6.45	17.0	6.34	219
	280	92.3	93.3	91.4	3.28	5.48	5.25	
para-Cresol	4.0	85.48	124	76.9	33.6	45.0	11.2	161
	40	74.2	115	67.6	5.09	14.9	5.12	
para-Nonylphenol (total)[2]	72	79.4	79.9	83.7	6.23	11.5	10.2	499
	720	86.5	86.0	86.3	7.43	5.47	7.21	
Pentachlorophenol[1]	16	52.7	445.2	54.2	44.1	35.1	19.8	520
	160	35.2	40.3	40.5	28.0	24.3	26.4	
Phenanthrene	4.0	78.2	84.9	80.8	4.72	9.98	3.87	20.7
	40	85.4	86.0	88.0	2.60	5.10	2.20	
Phenol[1]	4.0	20.9	20.8	87.5	32.8	37.8	76.4	38.2
	40	41.9	47.0	39.8	16.3	6.2	13.3	
Prometon	4.0	74.7	79.9	66.6	10.6	16.9	10.7	44.2
	40	88.6	74.4	73.3	5.12	10.2	6.67	
Pyrene	4.0	73.3	91.6	73.2	5.01	36.9	7.22	20.6
	40	82.7	80.9	83.2	2.14	5.62	3.10	

Table 5. Wastewater method mean bias and precision of spike recovery data for seven or eight replicates with compounds spiked at two concentrations ranging from 4 to 720 micrograms per sample in reagent-sand (including calculated method detection limits), river-sediment, and topsoil samples.—Continued

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

Compound name	Spike amount (µg)	Mean recovery (percent)			RSD (percent)			Initial MDL (µg/kg)
		Sand	River sediment	Topsoil	Sand	River sediment	Topsoil	
Tetrabromodiphenyl ether	4.0	79.6	79.0	83.5	4.29	9.88	6.60	19.1
	40	84.4	87.6	67.0	5.80	8.81	19.3	
Tri(2-butoxyethyl) phosphate	4.0	101	97.7	102	17.5	32.6	9.15	98.5
	40	87.9	87.8	89.3	2.35	3.74	1.01	
Tri(2-chloroethyl) phosphate[1]	4.0	49.4	39.3	39.3	25.4	20.8	59.7	70.3
	40	66.7	48.0	39.8	13.0	16.6	9.36	
Tri(dichloroisopropyl) phosphate[1]	4.0	47.0	48.1	66.6	27.8	22.3	30.6	73.0
	40	46.3	49.8	63.9	24.1	18.1	21.8	
Tributyl phosphate	4.0	86.5	84.7	85.7	8.10	18.3	7.02	39.6
	40	86.9	91.0	87.9	3.59	4.11	4.50	
Triclosan	4.0	82.9	70.9	86.6	10.7	12.2	13.1	49.6
	40	82.4	74.8	85.3	6.42	3.55	3.07	
Triphenyl phosphate[1]	4.0	47.8	47.9	61.4	17.2	29.3	29.0	46.0
	40	49.0	49.0	64.6	18.4	16.5	16.1	
Surrogate Compounds								
Fluoranthene-d_{10}	8	83.4	92.5	85.0	4.42	6.00	3.80	
	8	84.1	74.6	81.6	11.4	21.4	6.19	
Bisphenol A-d_3	8	68.2	70.5	64.1	9.36	12.0	18.9	
	8	56.8	44.1	60.7	7.43	9.71	6.67	
Decafluorobipheny[1]	8	56.7	55.2	62.5	12.3	11.6	14.1	
	8	65.7	44.8	66.6	11.7	9.78	11.4	

[1]Concentration is estimated because recovery is less than 60 percent or precision is greater than 25 percent RSD. This can be caused by instrumental or extraction difficulties.

[2]Concentration is estimated because the reference standard is from a technical mixture.

[3]Concentration is estimated because of potential blank contamination unless concentration is greater than 10 times the 95th percentile of all blank concentrations.

[*]Percent recovery corrected for background concentration in the unfortified sample.

Table 6. Wastewater method compounds that failed method acceptance criteria and are not included in this method. Mean bias and precision of spike recovery data for seven or eight replicates with compounds fortified at two concentrations ranging from 4 to 720 micrograms per sample in reagent-sand, river-sediment, and topsoil samples.

[µg, micrograms; RSD, relative standard deviation]

Compound name	Spike amount (µg)	Mean recovery (percent)			RSD (percent)		
		Sand	River sediment	Topsoil	Sand	River sediment	Topsoil
5-Methyl-1H-benzotriazole	16	11.2	4.50	8.01	98.1	67.4	98.1
	160	8.80	8.01	5.76	10.3	12.8	16.4
Caffeine	4.0	0	0	0	0	0	0
	40	0	0	0	0	0	0
Caffeine-$^{13}C_3$	8.0	0	0	0	0	0	0
	8.0	0	0	0	0	0	0
Cotinine	4.0	0	0	0	0	0	0
	40	0	0	0	0	0	0
Triethyl citrate (ethyl citrate)	4.0	0	0	0	0	0	0
	40	0	0	0	0	0	0
Carbaryl	4.0	4.98	8.23	25.7	106	89.1	186
	40	0.10	4.07	28.5	264	142	64.0
Dichlorvos	4.0	0	0	0	0	0	0
	40	5.83	5.36	11.9	66.7	71.3	50.1

Method detection limits (MDLs) and minimum reporting levels (MRLs)—The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the compound concentration is greater than zero (U.S. Environmental Protection Agency, 1997). Initial MDLs were determined according to the procedure outlined by the U.S. Environmental Protection Agency (1997), assuming a 25-g sample size.

The MDL was calculated according to the equation

$$MDL = S \times t_{(n-1,\ 1-\alpha = 0.99)} \quad (5)$$

where

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

n = number of replicate analyses; and

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

According to the USEPA procedure, at least seven replicate samples are fortified with compounds at concentrations of two to five times the estimated MDL. This concentration range was used to calculate initial MDLs for most of the compounds. However, initial MDLs for some method compounds were calculated by using concentrations higher than the desired spiking level so that the compound would be detected in each of the replicate reagent-sand samples. Initial MDLs that were calculated from this procedure for single-component compounds ranged from 12.5 to 852 µg/kg.

The initial minimum reporting levels (MRLs) have been set higher than the calculated initial MDLs (table 7). This precaution reduces the risk of reporting false positives in complex, varying matrices. All qualitatively identified compounds detected less than the MRL are reported as estimated with the "E" remark code, regardless of the established MRL, because the wastewater method is classified as an "information-rich" method, as are other MS methods (Childress and others, 1999).

Calculation of the MDL with data over a long time (6 to 12 months), including results from a sufficient number (n >30) of samples to reflect multiple instruments, analysts, and calibration curves, is referred to as a long-term method detection level (LT–MDL or operational MDL) (Childress and others, 1999). The spiking solution at a concentration of 4 µg (in reagent sand) will be used routinely throughout the year to calculate LT–MDLs for the wastewater method. The initial MDLs and initial MRLs will be updated annually by using data acquired from the NWQL (Childress and others, 1999).

*Reconnaissance Stu*dy—Figure 2 shows the results from a small reconnaissance study of 103 sediment and soil samples collected during 2003 throughout the United States. The samples are a mixture of river sediments and soils, the majority from urban sampling sites. The number of detections is listed

Table 7. Initial method detection limits for the wastewater method calculated from the precision data reported in table 5 using the eight replicate reagent-sand samples fortified with compound concentrations ranging from 4 to 72 micrograms.

[µg, micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; MDL, method detection limit; MRL, minimum reporting level; "E" Coded, remark placed on compounds for recovery greater than 120 percent or less than 30 percent or RSD greater than 25 percent]

Compound name	Spike amount (µg)	Mean recovery (percent)	RSD (percent)	Initial MDL (µg/kg)	Initial MRL (µg/kg)
1,4-Dichlorobenzene	4	70.1	7.0	27.6	50
1-Methylnaphthalene	4	76.7	6.5	27.8	50
2,6-Dimethylnaphthalene	4	75.7	5.9	24.8	50
2-Methylnaphthalene	4	76.7	6.5	27.8	50
3-*beta*-Coprostanol	16	106	15.2	360	500
3-Methyl-1H-indole (skatol)	4	83.1	6.7	30.9	50
3-*tert*-Butyl-4-hydroxyanisole (BHA)	4	79.0	22.9	101	100
4-Cumylphenol	4	85.9	7.0	33.7	50
4-*n*-Octylphenol	4	82.3	7.8	36.8	50
4-*tert*-Octylphenol	4	85.3	4.8	22.9	50
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	4	76.8	3.8	16.5	50
Anthracene	4	78.1	4.5	19.8	50
Anthraquinone	4	84.3	5.2	24.3	50
Atrazine	4	74.7	13.7	58.9	100
Benzo[*a*]pyrene	4	77.8	5.6	24.6	50
Benzophenone	4	88.8	6.4	31.8	50
beta-Sitosterol	16	97.4	16.7	363	500
beta-Stigmastanol	16	96.1	17.1	367	500
Camphor	4	79.1	6.1	27.0	50
Carbazole	4	82.9	4.8	22.4	50
Chlorpyrifos	4	60.4	9.9	33.6	50
Cholesterol	16	99.3	7.6	168	250
Diazinon	4	75.8	11.5	48.6	50
Diethyl phthalate	4	58.2	14.3	46.7	100
Diethylhexyl phthalate	4	153	16.1	138	250
Fluoranthene	4	81.0	5.1	23.2	50
Hexahydrohexamethyl-cyclo-pentabenzo-pyran (HHCB)	4	78.0	2.9	12.5	50
Indole	4	82.0	11.7	53.5	50
Isoborneol	4	86.5	8.1	39.3	50
Menthol	4	88.4	8.5	42.0	50
Metalaxyl	4	57.7	16.5	53.4	50
Metolachlor	4	83.9	7.9	37.2	50
Naphthalene	4	75.7	5.6	23.5	50
para-Cresol	4	85.5	33.6	161	250
Phenanthrene	4	78.2	4.7	20.7	50
Prometon	4	74.7	10.6	44.2	50

Table 7. Initial method detection limits for the wastewater method calculated from the precision data reported in table 5 using the eight replicate reagent-sand samples fortified with compound concentrations ranging from 4 to 72 micrograms.—Continued

[µg, micrograms; µg/kg, micrograms per kilogram; RSD, relative standard deviation; MDL, method detection limit; MRL, minimum reporting level; "E" Coded, remark placed on compounds for recovery greater than 120 percent or less than 30 percent or RSD greater than 25 percent]

Compound name	Spike amount (µg)	Mean recovery (percent)	RSD (percent)	Initial MDL (µg/kg)	Initial MRL (µg/kg)
Pyrene	4	73.3	5.0	20.6	50
Tetrabromodiphenyl ether	4	79.6	4.3	19.1	50
Tri(2-butoxyethyl) phosphate	4	101	17.5	98.5	100
Tributyl phosphate	4	86.5	8.1	39.3	50
Triclosan	4	82.9	10.7	49.6	50
"E" Coded Compounds					
3,4-Dichlorophenyl isocyanate	4	43.3	24.9	60.4	100
Acetophenone	4	45.0	40.0	100	100
Bisphenol A	4	64.5	8.8	31.2	50
Bromacil	16	62.8	20.7	254	500
d-Limonene	4	65.7	6.5	23.7	50
Isophorone	4	12.1	64.1	43.4	50
Isopropylbenzene (cumene)	4	54.4	28.4	86.6	100
Isoquinoline	4	59.5	25.0	83.1	100
Methyl salicylate	4	13.4	47.7	35.8	50
Nonylphenol, diethoxy- (total, NPEO2)	64	106	8.9	852	1,000
Nonylphenol, monoethoxy- (total, NPEO1)	32	93.7	8.0	336	500
Octylphenol, diethoxy-(OPEO2)	28	103	9.6	38.5	50
Octylphenol, monoethoxy-(OPEO1)	28	86.6	6.5	219	250
N,N-Diethyl-meta-toluamide(Deet)	4	76.3	13.2	56.2	50
para-Nonylphenol (total)	72	79.4	6.2	498	500
Pentachlorophenol	16	52.7	44.1	520	500
Phenol	4	20.9	32.8	38.3	50
Tri(2-chloroethyl) phosphate	4	49.4	25.4	70.3	100
Tri(dichloroisopropyl) phosphate	4	47.0	27.8	73.0	100
Triphenyl phosphate	4	47.8	17.2	46.0	50

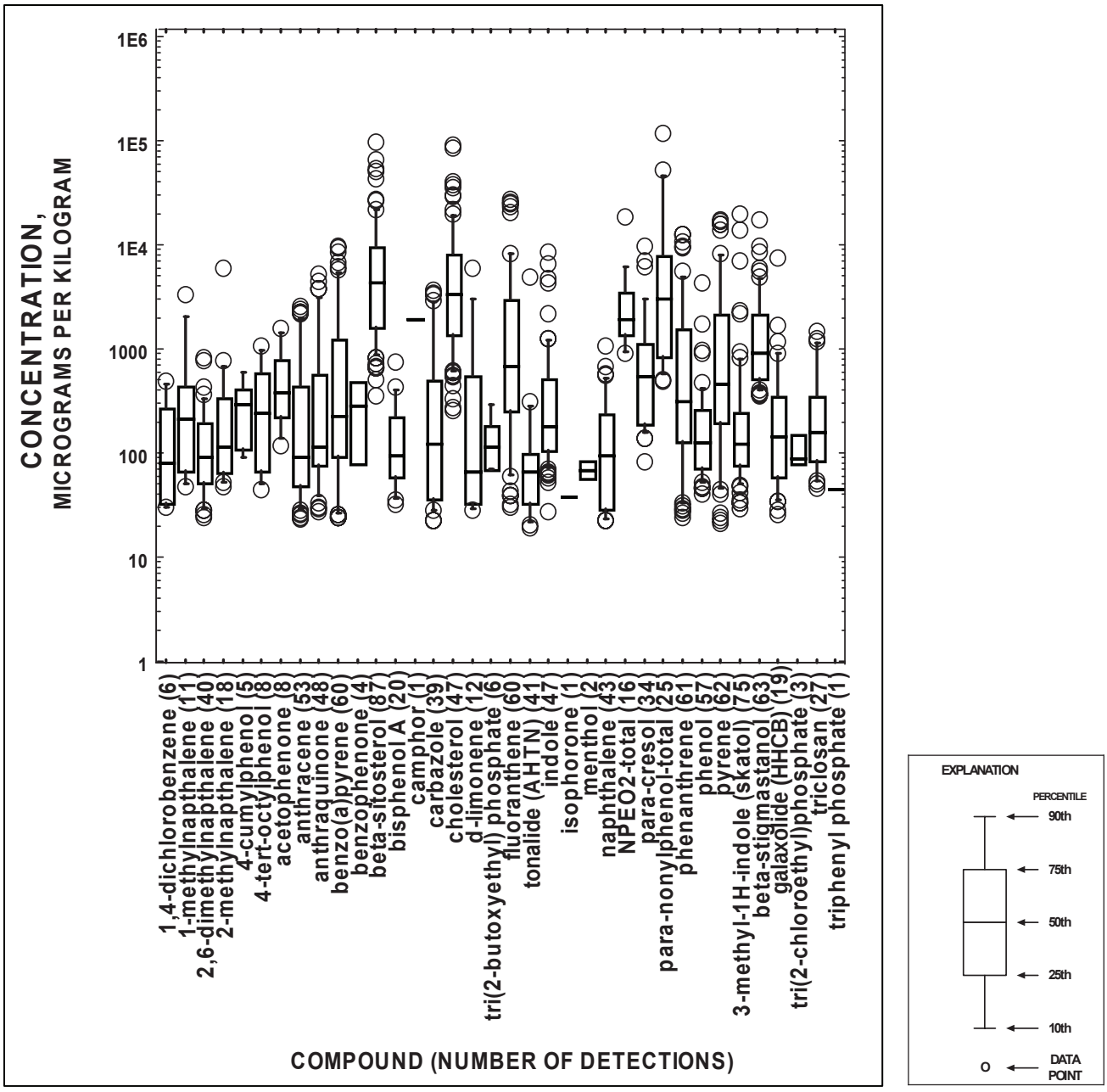

Figure 2. Analysis of 103 environmental sediment and soil samples. The concentration axis is in log scale to accommodate the large concentration ranges for the compounds of interest. The number of compound detections is listed after each compound name.

after the compound name. The data are reported using a log scale to accommodate the large concentration ranges for each compound. The results (concentration ranges and detection frequencies) demonstrate the ability of the described method to determine the compound classes of interest in various sediment and soil types.

One or more of the compounds in the method were found in 90 percent of the samples. This high frequency is caused, in part, by samples being collected primarily in urban environments. In addition, some of the compounds have natural sources, such as the plant sterols *beta*-sitosterol and *beta*-stigmastanol. The results presented are not necessarily representative of all sediments in the United States, but they do demonstrate the ability of the described method to measure concentrations of compounds of interest in environmental sediment and soil samples.

Thirty-six of 61 compounds of interest were detected in at least one environmental sample. The 36 must frequently detected compounds represent a wide variety of chemical classes and uses. Figure 2 shows the number of detections and the concentration ranges for the compounds of interest. Again, naturally present compounds as well as anthropogenic-sourced compounds are represented. Many of the detected compounds are recognized endocrine disruptors (alkylphenols, alkylphenols polyethoxlates, bisphenol A), whereas others, such as the fragrances, flame retardants, and fecal steroids, are excellent indicators of wastewater.

Summary and Conclusions

The U.S. Geological Survey (USGS) National Water Quality Laboratory has developed an analytical method for the determination of 61 compounds in environmental sediment and soil samples. This method provides an efficient means of detecting important toxic and estrogenic compounds that otherwise might not be reported because they are unregulated or not included in other USGS or U.S. Environmental Protection Agency methods. Sediment samples are collected and the compounds of interest are isolated by pressurized solvent extraction, solid-phase isolation, and are determined by capillary-column gas chromatography/mass spectrometry (GC/MS). The method focuses on the determination of compounds indicative of wastewater. The compounds were chosen on the basis of potential toxicity or endocrine disruption. Analysis of the alkylphenol ethoxylate nonionic surfactant compounds is particularly important because they are persistent indicators of wastewater. Other method compounds are representative of fragrances, food additives, antioxidants, phosphate flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, polycyclic aromatic hydrocarbons, and high-use domestic pesticides.

Average recovery of all method compounds for short-term single-operator results from reagent-sand samples fortified at 4 to72 micrograms was 76 ±13 percent relative standard deviation. Initial method detection limits for single-component compounds ranged from 12.5 to 852 micrograms per kilogram.

There are advantages for the analytical laboratory as well as the data user by adopting this new method. For the laboratory, (1) short overall sample-extraction times and (2) the use of less organic solvent than for previous methods will reduce cost and work-place exposure. Data users, on the other hand, (3) will gain clean sample extracts, allowing for improved method detection limits; (4) will be able to monitor several classes of compounds with varied endocrine-disruption potential; and (5) will benefit from demonstrated low bias and high precision.

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Glossary

Continuing calibration verification (CCV)

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

Internal standard (IS)

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

Long-term method detection level (LT–MDL)

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

Method detection limit (MDL)

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

Minimum reporting level (MRL)

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

Surrogate

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

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