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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Wastewater Compounds by Polystyrene-Divinylbenzene Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry

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Water-Resources Investigations Report 01-4186

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

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CONTENTS

FIGURES

TABLES

CONVERSION FACTORS

Multiply	By	To obtain
	Length	
centimeter (cm)	3.94×10^{-1}	inch
micrometer (µm)	3.94×10^{-5}	inch
millimeter (mm)	3.94×10^{-2}	inch
meter (m)	3.94×10^{-1}	inch
	Mass	
gram (g)	3.53×10^{-2}	ounce, avoirdupois
kilogram (kg)	3.53×10^{-1}	ounce, avoirdupois
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter per minute (mL/min)	3.38×10^{-2}	ounce per minute
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
	Volume	
liter (L)	2.64×10^{-1}	gallon
microliter (µL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon

Degree Celsius (^{o}C) may be converted to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F = 9/5\ (^{o}C) + 32.$$

ACRONYMS AND ABBREVIATIONS

in.	inch
min	minute
mg/kg	milligram per kilogram
mg/mL	milligram per milliliter
µg/L	microgram per liter
ng/µL	nanogram per microliter
AHTM	acetyl-hexamethyl-tetrahydronaphthalene
AP	alkylphenol
APEC	alkylphenol ethoxycarboxylate
APEO	alkylphenol polyethoxylate
CAS	Chemical Abstracts Service
CCV	continuing calibration verification solution
DCM	dichloromethane
CLLE	continuous liquid-liquid extraction
EE	diethyl ether
ETFE	ethylenetetrafluoroethylene
GC	gas chromatograph
GCC	glass bottle, amber
GC/MS	gas chromatography/mass spectrometry

HHCB	hexahydrohexamethyl-cyclopentabenzopyran
K-D	Kuderna-Danish
LT–MDL	long-term method detection level
MDL	method detection limit
MRL	minimum reporting level
MS	mass spectrometry
m/z	mass-to-charge ratio
N-Evap	nitrogen evaporative concentrator
NP	nonylphenol
NPEO	nonylphenol ethoxylate
NWQL	National Water Quality Laboratory
N/A	not applicable
OPEO	octylphenol ethoxylate
PAH	polycyclicaromatic hydrocarbon
PCB	polychlorinated biphenyl
PSDVB	polystyrene-divinylbenzene
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

GLOSSARY

Continuing calibration verification – The continuing calibration verification (CCV) is a calibration standard that 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 variability 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 variability and establish more realistic minimum reporting levels.

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

Procedural internal standard quantitation – A quantitation method where the internal standard is added during sample processing prior to transferring the sample extract to a vial. The addition of the procedural internal standard during sample processing compensates for quantitation losses in those processing steps after the internal standard is added.

Surrogate – A compound not expected to be found in any environmental sample, which 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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Abstract

A method for the determination of 67 compounds typically found in domestic and industrial wastewater is described. The method was developed in response to increasing concern over the impact of endocrine-disrupting chemicals in wastewater on aquatic organisms. This method also may be useful for evaluating the impact of combined sanitary and storm-sewer overflow on the water quality of urban streams. The method focuses on the determination of compounds that are an indicator of wastewater or that have been 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, polycyclicaromatic hydrocarbons, and high-use domestic pesticides.

Water samples are filtered to remove suspended particulate matter and then are extracted by vacuum through disposable solid-phase cartridges that contain polystyrene-divinylbenzene resin. Cartridges are dried with nitrogen gas, and then sorbed compounds are eluted with dichloromethane-diethyl ether (4:1) and determined by capillary-column gas chromatography/mass spectrometry. Recoveries in reagent-water samples fortified at 4 micrograms per liter averaged 74 percent ± 7 percent relative standard deviation for all method compounds. Initial method detection limits for single-component compounds (excluding hormones and sterols) averaged 0.15 microgram per liter. Samples are preserved by filtration, the addition of 60 grams NaCl, and storage at 4 degrees Celsius. The laboratory has established a sample-holding time (prior to sample extraction) of 14 days from the date of sample collection until a statistically accepted method can be used to determine the effectiveness of these sample-preservation procedures.

INTRODUCTION

Industrial and domestic waste must be managed effectively to meet the challenges of increasing population, stringent regulatory requirements, and aging wastewater-treatment facilities in the United States. Specific analytical methods are available to monitor chemical compounds in wastewater to meet these challenges. Many compounds are regulated by the U.S. Environmental Protection Agency (USEPA), 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 matrix, 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 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) and National Research Program have developed an analytical method that uses representative compounds from various chemical classes to monitor unregulated and regulated contaminants.

Traditional methods for determining organic compounds in natural-water samples generally are optimized for one or two classes of compounds and use liquid-liquid extraction with an organic solvent followed by analysis with gas chromatography (GC) and nitrogen-phosphorus, electron-capture, or mass spectrometry (MS) detection. Analytical methods that use solid-phase extraction (SPE) as an alternative to liquid-liquid extraction have been implemented at the NWQL for the determination of pesticides in water (Lindley and others, 1996; Werner and others, 1996; Furlong and others, 2001; Sandstrom and others, 1992 and 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.

This report describes a method for determining a broad range of wastewater compounds in filtered natural-water samples. It is rapid and efficient compared to older USGS methods (Wershaw and others, 1987) and was developed potentially to replace or augment separatory-funnel or continuous liquid-liquid extraction (CLLE) 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) and by Fishman (1993). A prototype wastewater method that uses CLLE instead of SPE for sample preparation was implemented at the NWQL in October 1998 on a custom basis (Brown and others, 1999). A comparison of results for over 30 environmental samples between the CLLE and the SPE methods demonstrated, as expected, that concentrations for hydrophobic (low-water solubility) compounds were much less (up to 400 percent) when determined by SPE because of sample filtration, whereas results for hydrophilic compounds were identical. Application of this SPE method will provide data for dissolved wastewater compounds to supplement available whole-water CLLE data used to identify urban sanitary-sewer and storm-sewer problems (Wilkison and others, 2000), as well as emerging contaminants in concentrated animal feedlot runoff for the USGS's Toxic Substances Hydrology Program. This new SPE method has been used at the NWQL as a conditional method since January 1, 2001. It officially was approved and implemented at the NWQL on June 27, 2001.

This report provides a detailed description of all aspects of the method, including the equipment, reagents, sampling protocol, instrument calibration, and SPE procedure required for sample analysis. Method performance (bias and variability) and estimated **method detection limits**[1] for 67 compounds are presented.

[1]Words in boldface are defined in Glossary.

The scope of the study includes determination of method performance in reagent-water and filtered natural-water samples from ground water obtained in a domestic well near Evergreen, Colorado, and a surface-water sample obtained from the Platte River near Confluence Park in Denver, Colorado. Method performance was determined at two appropriate concentrations for each compound (0.50 and 4.0 µg/L for most compounds) in each water type. Method detection limits were determined according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1997).

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Pesticides and degradates, filtered water, gas chromatography/ mass spectrometry, O-1433-01 (see table 1)

1. Scope and Application

This manual method is suitable for the determination of microgram-per-liter concentrations of compounds in filtered wastewater and natural-water samples. The method is applicable to compounds that are efficiently partitioned from the water phase onto the polystyrene-divinylbenzene (PSDVB) organic phase, and are sufficiently volatile and thermally stable for gas chromatography. Samples are filtered to remove suspended particulate matter, so this method is suitable only for dissolved-phase compounds.

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 (table 1).

The environmental implications of nonionic surfactants is unknown, thus, making it important to determine as many compounds and their degradates as possible in this chemical class (Barber and others, 2000). The alkylphenol polyethoxylates (APEOs) are nonionic surfactants, and those of particular interest consist of the nonylphenol polyethoxylates (NPEOs) and the octylphenol polyethoxylates (OPEOs). The APEO surfactants generally contain up to about 20 ethoxy-units. These compounds eventually degrade in the environment to form alkylphenol diethoxylates (APEO2), which are represented in the method by OPEO2 and NPEO2 (total), and mono-ethoxylates, which are represented in the method by OPEO1 (see table 1). All of these compounds are known for their estrogenic activity in aquatic organisms (Jobling and Sumpter, 1993). The alkylphenol mono- and diethoxylates degrade further to form alkylphenols (APs) and alkylphenol ethoxycarboxylates (APEC). The APs are represented in the method (see table 1) by *para*-nonylphenol, 4-cumylphenol, 4-*n*-octylphenol, and 4-*tert*-octylphenol, and are less estrogenic than their ethoxylated counterparts. Unfortunately, the APECs are too polar to be analyzed by this method. A comprehensive analysis of this family of compounds (APEOs and their degradates) is needed to understand their fate and transport in the environment. The hormonal disrupting effect of this compound class on aquatic life has been documented, and is exemplified by a study with rainbow trout: male fish exposed to concentrations of APs greater than about 20 µg/L produced vitellogenin, a yolk protein normally found only in females (Jobling and Sumpter, 1993).

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

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

Compound name	EDP[1]	CAS number	Parameter/ method codes[2]	Possible compound uses or sources[3]
1,4-Dichlorobenzene[4]	S	106-46-7	34572A	Moth repellant, fumigant, deodorant
17*beta*-Estradiol	K	50-28-2	62053A	Estrogen replacement therapy, estrogen metabolite
1-Methylnaphthalene	--	90-12-0	62054A	2-5% of gasoline, diesel fuel, or crude oil
2,6-Dimethylnaphthalene[4]	--	581-42-0	62055A	Present in diesel/kerosene (trace in gasoline)
2-Methylnaphthalene	--	91-57-6	62056A	2-5% of gasoline, diesel fuel, or crude oil
3*beta*-Coprostanol	--	360-68-9	62057A	Carnivore fecal indicator
3-Methyl-1H-indole (skatol)	--	83-34-1	62058A	Fragrance, stench in feces and coal tar
3-*tert*-Butyl-4-hydroxyanisole (BHA)	K	25013-16-5	62059A	Antioxidant, general preservative
4-Cumylphenol	K	599-64-4	62060A	Nonionic detergent metabolite
4-*n*-Octylphenol	K	1806-26-4	62061A	Nonionic detergent metabolite
4-*tert*-Octylphenol	K	140-66-9	62062A	Nonionic detergent metabolite
5-Methyl-1H-benzotriazole	--	136-85-6	62063A	Antioxidant in antifreeze and deicers
Acetophenone	--	98-86-2	62064A	Fragrance in detergent and tobacco, flavor in beverages
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	--	21145-77-7	62065A	Musk fragrance (widespread usage) persistent in ground water
Anthracene[4]	--	120-12-7	34221A	Wood preservative, component of tar, diesel, or crude oil, CP
Anthraquinone[4]	--	84-65-1	62066A	Manuf dye/textiles, seed treatment, bird repellant
Benzo[*a*]pyrene[4]	K	50-32-8	34248A	Regulated PAH, used in cancer research, CP
Benzophenone	S	119-61-9	62067A	Fixative for perfumes and soaps
beta-Sitosterol	--	83-46-5	62068A	Plant sterol
beta-Stigmastanol	--	19466-47-8	62086A	Plant sterol
Bisphenol A	K	80-05-7	62069A	Manuf polycarbonate resins, antioxidant, FR
Bromacil[4]	--	314-40-9	04029E	H (GUP), >80% noncrop usage on grass/brush
Bromoform[4]	--	75-25-2	34288A	WW ozination byproduct, military/explosives
Caffeine[4]	--	58-08-2	50305B	Beverages, diuretic, very mobile/biodegradable
Camphor	--	76-22-2	62070A	Flavor, odorant, ointments
Carbaryl[4]	K	63-25-2	82680F	I, crop and garden uses, low persistence
Carbazole	--	86-74-8	62071A	I, Manuf dyes, explosives, and lubricants
Chlorpyrifos[4]	K	2921-88-2	38933F	I, domestic pest and termite control (domestic use restricted as of 2001)
Cholesterol	--	57-88-5	62072A	Often a fecal indicator, also a plant sterol
Cotinine	--	486-56-6	62005A	Primary nicotine metabolite
Diazinon[4]	K	333-41-5	39572F	I, > 40% nonagricultural usage, ants, flies
Dichlorvos[4]	S	62-73-7	38775B	I, pet collars, flies, also a degradate of naled or trichlofon
d-Limonene	--	5989-27-5	62073A	F, antimicrobial, antiviral, fragrance in aerosols
Equilenin	--	517-09-9	62074A	Hormone replacement therapy drug
Estrone	--	53-16-7	62484A	Biogenic hormone
Ethynyl estradiol	K	57-63-6	62052A	Oral contraceptive

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

Compound name	EDP[1]	CAS number	Parameter/ method codes[2]	Possible compound uses or sources[3]
Fluoranthene[4]	--	206-44-0	34377A	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	--	1222-05-5	62075A	Musk fragrance (widespread usage) persistent in ground water
Indole	--	120-72-9	62076A	Pesticide inert ingredient, fragrance in coffee
Isoborneol	--	124-76-5	62077A	Fragrance in perfumery, in disinfectants
Isophorone[4]	--	78-59-1	34409A	Solvent for lacquer, plastic, oil, silicon, resin
Isopropylbenzene (cumene)	--	98-82-8	62078A	Manuf phenol/acetone, fuels and paint thinner
Isoquinoline[4]	--	119-65-3	62079A	Flavors and fragrances
Menthol	--	89-78-1	62080A	Cigarettes, cough drops, liniment, mouthwash
Metalaxyl[4]	--	57837-19-1	50359B	H, F (GUP), mildew, blight, pathogens, golf/turf
Methyl salicylate	--	119-36-8	62081A	Liniment, food, beverage, UV-absorbing lotion
Metolachlor[4]	--	51218-45-2	39415F	H (GUP), indicator of agricultural drainage
N,N-diethyl-*meta*-toluamide (Deet)	--	134-62-3	62082A	I, urban uses, mosquito repellent
Naphthalene[4]	--	91-20-3	34443A	Fumigant, moth repellent, major component (about 10%) of gasoline
Nonylphenol, diethoxy- (total, NPEO2)	K	NA	62083A	Nonionic detergent metabolite
Octylphenol, diethoxy- (OPEO2)	K	NA	61705A	Nonionic detergent metabolite
Octylphenol, monoethoxy- (OPEO1)	K	NA	61706A	Nonionic detergent metabolite
para-Cresol[4]	S	106-44-5	62084A	Wood preservative
para-Nonylphenol (total)	K	84852-15-3	62085A	Nonionic detergent metabolite
Pentachlorophenol[4]	S	87-86-5	34459A	H, F, wood preservative, termite control
Phenanthrene[4]	--	85-01-8	34462A	Manuf explosives, component of tar, diesel fuel, or crude oil, CP
Phenol[4]	--	108-95-2	34466A	Disinfectant, manuf several products, leachate
Prometon[4]	--	1610-18-0	04037F	H (noncrop only), applied prior to blacktop
Pyrene[4]	--	129-00-0	34470A	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Tetrachloroethylene[4]	--	127-18-4	34476A	Solvent, degreaser, veterinary anthelmintic
Tri(2-chloroethyl) phosphate	S	115-96-8	62087A	Plasticizer, flame retardant
Tri(dichloroisopropyl) phosphate	S	13674-87-8	62088A	Flame retardant
Tributyl phosphate	--	126-73-8	62089A	Antifoaming agent, flame retardant
Triclosan	S	3380-34-5	62090A	Disinfectant, antimicrobial (concern for acquired microbial resistance)
Triethyl citrate (ethyl citrate)	--	77-93-0	62091A	Cosmetics, pharmaceuticals
Triphenyl phosphate	--	115-86-6	62092A	Plasticizer, resin, wax, finish, roofing paper, FR
Tri(2-butoxyethyl) phosphate	--	78-51-3	62093A	Flame retardant

[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.

[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.

The APEOs also are degraded during sewage treatment (Geiger and others, 1984). Therefore, sewage-treatment plant effluents can be major point sources for the hydrophobic APs and APECs. The more polar APECs cannot be determined by this method because they thermally degrade on the GC, which is unfortunate, because they have a higher potential for leaching into ground water than do APs. The volatility and availability of reference standard APEOs limit the method to the determination of OPEO1, OPEO2, and NPEO2, even though APEOs typically contain up to about 20 ethoxy-units.

Alkylphenols exhibit long-term persistence and bioaccumulation potential in the environment. Research on the distribution of alkylphenols in rivers and estuaries of England (Blackburn and Waldock, 1995) suggests that the majority of APs entering rivers will sorb onto particulate matter and ultimately accumulate in sediments. Water solubility and sediment/water partition data for these compounds indicate that if the total concentration of APs in the particulate plus dissolved phases exceeds about 20 µg/L, then the majority of the APs are present in the particulate phase, and, at concentrations less than 20 µg/L, the higher concentration remains in solution (Blackburn and Waldock, 1995). Various investigators have reported concentrations of APs ranging from 10 to 100 mg/kg in sediment samples near sewage-treatment plants. Hale and others (2000) detected concentrations of NPs at more than 50 mg/kg in some sediment samples near a treatment plant that had ceased operation 20 years earlier. Complementary methods are needed at the NWQL to determine APs and other hydrophobic compounds associated with suspended particles and sediments because this filtered-water method is applicable to the determination of compounds in the dissolved phase.

Detection of caffeine can be an important indicator of wastewater contamination in surface-water samples, however, caffeine is not persistent in the environment because of rapid degradation by bacteria. Caffeine usually will not be detected in ground-water samples even though its detection might be expected on the basis of surface-water concentrations (Seiler and others, 1999).

Coprostanol has been a traditional indicator of sewage contamination, because it is produced almost exclusively in the digestive tract of higher mammals (humans, pigs, and cats) and often correlates with the presence of other sewage-derived pollutants, such as pathogens, toxic metals, organic compounds, and hormones. Coprostanol is persistent in the environment under anaerobic conditions and is degraded by aerobic bacteria (Shigenaka and Price, 1988). Although the method is not particularly sensitive for fecal sterols, mainly because compound derivatization is not used, their presence with polychlorinated-biphenyls (PCBs), polycyclicaromatic hydrocarbons (PAHs), nonylphenols (NPs) and other hydrophobic, environmentally "resistant" compounds might be useful to determine sources of contaminants associated with suspended sediment. The need to detect sterols in the suspended-sediment phase also indicates the need to implement a complementary suspended-phase method at the NWQL.

The detection of *beta*-stigmastanol and *beta*-sitosterol in the same sample generally indicates a substantial contribution from plant sterols. The detection of *beta*-coprostanol generally is associated with higher mammals. Cholesterol, on the other hand, can originate from plant and animal sources.

Other important compounds determined by this method are organochlorine flame retardants, tri(2-chloroethyl) phosphate (Fyrol

CEF ™) and tri(dichloroisopropyl) phosphate (Fyrol FR 2 ™). These compounds have been detected frequently during custom implementation of this method at the NWQL, even though they have been replaced in most industrial applications by the polybrominated, flame retardants because they are less toxic if they ignite. The polybrominated diphenylethers and other polybrominated flame-retarding chemicals have the potential to become a widespread, persistent environmental problem similar to the PCBs (de Boer and others, 1998) because they have been used extensively in many common products. Moreover, these compounds are difficult to analyze because of their extremely low water solubilities and high molecular weights. The NWQL currently (2002) is evaluating several specific brominated fire-retardant compounds to include in this method because of their environmental significance. Generally, water treatment is not sufficient to remove halogenated flame retardants, and the Fyrols™ have been detected at 0.5 to 3 µg/L in samples before and after wastewater treatment (van Stee and others, 1999).

Triclosan is another chlorinated compound that is widely used as an antimicrobial agent in household products, such as hand soaps, shampoos, antiperspirant products, and toothpaste. In contrast to the halogenated flame retardant compounds, van Stee and others (1999) reported that about 80 percent of triclosan is removed during water treatment. There is recent evidence (McMurry and others, 1998) that bacteria might become resistant to triclosan, which is cause for concern, especially considering its widespread use. Triclosan also has been detected in greater than 25 percent of surface-water samples analyzed by using the CLLE wastewater method at the NWQL.

Several fragrance compounds have been included in the wastewater method because of their widespread use in numerous domestic products and detergents. Use of the synthetic polycyclic musks, acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) and hexahydrohexamethyl-cyclopentabenzopyran (HHCB), has surpassed that of the once used (prior to 1978) and highly controversial nitro-musks (Fromme and others, 1999). There also is recent evidence (Franke and others, 1999) concerning bioaccumulation and potential toxicity of the synthetic polycyclic musk compounds in aquatic life. Treatment of wastewater in a survey of 25 sewage-treatment plants near the Ruhr River in Germany indicated that primary water treatment only reduces the concentration of polycyclic musk compounds by about 30 percent, whereas secondary water treatment removes about 85 percent (Simonich and others, 2000). AHTN and HHCB have been detected in wastewater samples of the United States (Standley and others, 2000), and because of their persistence and widespread use, are expected to be more reliable than caffeine for correlating and evaluating potential wastewater problems. The synthetic musks tentatively were identified in about 5 percent of wastewater samples (both ground-water and surface-water) at the NWQL, but until standard compounds were obtained, positive identification was impossible. These compounds should prove to be invaluable for hydrologic studies because of their mobility, widespread use, and recalcitrant properties.

2. Summary of Method

Water samples are filtered in the field by using glass-fiber filters (0.7-µm nominal pore diameter) to remove suspended particulate matter (Sandstrom, 1995) before they are sent to the NWQL. Filtered 1-L water samples are extracted with disposable, polypropylene SPE cartridges that contain polystyrene-divinylbenzene phase. The SPE

cartridges are dried thoroughly by using a flow rate of 2 L/min of pressurized nitrogen, which takes about 45 minutes.

After the SPE cartridges have dried, the sample bottles are rinsed thoroughly with a mixture of 15 mL dichloromethane (DCM) and diethyl ether (EE), at 4:1. The DCM-EE rinsate also is used to elute sorbed compounds from the corresponding SPE cartridges. Next, the extract is evaporated by using a gentle stream of nitrogen to a final volume of 0.4 mL and then is transferred to an autosampler vial that contains a 400-µL glass insert. Finally, the concentrated extracts are determined by capillary-column gas chromatography/mass spectrometry (GC/MS).

3. Interferences

Organic compounds that have gas-chromatographic retention times and characteristic ions with a mass identical to those of the compounds of interest might interfere, and because of the complex nature of wastewater, there are often unknown compounds that interfere.

Phthalates and preservatives (BHT and related compounds) in the cartridge material 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 7.1, Field Sampling) because some method compounds are contained in commonly used products. Sample-collection protocols and cleaning procedures for field equipment (Radke and others, 1998a and 1998b) need to be followed to reduce interference.

4. Apparatus and Instrumentation

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

4.2 *O-rings* — Viton, 3.25 cm (1 9/32 in.) outside diameter by 2.62 cm (1 1/32 in.) inside diameter.

4.3 *Teflon tubing* — 0.317 cm (⅛ in.) outside diameter by about 1 m (39.4 in.) length, for vacuum pumping samples through SPE cartridges.

4.4 *Extraction caps* — Teflon, 32/133 threads to fit sample bottles and tapered opening to fit the Luer end of SPE cartridges.

4.5 *Luer stopcock* — Teflon flow-control valves (on-off valves).

4.6 *Carboy* — Nalgene™, thick-walled, capable of maintaining 200 kPa (29 in.) mercury vacuum, 20-L volume, VWR Scientific Inc., catalog number 36494-092 or equivalent.

4.7 *Tefzel-ethylenetetrafluoroethylene (Tefzel-ETFE) female Luer connector* — 1/4-28 thread, Tefzel-ETFE union with 1/4-28 thread; Upchurch Scientific or equivalent.

4.8 *Bottle-top solvent dispensers* — Adjustable from 2 to 5 mL and 5 to 25 mL; Brinkman Dispensette, Van Waters & Rogers (VWR) Scientific or equivalent.

4.9 *25-mL graduated Kuderna-Danish receivers (concentrator tubes*) — Kontes part number 570081-2526 or equivalent.

4.10 *Solvent reservoirs* — Polypropylene, 30-mL column.

4.11 *Adapters* — Teflon, connects SPE cartridge barrel to male Luer fitting.

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

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

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

4.15 *Micropipets* — 50-, 100-, and 200-µL fixed-volume and variable-volume micropipets with disposable glass bores; VWR Scientific or equivalent.

4.16 *Glass syringes* — 10-, 50-, 100-, 250-, and 500-µL volume.

4.17 *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 polyphenyl-methylsilicone; Hewlett-Packard HP-trace analysis column or equivalent.

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

4.18.1 *Recommended GC conditions.* 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 9 mL/min; injection volume, 2 µL, splitless injection.

4.18.2 Recommended 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.

5. Reagents and Consumable Materials

5.1 *Helium carrier gas* (99.999 percent).

5.2 *Sodium sulfate drying cartridges*, Luer-Lok, 3-mL volume, 2.5 g Na_2SO_4 ; International Sorbent Technology, Ltd., catalog number 802-0250-M or equivalent.

5.3 *Nitrogen gas*, for evaporation, ultrapure.

5.4 *Sodium chloride*, reagent grade, baked 8 hours at 450°C, VWR or equivalent.

5.5 *Acetic acid*, glacial, reagent grade, Sigma Scientific Inc. or equivalent.

5.6 Sodium acetate, anhydrous, reagent grade, Sigma Scientific Inc. or equivalent.

5.7 SPE cartridges, 6-mL barrel, packed with 500 mg of PSDVB; Oasis polystyrene-divinylbenzene packing material, Waters Inc., catalog number 186000115 or equivalent.

5.8 Glass-fiber filters, 0.7-µm nominal pore diameter (GF/F grade), baked at 450°C for 2 hours; Whatman, Inc. or equivalent.

5.9 Glass bottles, amber, 1,000-mL, 33-mm neck, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps; NWQL GCC or equivalent.

5.10 Solvents, dichloromethane (DCM) and diethyl ether (EE); B&J Brand pesticide grade or equivalent.

5.11 Solution 2000 water, prepared by Solution 2000 purification system or equivalent.

5.12 Acetic acid/sodium acetate buffer, pH 4.3 (dilute 30 g acetic acid and 15 g sodium acetate in 1 L reagent water).

5.13 Potassium phosphate buffer, pH 7.0 (dilute 30 g dipotassium hydrogen phosphate and 20 g potassium dihydrogen phosphate in 1 L reagent water).

5.14 Dichloromethane: diethyl ether mixture, 80:20 volume per volume.

6. Standards

6.1 *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*-NP, OPEO1, and OPEO2) are only available in technical mixtures. For the technical grade nonylphenol (NP) mixture (*ortho*-NP and *para*-NP) and the Igepal 210 (Dupont, Inc.) mixture (OPEO1 and OPEO2), the final concentration of 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, Calibration).

The 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, note how the qualification ion profiles (m/z 220 and 107) must coincide in a similar pattern with ion 135. 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).

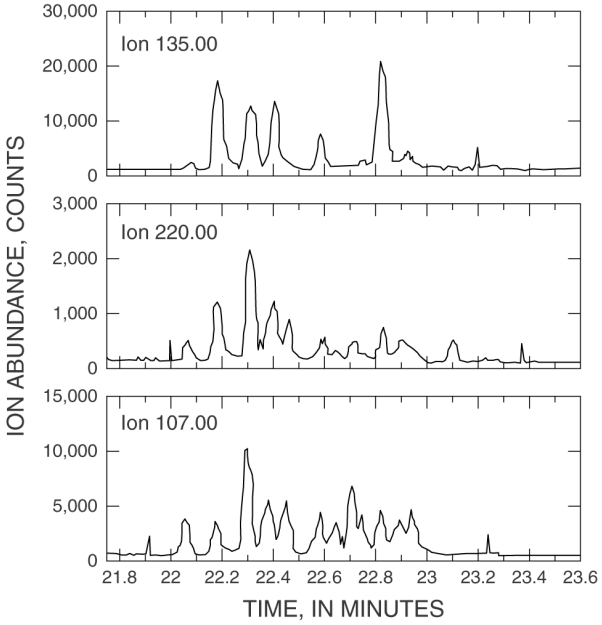

Figure 1. Manual integration of the extracted ion profile for the quantitation ion (mass-to-charge ratio 135) of *para*-nonylphenol from the 2 nanogram-per-microliter calibration solution for the wastewater method.

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.

During development of the custom wastewater method, NPEO1 and NPEO2 only were available in a technical mixture. A source of NPEO2 standard has been identified and evaluated for purity for inclusion in this method. Standards of the NPEO1 compounds also recently have become available and currently (2002) are being evaluated for composition and purity. It is anticipated that they will be included in the method in 2002.

6.2 *Intermediate method compound standard solution at 100 ng/µL* — Prepare a mixed stock standard solution at 100 ng/µL that contains each method compound stock standard solution at 100 ng/µL (not surrogate compounds). Use an adjustable 100-µL dispenser and a 10-mL volumetric flask to prepare this intermediate method compound standard solution and dilute with DCM.

6.3 *Surrogate spike solution at 20 ng/µL* — Combine 100 µL of stock standard solution at 10,000 ng/µL for each **surrogate compound** listed in table 2 (see Section 10, Calibration) in a 50-mL volumetric flask and dilute with methanol. Add 100 µL of the 20-ng/µL standard solution to a 1-L sample to obtain a surrogate spike solution of 2.0 µg/L. A surrogate concentration of 5.0 ng/µL is expected in a 0.40-mL extract if 100 percent of the surrogate is recovered through the sample preparation procedure.

6.4 *Mixed surrogate and method compounds solution at 50 ng/µL* — Add 5.0 mL of the 100-ng/µL intermediate method compound standard solution (see section 6.2) to a 10-mL flask. Add 50 µL of each of the stock standard solutions at 10,000 ng/µL (see section 6.1) and dilute with DCM. This mixture is used to prepare the calibration solutions (section 6.7).

6.5 *Compound spike 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 methanol. Add 100 µL to a 1-L sample to obtain a compound concentration of 2.0 µg/L. A concentration of 5.0 ng/µL is expected in a 0.40-mL extract if 100 percent of the spike is recovered.

6.6 *PAH procedural internal standard solution at 100 ng/µL* — The internal standards (see table 2, Section 10, 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 0.40-mL extract is equivalent to a concentration of 5 ng/µL.

6.7 *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 compounds in the calibration mixture that respond poorly by GC/MS (cholesterol, 3*beta*-coprostanol, 17*beta*-estradiol, *beta*-stigmastanol, *beta*-stitosterol, ethynyl estradiol, OPEO1, and 5-methyl-1H-benzotriazole) is 4 times that of the other single-component compounds. The concentration of the multicomponent compounds in the calibration mixture, NP (total) and NPEO2 (total), is 20 and 16 times, respectively, that of the single-component compounds in the calibration mixture. The concentration of the PAH procedural internal standard compounds in the calibration

mixtures is kept constant at 5.0 ng/µL. Prepare these calibration solutions by adding the appropriate volumes of the mixed surrogate and method compounds 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.

7. Procedure

7.1 *Field sampling* — Collect samples and filter them through 0.7-µm nominal pore-size diameter glass-fiber filters (Sandstrom, 1995) into 1-L amber glass pesticide bottles (NWQL type GCC) before shipping at 4ºC to the NWQL, preferably by express mail. Field-sampling procedures should follow those typically used to collect samples for trace organic compound analyses (Hardy and others, 1989; Ward and Harr, 1990; Radke and others, 1998a, 1998b). Some of the compounds that are determined by this method are found in commonly used products, such as coffee, tea, cola, soap, and insecticide repellant.

CAUTION: 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, field blanks should be analyzed routinely by using EM Science, Inc. Omni Solv® water to monitor for potential sample contamination.

7.2 *Initial sample preparation* — Samples received at the NWQL must be visually examined to determine if they have been filtered in the field, and if not, they must be filtered (Sandstrom, 1995). If the sample bottle has less than about 30 mL of headspace after filtration, then discard a minimum amount of water to provide enough headspace for later addition of 60 g NaCl. Weigh the sample and bottle and record the gross sample weight (±1 g). After sample filtration, and the gross weight has been recorded, add 60 ± 10 g NaCl (baked) to make the sample about 1 molar NaCl. Store filtered samples in a refrigerator at 4°C for up to 14 days from the time of sample collection.

NOTE: Addition of NaCl to samples increases the ionic strength and improves recovery of polar compounds during extraction. Addition of NaCl also might augment sample filtration to preserve samples from biodegradation.

7.3 *SPE cartridge cleaning* — Assemble the Na_2SO_4 drying cartridges, stopcocks, and SPE cartridges vertically in that order. Attach them to the Luer-Lok fittings on the vacuum/elution manifold by twisting them clockwise to ensure that the fittings are closed. Add 5 mL (the SPE barrel volume) of the elution solvent (DCM-EE, 4:1) to rinse the SPE and Na_2SO_4 drying 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 5 mL of DCM-EE (4:1) and allow at least 10 minutes for the vacuum to remove any residual solvent. Attach the polypropylene 25-mL empty sample reservoirs to the Luer-Lok fittings on the vacuum/elution manifold and clean them by rinsing with DCM-EE (4:1).

NOTE: Unlike most other SPE phases, it is permissible for PSDVB to dry prior to sample extraction, thus making it possible to prepare SPE cartridges up to a day in advance of sample extraction.

7.4 *Sample extraction* — Before the 14-day holding time expires, obtain the samples from the refrigerator and acidify with 3 mL of the acetic acid/sodium acetate buffer (pH 4.3). Prepare a laboratory reagent water set blank and set spike sample with each set of samples. Add 100 µL of the surrogate spike solution (20 ng/µL; see section 6.3) to each sample, set spike, and set blank by using a stepper syringe to make the 100-µL additions. Fortify the spike sample with 100 µL of the compound spike solution (20 ng/µL; see section 6.5) by using a micropipet dispenser and 100-µL disposable glass bore. (This step results in a concentration of 2.0 µg/L for the fortified spike compounds and surrogate compounds in a 1-L sample.)

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

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.

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.

Attach the SPE cartridges to the vacuum lines from the waste carboy manifold assembly (fig. 2) by using an adapter (not shown).

CAUTION: Ensure that the 20-L carboys have enough headspace (empty volume) remaining to accommodate the total water volume from all samples before a new sample set is extracted, otherwise it might be difficult to exchange carboys during the extraction.

Attach Teflon bottle caps to sample bottles. Turn on the vacuum pump, and attach the male Luer end of the SPE cartridge to the bottle cap before inverting the sample bottles and placing them in the rack (fig. 3).

Ensure that there are no leaks or sources of bubbles in the system. Small bubbles might form as the sample is pumped through the tubing and will slow the extraction process. Large air bubbles can be a problem if they cause uneven flow (channeling) through the cartridge packing. One advantage of operating under vacuum, as opposed to positive pressure, is that system leaks usually do not result in sample loss. The desired extraction flow-rate range (between 25 to 50 mL/min) is obtained by loosening or tightening the sample bottle caps, which might need to be done once or twice during sample extraction.

NOTE: Reasonable extraction times range from 20 to 40 minutes for 1-L samples and correspond to flow rates between 25 and 50 mL/min. No adverse effects on compound recoveries have been observed when flow rates are maintained in this operating range.

Pump the entire sample through the SPE cartridge. Unscrew the sample bottle from the Teflon bottle cap. Place the Teflon bottle cap back on the rack. Add 20 mL of phosphate buffer (pH 7) to the cap and draw it by vacuum through the cartridge; this buffer is added to remove excess salt from the cartridge prior to the drying step and adjusts the pH of the cartridge to neutral prior to the elution step. Salt deposits formed while drying the SPE cartridge might lead to channeling and variable recovery during the subsequent elution step. Adjusting the pH of the cartridge to neutral will improve the elution of basic compounds that otherwise remain partially bound to the sorbent. Turn off the vacuum pump after all of the buffer solution has passed through the cartridge.

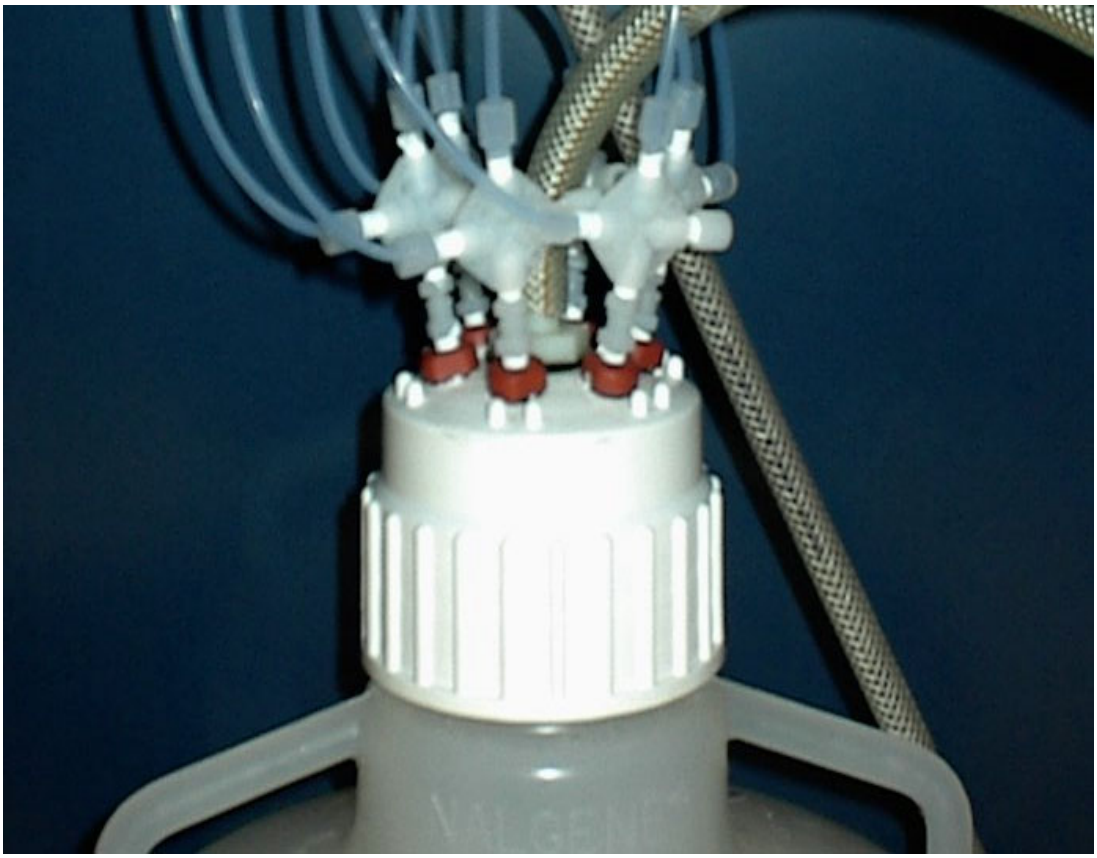

Figure 2. Manifold assembly cap on a 20-liter carboy for collecting extracted sample water from the wastewater method.

NOTE: Equipment cleanup is minimized because there is no possibility for sample cross-contamination except from the Teflon bottle caps, an advantage of using this procedure.

7.5 *Cartridge drying* — Attach the male Luer end of the SPE cartridge to the female Luer-Lok fitting on the gas-pressure module of the SPE vacuum manifold. Dry the cartridges by using a positive pressure of nitrogen (2 L/min through each cartridge for about 45 minutes) to remove all interstitial water.

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 is completely dry prior to elution, or compound recoveries might be unacceptable.

Remove cartridges from nitrogen gas as soon as possible after determining that they are dry. Excessive gas-flow time results in compound losses caused by volatilization.

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 nitrogen gas flow beyond 20 minutes past dry.

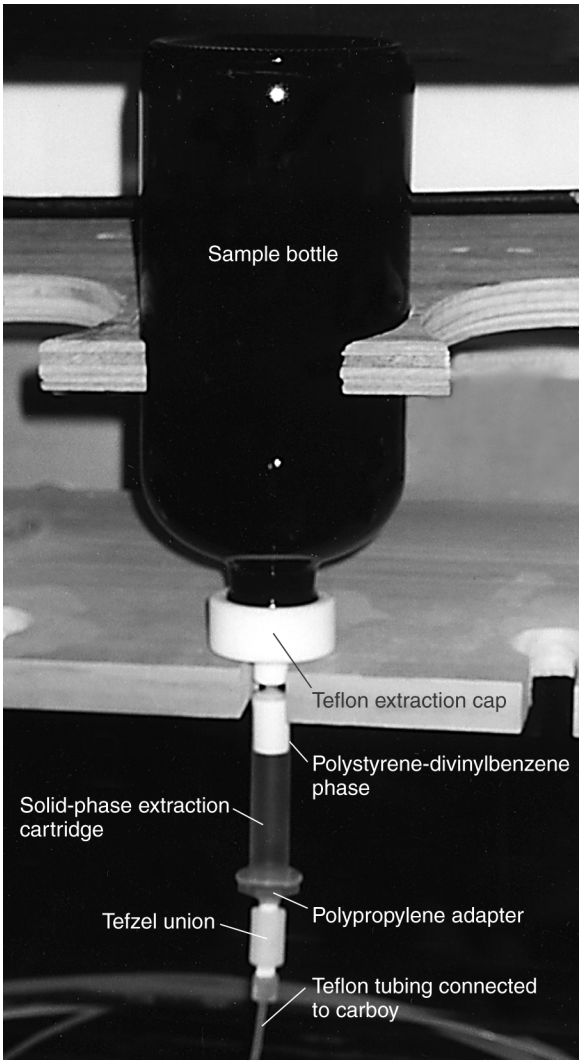

Figure 3. Solid-phase extraction sample assembly for the wastewater method.

7.6 *Compound elution* — The sample bottle is rinsed with DCM-EE (4:1) to remove hydrophobic compounds that adhere to the glass surface. The solvent rinse from the bottle then is used to elute the dry SPE cartridge.

Slide the Viton O-ring over the mouth and just past the threads of the sample bottle. Screw on the Teflon bottle cap until it comes in contact with the Viton O-ring to form an air-tight seal. In a hood, add 15 mL of DCM-EE (4:1) to the sample bottles through the hole in the top of each bottle cap. Attach a stopcock and Na_2SO_4 drying cartridge to each bottle cap by twisting slightly clockwise to ensure that the Luer-Lok connections are secure (fig. 4). Set stopcocks in the closed position before rinsing sample bottles. Rinse each bottle thoroughly by rotating the bottle, thus ensuring that the solvent contacts all inside surfaces.

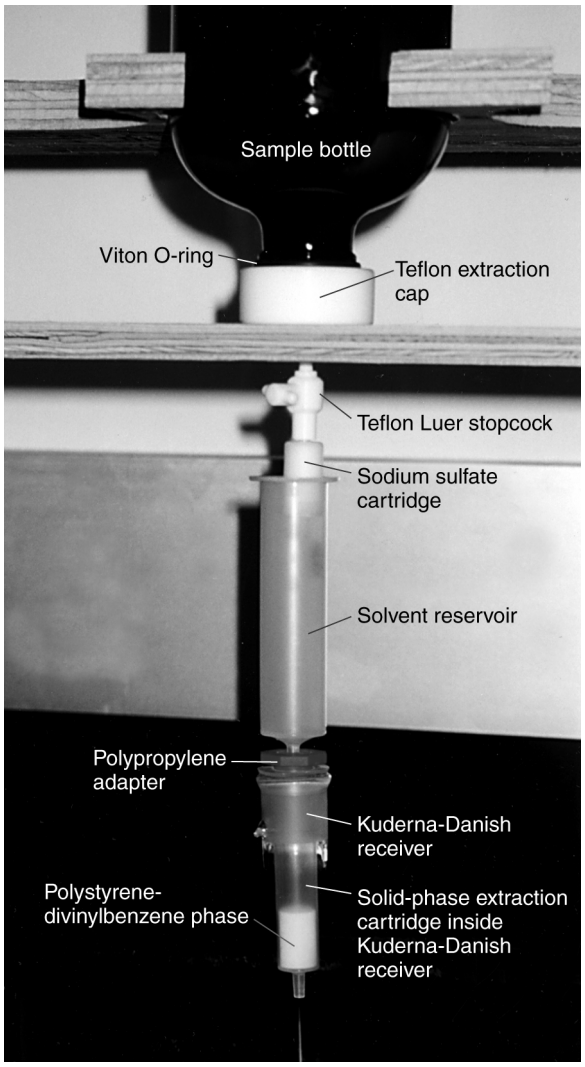

Figure 4. Solid-phase cartridge elution apparatus for the wastewater method.

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

Attach 25-mL solvent reservoirs to dried SPE cartridges with a Teflon adapter and place in 25-mL K-D receivers. Invert the sample bottles and place them in the elution rack with the male Luer end of the drying cartridge positioned above the appropriately labeled receiver (fig. 4).

Add 3 mL of EE to the 25-mL solvent reservoir to elute the SPE cartridge and ensure that any residual water is removed from the SPE sorbent prior to solvent elution with DCM-EE (4:1) from the bottle rinse. This first diethyl ether fraction is collected in the K-D receiver and is processed later as part of the sample extract. After EE has drained from the SPE cartridge, open the stopcock and allow the DCM-EE (4:1) solvent rinse from the sample bottle to drain into the solvent reservoir so that compounds from the SPE cartridge can be eluted by gravity into the K-D receiver (about 20 minutes). Finally, add another 3 mL of EE to the 25-mL solvent reservoir to displace any remaining DCM-EE (4:1) solvent from the SPE sorbent. This final EE fraction also is collected in the K-D receiver with the extract.

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 incomplete removal of water from the SPE cartridges.

7.7 *Weigh bottles* — Record empty sample bottle weights to ± 1 g.

7.8 *Solvent evaporation* — Prepare the 24-position N-Evap nitrogen evaporator by attaching cleaned and burned stainless-steel needles in each position. Set the nitrogen flow rate to about 3.5 L/min and adjust the flow visually so that a slightly detectable ripple can be seen on the surface of the extracts. When the extract volume is between 2.5 and 4 mL, add 20 µL of the PAH procedural internal standard solution (100 ng/µL) by using a 1.0-mL stepper syringe. Remove the extracts when the final volume is 0.4 mL. Maintain a consistent flow rate by leaving the needles attached to the N-Evap with the flow of nitrogen remaining unaltered. Concentrate the DCM-EE extract at ambient temperature and periodically check the extract; at no time should the extract be allowed to evaporate completely. Allow about 40 to 50 minutes for evaporation of nearly 15 mL of DCM-EE to 0.4 µL.

7.9 *Vial 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 that contain 400-µL glass inserts. Store extracts in a freezer prior to GC/MS analysis.

8. Safety Precautions and Waste Disposal

8.1 Method compounds may be extracted on a laboratory bench, but all steps in the method that require the use of organic solvents, such as cartridge cleaning, bottle rinsing, cartridge elution, and extract concentration, must be conducted in a fume hood. Eye protection, gloves, and protective clothing must be worn in the laboratory area and when handling reagents, solvents, or any corrosive materials, such as acetic acid buffer. Typical laboratory disposable, nitrile gloves do not provide adequate protection from DCM, so avoid contact with DCM.

8.2 The waste stream produced during sample preparation is about 1 molar NaCl and pH 7. It is collected in thick-walled carboys, and must be disposed of according to local regulations. Solvent used to clean or rinse glassware, equipment, and cartridges also must be disposed of in the appropriate waste containers.

9. Gas Chromatograph/Mass Spectrometer Performance

Check instrument performance at least every 24 hours to ensure that it meets quality-assurance guidelines of sensitivity and accuracy necessary to obtain reproducible sample results.

9.1 Gas Chromatograph Performance Evaluation

9.1.1 Gas chromatograph 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 NP compounds is shown in the selected ion chromatogram (fig. 1) of a 2.0-ng/µL calibration solution. If peak shape and resolution deteriorates (indicated by a loss in the number of resolved NP isomers, fig. 1) or if compounds fail to meet the calibration criteria (see section 10, Calibration), change the injection port liner or perform maintenance on the capillary column to bring the gas chromatograph into compliance. 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. 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 perfluorotributylamine tuning compound, locate and fix the leaks. Also, check the instrument every 24 hours during a series of sample analyses to ensure that mass spectrometer performance is in accordance with the perfluorotributylamine tuning criteria outlined below. In addition, initially adjust the mass spectrometer response (also outlined below) to ensure that the established **minimum reporting level (MRL)** for each selected compound can be achieved.

9.2.2 Check the mass spectrometer tune daily.

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.

Mass axis and MS peak-width adjustment characteristics must be set to give ±0.15-atomic mass unit accuracy at masses 69, 219, and 502 in the spectrum of perfluorotributylamine. Adjust the electron multiplier voltage to achieve about 1,000,000 counts for the mass 69 ion. This setting generally will provide 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 resolution so that m/z ion 69 has 100-percent abundance, mass 219 ion is 40±20 percent, and mass 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 ions 69, 219, and 502 so that they range from about 0.5 to 0.65 atomic mass unit. Adjustment of tune settings normally will require recalibrating the method compounds.

10. Calibration

10.1 Acquire initial calibration data by using a new capillary column and the latest calibration solutions. 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 solution (or solutions) that contain all of the method compounds to ensure that GC/MS performance is in compliance with established performance criteria (see section 9.2). The calculated concentration of method compounds in the **continuing calibration verification solutions (CCVs)**, using the initial calibration curve, generally needs to be within ±20 percent of the expected concentration.

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 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, 2001).

10.4 See table 2 for compound quantitation ions and their respective PAH internal-standard reference compounds used for these calculations. The concentration of chrysene-d_{12} in the procedural internal standard solution was changed inadvertently so that it was not consistent with the concentration of the other internal standard compounds and could no longer be used during method development. Phenanthrene-d_{10} was used successfully in its place, but it is anticipated that chrysene-d_{12} might be used when new standard solutions are prepared.

10.5 *Calibration of multicomponent compounds* — The *para*-NPs and NPEO2 mixtures are each composed of 10 to 20 discernible isomers. They are calibrated by manually integrating the area of their respective quantitation ion peaks that are present in the expected range of the retention time window (table 2). This approach also was used for determining the concentration of compounds in the preparation of stock standard solutions (section 6.1, fig. 1) and also has been used in other studies (Blackburn and Waldock, 1995).

11. Quality Assurance and Quality Control

The NWQL has prepared a quality-assurance and quality-control (QA/QC) guidance document (Merle Shockey, U.S. Geological Survey, written commun., 1998) for the Organic Chemistry Program that is followed for this wastewater 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.

First, the sample matrix must be consistent with the requirements of the method (filtered water). Problematic sample matrices will affect the performance of the method during sample preparation and analysis. Extremely dirty sample matrices, such as raw sewage, are discouraged because

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

[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
Tetrachloroethylene	7.021	164	166	131	IS1
Bromoform	10.233	173	171	175	IS1
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
Dichlorvos	22.374	109	85	220	IS2
Isoquinoline	22.834	129	102	--	IS2
Indole	23.418	117	89	--	IS2
2-Methylnaphthalene	23.568	142	141	115	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
3-*tert*-Butyl-4-hydroxyanisole (BHA)	26.606	180	165	137	IS3
5-Methyl-1H-benzotriazole	27.918	103	104	77	IS3
N,N-diethyl-*meta*-toluamide (Deet)	27.983	119	190	91	IS3
4-*tert*-Octylphenol	28.320	135	206	107	IS3
Benzophenone	28.806	182	105	77	IS3
Tributyl phosphate	28.830	99	155	211	IS3
Triethyl citrate (ethyl citrate)	28.914	157	115	203	IS4
Cotinine	29.761	98	176	147	IS4
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

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

Compound name	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Confirmation ion (m/z)	Internal standard reference
Phenanthrene	30.903	178	176	89	IS4
Octylphenol, monoethoxy- (OPEO1)	30.903	135	107	179	IS4
Anthracene	31.044	178	176	89	IS4
Caffeine	31.444	194	109	82	IS4
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	31.468	243	258	213	IS4
Carbazole	31.524	167	139	166	IS4
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	31.538	243	258	197	IS4
4-Cumylphenol	31.576	197	212	--	IS4
Carbaryl	32.120	144	115	116	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
Pyrene	34.731	202	101	203	IS4
Bisphenol A	34.994	213	228	119	IS4
Octylphenol, diethoxy- (OPEO2)	35.168	223	135	294	IS4
Nonylphenol, diethoxy- (total, NPEO2)	35.7–36.5	237	223	279	IS4
Tri(dichloroisopropyl) phosphate	36.400	379	383	381	IS4
Tri(2-butoxyethyl) phosphate	37.054	299	199	125	IS4
Triphenyl phosphate	37.176	326	325	215	IS4
Estrone	39.395	270	185	146	IS4
17*beta*-Estradiol	39.574	272	213	172	IS4
Ethynyl estradiol	40.120	213	296	160	IS6
Equilenin	40.294	266	223	210	IS6
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

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

Compound name	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Confirmation ion (m/z)	Internal standard reference
Surrogates					
Decafluorobiphenyl	18.786	334	265	--	IS2
Caffeine-$^{13}C_3$	31.444	197	110	--	IS4
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	--	--

they contaminate sample preparation equipment and instrumentation, thus affecting the results of subsequent samples. Unknowingly processing raw sewage or unfiltered samples with this method could have deleterious effects on subsequent sample results. On the other hand, reagent water 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 water often are less than or greater than recoveries obtained from environmental sample matrices, which demonstrate some of the limitations of making comparisons among different sample matrices.

Before sample expiration, each environmental sample is prepared for analysis as part of a sample preparation set that contains a laboratory reagent spike and blank (control) to monitor general laboratory conditions and procedures. There is no guarantee, however, that each unique sample matrix will perform similarly to the recoveries of compounds and surrogates obtained from the set spike and blank. Consequently, spiking at the laboratory of field duplicate samples is encouraged to gain some indication of how method compounds perform in a particular sample matrix. Laboratory set spikes are of limited use because they are prepared in reagent water, which usually is not indicative of the sample matrix. Furthermore, just because surrogate compounds perform well in a given sample matrix does not necessarily mean that method compounds will perform equally well. Historical, 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. Control limits for laboratory spikes in reagent water are set at the mean percent recovery ± 3 standard deviations.

Surrogate compounds (not necessarily chemically representative of every method compound) 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 are set at the mean percent recovery ± 3 standard deviations as compiled from reagent water, laboratory set

spike and blank samples. The recoveries of caffeine-$^{-13}C_3$ 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 should be used to evaluate specific sample preparation steps and are of limited use for assessing method compound recoveries. Concentrations reported by the NWQL for compounds and surrogates in environmental samples are never corrected for spike or surrogate recoveries.

Set blanks provide information regarding possible contamination introduced to the sample at the laboratory. Possible contamination from field and sample handling is not monitored unless the appropriate field blanks are submitted to the laboratory for analysis. Even then, only limited information can be inferred because each individual sample is handled separately. Some compounds in the wastewater method are common in personal-care products, and might be detected occasionally in laboratory blanks. If compounds are detected in more than 10 percent of the historical laboratory 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 MDL calculation.

Sample extract(s) are analyzed in an instrument batch or sequence to provide additional information for quality assurance and facilitate corrective actions that might be required if performance criteria are not met. The analytical sequence includes a set spike and blank sample, as well as bracketing 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 acceptable. Finally, a low-concentration standard equivalent to 1 µg/L (or less) is analyzed in each sequence after the environmental samples to ensure that instrument sensitivity is maintained throughout the sample set. If available, field matrix spike samples at concentrations between 2 and 5 times the expected MDL also can be analyzed to ensure method sensitivity for different sample matrices.

If the instrument does not meet acceptance criteria, then follow recommended procedures of cleaning and maintenance (see section 9.1, GC performance evaluation) 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 might be required to meet performance criteria for other sample results.

Each sample also has procedural internal standard compounds added to correct automatically for any differences (generally less than ± 10 percent) in extract volume analyzed, as well as automatically adjust for slight variations in instrumental performance. The procedural internal standards are added prior to instrument analysis and are used to monitor instrument conditions, such as extract injection errors, unexpected GC compound retention time shifts, or instrument abnormalities caused by power interruptions or component malfunctions.

It is difficult to troubleshoot partial QA/QC problems caused by 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 a duplicate 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 unsalvageable and should not be reported.

12. Calculation of Results

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

12.1 Qualitative Identification

12.1.1 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, ensure that the profiles of the qualification and quantification ion peaks 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 (see table 2) 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 should 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 after a compound has passed qualitative criteria according to the calibration curve used to establish the best fit between the calibration points. Curve-fitting routines provided by the instrument manufacturer, and summarized in a similar NWQL method report (Sandstrom, 2001), 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 must 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 and NPEO2 mixtures are each composed of 10 to 20 discernable isomers. Manually integrate the isomeric peak areas of their respective quantitation ions present in their expected retention time window range (table 2), similar to the calibration process described earlier (Section 10, Calibration) for these compounds. If interferences cause the ratios of the qualification ions to the quantification ion 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 qualification ions for *para*-NP and NPEO2 compounds normally are unique from coeluting interference**.**

12.3 Reporting Results

The wastewater method requires that the most accurate information be transmitted to project investigators and data interpreters because it is used to report data for calculating the presence, fate, and transport of important compounds in the environment. Therefore, data are reported according to the latest laboratory quality-assurance information (Merle Shockey, U.S. Geological Survey, written commun., 1998; 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 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 0.05 µg/L), 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 (Merle Shockey, U.S. Geological Survey, written commun., 1998; Childress and others, 1999). They include such situations as matrix interferences, method compounds that have been permanently assigned an “E” code, and those compounds that do not meet quality-assurance criteria, such as being out of calibration by more than ± 20 percent. If the result is greater than 120 percent of 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 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 should not decrease

confidence in qualitative identification. However, concentrations reported near or less than the MDL must be interpreted cautiously. 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 MRL) is appropriate.

METHOD PERFORMANCE

Reagent-water (Solution 2000 water) samples and surface-water samples collected from the Platte River in Confluence Park, Denver, Colo., and ground-water samples collected in a domestic well near Evergreen, Colo., were used to test method performance. The surface-water and ground-water samples were filtered into 1-L sample bottles prior to extraction according to the method protocol. One set of the filtered 1-L subsamples was fortified at a lower concentration (0.5 – 8 µg/L) of each compound and the other set was fortified at a higher concentration (4.0 – 80 µg/L) of each compound. In addition, the three sample matrices were extracted and analyzed (unfortified) to determine the natural presence of any method compounds (table 3). The presence of 10 compounds in the reagent-water sample at barely detectable concentrations reemphasizes the ubiquitous nature of about half of the method compounds, as well as the importance of avoiding contamination throughout sample collection, preparation, and analysis. Isophorone, for example, was detected in all three sample matrices (see table 3) and since has been found at trace levels in opened bottles of methylene chloride. The subsequent isolation of methylene chloride from other laboratory solvents has reduced this contamination problem.

Each fortified sample set was extracted and analyzed on different days, so comparisons of different matrices and concentrations include day-to-day variation. Mean bias and variability data from the analyses are listed in table 4.

The concentration of 16 compounds always is reported as estimated for one of three reasons: unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25 percent RSD), unstable instrument response, or reference standards prepared from technical mixtures. Initial MDLs were calculated for compounds in reagent water by using the corresponding spike concentration as indicated in table 4.

Method detection limits and minimum reporting levels — Initial MDLs were determined according to the procedure outlined by the U.S. Environmental Protection Agency (1997).

The MDL was calculated according to the equation

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

where S = standard deviation of replicate analyses, in microgram per liter, 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 reagent-water samples are fortified with compounds at concentrations of two to five times the calculated MDL. This concentration range

Table 3. Wastewater method compounds detected in unfortified reagent-water, ground-water, and surface-water samples

[µg/L, micrograms per liter; --, not detected]

Compound name	Concentration (µg/L)		
	Reagent	Ground	Surface
1,4-Dichlorobenzene	--	--	--
17*beta*-Estradiol	--	--	--
1-Methylnaphthalene	--	--	--
2,6-Dimethylnaphthalene	--	--	--
2-Methylnaphthalene	--	--	--
3*beta*-Coprostanol	--	--	0.26
3-Methyl-1H-indole (skatol)	--	--	--
3-*tert*-Butyl-4-hydroxyanisole (BHA)	--	--	--
4-Cumylphenol	--	--	--
4-*n*-Octylphenol	--	--	--
4-*tert*-Octylphenol	--	--	.04
5-Methyl-1H-benzotriazole	--	--	1.92
Acetophenone	0.08	--	--
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	--	--	--
Anthracene	--	--	--
Anthraquinone	--	--	--
Benzo[*a*]pyrene	--	--	--
Benzophenone	--	--	.06
beta-Sitosterol	--	--	--
beta-Stigmastanol	--	--	--
Bisphenol A	.04	--	--
Bromacil	--	--	--
Bromoform	--	--	--
Caffeine	.01	--	.33
Camphor	--	--	.11
Carbaryl	--	--	.08
Carbazole	--	--	.02
Chlorpyrifos	--	--	--
Cholesterol	.50	--	.96
Cotinine	--	--	.11
Diazinon	--	--	.15
Dichlorvos	--	--	--
d-Limonene	--	--	--
Equilenin	--	--	--
Estrone	--	--	--

Compound name	Concentration (µg/L)		
	Reagent	Ground	Surface
Ethynyl estradiol	--	--	--
Fluoranthene	--	--	--
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	.01	--	.48
Indole	--	--	--
Isoborneol	--	--	--
Isophorone	0.11	0.40	0.26
Isopropylbenzene (cumene)	--	--	--
Isoquinoline	--	--	--
Menthol	--	--	--
Metalaxyl	--	--	--
Methyl salicylate	--	--	--
Metolachlor	--	--	--
N,N-diethyl-*meta*-toluamide (Deet)	--	--	.12
Naphthalene	.03	--	--
Naphthalene	.03	--	--
Nonylphenol, diethoxy- (total, NPEO2)	--	--	6.64
Octylphenol, diethoxy- (OPEO2)	--	--	1.10
Octylphenol, monoethoxy- (OPEO1)	--	--	--
para-Cresol	--	--	--
para-Nonylphenol (total)	.31	--	.80
Pentachlorophenol	--	--	--
Phenanthrene	--	--	.02
Phenol	--	--	--
Prometon	--	--	--
Pyrene	--	--	--
Tetrachloroethylene	--	--	--
Tri(2-chloroethyl) phosphate	--	--	.19
Tri(dichloroisopropyl) phosphate	--	--	.15
Tributyl phosphate	--	--	--
Triclosan	.11	--	.25
Triethyl citrate (ethyl citrate)	--	--	--
Triphenyl phosphate	.01	--	.07
Tri(2-butoxyethyl) phosphate	--	--	.71

Table 4. Wastewater method mean bias and variability of spike recovery data for eight replicates with compounds spiked at two concentrations that range from 0.5 to 80 micrograms per liter in reagent-water (including calculated method detection limits), ground-water, and surface-water samples

[µg/L, micrograms per liter; %, percent; RSD, relative standard deviation; MDL, method detection limit; --, not applicable; <, less than; ND, not determined]

Compound name	Spike amount (µg/L)	Mean% recovery			% RSD			Initial MDL (µg/L)
		Reagent	Ground	Surface	Reagent	Ground	Surface	
1,4-Dichlorobenzene	4.0	44.38	48.34	64.62	10.53	11.03	7.46	
	.5	29.94	45.15	49.63	13.77	20.55	6.65	0.28
17*beta*-Estradiol	16.0	75.03	67.03	79.10	3.93	10.06	3.16	1.64
	2.0	35.77	39.73	38.11	52.29	84.25	77.13	
1-Methylnaphthalene	4.0	69.71	68.09	77.35	2.58	3.47	3.87	
	0.5	58.17	69.53	68.34	14.98	5.67	5.78	.13
2,6-Dimethylnaphthalene	4.0	69.70	67.82	76.86	2.36	3.69	5.12	
	.5	54.47	65.55	67.50	11.85	9.21	6.29	.10
2-Methylnaphthalene	4.0	67.78	66.20	77.62	3.06	3.49	4.12	
	.5	55.44	68.34	68.23	15.12	7.17	6.51	.13
3*beta*-Coprostanol	16.0	76.38	76.72	56.90*	8.93	26.15	9.85	
	2.0	81.98	84.11	56.95*	10.58	20.49	11.80	.52
3-Methyl-1H-indole	4.0	81.66	67.04	82.42	5.89	10.91	7.27	
(skatol)	.5	50.42	45.39	33.92	39.49	64.38	66.59	.30
4-Cumylphenol	4.0	78.49	79.38	71.98	2.44	7.84	4.05	
	.5	58.85	52.27	50.94	41.38	66.64	50.59	.37
4-*n*-Octylphenol	4.0	79.04	71.78	71.22	2.81	7.83	7.50	
	.5	38.49	39.97	42.55	57.43	75.09	72.90	.33
4-*tert*-Octylphenol	4.0	82.62	85.15	81.62*	3.03	8.56	7.52	
	.5	43.06	42.09	42.02*	56.19	77.60	76.32	.37
5-Methyl-1H-benzotriazle	16.0	99.03	88.25	108.46*	2.40	14.05	11.42	.92
	2.0	107.15	123.20	353.25*	22.14	16.87	27.56	
Acetophenone	4.0	82.30	79.46	83.05	1.50	3.30	3.25	
	.5	73.40	85.94	94.40	6.14	3.94	6.08	.09
Acetyl-hexamethyl-	4.0	74.80	78.15	65.80	3.97	6.38	6.48	
tetrahydro-naphthalene (AHTN)	.5	76.06	76.95	67.30	7.81	5.22	3.83	.12
Anthracene	4.0	72.86	71.53	73.45	3.27	3.07	6.35	
	.5	72.93	61.30	59.71	9.67	14.68	16.98	.11
Anthraquinone	4.0	83.75	77.09	81.89	4.10	5.35	6.15	
	.5	94.80	97.60	109.10	7.20	6.37	7.13	.11
Benzo[*a*]pyrene	4.0	75.95	70.76	69.38	3.36	4.18	10.49	
	.5	65.06	68.51	51.64	7.81	24.16	11.86	.08
Benzophenone	4.0	87.42	88.66	89.91*	3.59	4.18	4.65	
	.5	95.90	90.74	90.70*	7.99	5.50	4.84	.12
beta-Sitosterol	16.0	100.70	97.89	70.16	9.33	16.73	7.75	
	2.0	92.55	100.54	84.25	11.10	19.24	8.04	.60
beta-Stigmastanol	16.0	97.3	98.44	63.71	10.13	16.31	6.00	
	2.0	101.40	96.09	73.35	11.71	19.58	12.65	.72
Bisphenol A	4.0	74.25*	68.36	65.15	3.98	8.92	5.46	.38
	.5	28.16*	37.51	55.56	55.91	89.92	61.15	
Bromacil	4.0	85.02	83.29	85.51	3.72	4.20	2.03	
	.5	119.30	116.11	110.40	5.39	5.66	3.17	.10

Table 4. Wastewater method mean bias and variability of spike recovery data for eight replicates with compounds spiked at two concentrations that range from 0.5 to 80 micrograms per liter in reagent-water (including calculated method detection limits), ground-water, and surface-water samples—Continued

Compound name	Spike amount (µg/L)	Mean% recovery			% RSD			Initial MDL (µg/L)
		Reagent	Ground	Surface	Reagent	Ground	Surface	
Caffeine	4.0	83.04*	87.20	82.55*	2.86	2.96	2.41	
	.5	89.90*	87.20	82.30*	6.72	6.99	6.22	0.09
Camphor	4.0	79.00	77.86	77.33*	2.02	2.88	1.54	
	.5	80.05	75.05	51.51*	6.95	3.50	3.90	.09
Carbazole	4.0	81.60	78.91	84.10*	4.55	3.70	6.50	
	.5	93.70	93.94	86.00*	7.86	5.65	4.63	.11
Chlorpyrifos	4.0	75.66	78.18	69.27	5.26	7.01	6.45	
	.5	91.90	84.79	79.60	5.13	7.00	3.71	.08
Cholesterol	16.0	96.12*	96.60	54.66*	10.23	22.25	9.37	
	2.0	27.48*	95.80	52.90*	13.27	17.13	47.22	.71
Cotinine	4.0	49.82	82.34	75.58*	2.32	2.86	2.78	
	.5	65.88	89.09	66.38*	8.44	4.85	4.62	.33
Diazinon	4.0	78.16	82.25	71.40*	3.32	6.88	4.62	
	.5	92.70	89.14	73.90*	4.48	5.95	4.31	.07
Ethynyl estradiol	16.0	67.10	66.66	50.75	5.71	26.24	5.42	2.08
	2.0	33.09	32.01	35.59	55.05	81.25	74.75	
Fluoranthene	4.0	74.69	77.49	70.29	2.84	3.82	6.11	
	.5	82.39	39.01	71.24	6.35	7.42	3.18	.08
Hexahydrohexamethyl-cyclo-pentabenzopyran (HHCB)	4.0	73.02*	75.70	66.64*	3.77	5.64	5.82	
	.5	77.59*	73.76	56.10*	6.85	4.63	6.83	.08
Indole	4.0	79.44	78.07	85.74	2.43	3.81	4.62	
	.5	73.84	68.53	55.05	12.14	17.63	16.87	.14
Isoborneol	4.0	80.93	79.05	81.14	2.35	2.92	1.52	
	.5	88.20	80.86	73.02	8.07	4.36	5.65	.11
Isophorone	4.0	86.48*	77.35*	87.53*	14.45	3.52	25.43	
	.5	85.80*	43.31*	58.60*	11.64	28.46	6.30	.19
Isoquinoline	4.0	85.41	85.33	83.78	2.60	4.58	4.58	
	.5	84.36	80.98	92.30	8.21	7.83	6.73	.11
Menthol	4.0	81.46	79.47	81.15	2.46	2.88	2.02	
	.5	86.70	79.94	68.83	5.75	2.40	6.84	.08
Metalaxyl	4.0	80.56	85.51	76.73	3.19	7.02	1.13	
	.5	48.00	90.86	83.84	4.90	5.35	4.25	.08
Methyl salicylate	4.0	82.98	77.04	82.16	2.37	2.51	1.86	
	.5	87.50	84.95	84.00	5.94	3.70	4.38	.08
Metolachlor	4.0	77.44	82.48	71.1	3.86	6.91	4.09	
	.5	91.40	88.57	79.66	5.53	6.32	4.09	.08
N,N-diethyl-*meta*-toluamide (Deet)	4.0	85.15	96.38	90.45*	3.88	4.63	6.92	
	.5	101.90	100.34	87.00*	9.25	6.22	4.11	.14
Naphthalene	4.0	60.07*	66.20	76.72	5.02	3.98	3.24	
	.5	56.14*	66.41	66.22	17.56	7.66	4.07	.15
para-Cresol	4.0	85.49	71.58	85.44	4.83	7.25	4.14	
	.5	35.70	36.57	41.07	51.73	75.13	71.38	.27
Phenanthrene	4.0	77.95	75.47	74.22	1.78	2.58	5.00	
	.5	79.76	73.62	72.17*	6.36	3.46	3.01	.08
Phenol	4.0	86.25	98.16	89.05*	2.87	10.60	3.20	
	.5	92.50	254.65	95.88	7.84	65.64	43.27	.11
Prometon	4.0	83.26	84.75	77.67	2.65	6.40	2.25	
	.5	101.00	96.57	91.00	7.54	7.90	5.39	.12

Table 4. Wastewater method mean bias and variability of spike recovery data for eight replicates with compounds spiked at two concentrations that range from 0.5 to 80 micrograms per liter in reagent-water (including calculated method detection limits), ground-water, and surface-water samples—Continued

Compound name	Spike amount (µg/L)	Mean% recovery			% RSD			Initial MDL (µg/L)
		Reagent	Ground	Surface	Reagent	Ground	Surface	
Pyrene	4.0	73.84	77.27	69.26	3.03	3.88	6.21	
	.5	81.18	77.86	71.02	5.81	9.22	3.21	0.08
Tri(2-chloroethyl)	4.0	84.25	85.26	79.07*	3.34	5.81	1.21	
phosphate	.5	103.10	91.77	77.80*	5.04	4.87	4.09	.08
Tri(dichloroisopropyl)	4.0	79.86	84.62	71.68*	5.40	7.52	4.95	
phosphate	.5	96.40	96.00	72.30*	5.29	10.80	4.41	.08
Tributyl phosphate	4.0	87.53	98.24	87.70	3.88	5.66	7.00	
	.5	112.40	17.37	122.70	5.97	7.42	4.54	.10
Triclosan	4.0	84.50*	76.93	80.42*	5.00	6.73	5.18	.48
	.5	69.21*	78.50	85.63*	31.68	61.58	100.65	
Triethyl citrate	4.0	84.02	83.78	78.80	2.12	5.62	2.05	
(ethyl citrate)	.5	98.20	93.37	96.30	5.59	5.63	3.74	.09
Triphenyl phosphate	4.0	74.94*	81.98	69.40*	6.07	6.31	5.92	
	.5	90.00*	93.37	80.30*	4.48	11.74	4.25	.06
Tri(2-butoxyethyl)	4.0	79.47	82.11	78.49*	6.37	7.66	5.20	
phosphate	.5	103.40	115.43	90.40*	12.52	9.44	6.32	.20
Compounds with low recovery[1], high variable recovery (RSD)[1], unstable instrument response[2], or from a technical mixture[3] to be reported with an "E" code (estimated concentration)								
1,4-Dichlorobenzene[1]	4.0	44.38	48.34	64.62	10.53	11.03	7.46	
	.5	29.94	45.15	49.63	13.77	20.55	6.65	.28
17*beta*-Estradiol[1]	16.0	75.03	67.03	79.10	3.93	10.06	3.16	1.64
	2.0	35.77	39.75	38.11	52.29	84.25	77.13	
3-*tert*-Butyl-4-	4.0	51.42	24.88	22.05	46.23	107.68	106.99	3.07
hydroxyanisole (BHA)[1]	.5	17.64	19.42	16.82	13.44	51.47	27.53	
Bromoform[1]	4.0	54.58	62.75	71.80	5.39	5.39	4.03	
	.5	43.03	51.14	57.23	27.56	19.74	6.53	.18
Carbaryl[2]	4.0	101.24	86.00	100.06*	4.79	12.06	3.53	
	.5	161.10	132.80	155.20*	13.19	18.04	5.01	.44
Dichlorvos[1]	4.0	6.7	23.17	31.31	44.73	43.07	23.11	
	.5	14.24	9.30	48.55	44.38	27.02	37.25	.10
d-Limonene[1]	4.0	29.58	34.11	50.70	16.99	17.30	14.35	
	.05	18.51	18.46	23.73	19.06	34.73	26.80	.05
Equilenin[1]	4.0	58.02	27.58	39.73	19.99	81.45	28.61	1.80
	.5	1.79	16.95	21.43	49.15	55.79	110.32	
Estrone[1]	4.0	84.33	28.34	129.58	18.91	39.31	45.61	
	.5	21.22	30.67	52.53	46.82	74.20	68.84	1.12
Isopropylbenzene	4.0	33.24	39.07	53.2	15.16	13.57	13.14	
(cumene)[1]	.5	20.64	27.98	34.88	12.42	24.49	13.46	.04
Nonylphenol, diethoxy-	64.0	78.30	79.84	61.15*	6.34	6.40	7.70	
(total, NPEO2)[3]	8.0	83.69	89.55	98.94*	12.59	35.26	5.30	2.52
Octylphenol, diethoxy-	.8	122.59	118.58	61.42*	2.24	14.04	7.63	.04
(OPEO2)[3]	.1	110.67	159.20	<0.0*	17.33	2.39	ND	
Octylphenol,	16.0	75.31	73.42	68.06	4.86	9.52	7.16	.29
monoethoxy-(OPEO1)[3]	2.0	45.18	44.41	65.93	42.73	76.05	52.89	

Table 4. Wastewater method mean bias and variability of spike recovery data for eight replicates with compounds spiked at two concentrations that range from 0.5 to 80 micrograms per liter in reagent-water (including calculated method detection limits), ground-water, and surface-water samples—Continued

Compound name	Spike amount (µg/L)	Mean% recovery			% RSD			Initial MDL (µg/L)
		Reagent	Ground	Surface	Reagent	Ground	Surface	
para-Nonylphenol (total)[3]	80.0	73.62*	79.56	64.94*	5.45	8.44	5.90	
	10.0	36.78	36.95	38.40*	53.73	88.83	73.91	6.40
Pentachlorophenol[2]	4.0	80.49	76.50	90.66	6.25	9.11	3.14	.39
	.5	111.35	92.43	62.07	28.06	45.63	43.74	
Tetrachloroethylene[1]	4.0	25.36	33.05	41.65	16.34	12.91	13.48	
	.5	18.49	36.46	28.29	10.39	22.51	15.05	.03
Surrogate compounds								
Caffeine-$^{13}C_3$	2.0	91.33	90.00	86.82	2.81	2.79	2.58	--
	.5	80.10	84.91	82.56	3.75	4.38	6.15	
Fluoranthene-d_{10}	2.0	73.17	79.53	68.98	2.66	3.18	2.47	--
	.5	71.60	71.43	83.45	2.59	4.76	4.23	
Bisphenol A-d_3	2.0	40.42	41.27	67.55	3.66	6.33	3.91	--
	.5	28.12	65.75	73.13	61.67	100.80	88.18	
Decafluorobiphenyl	2.0	35.10	70.90	55.18	4.89	6.06	9.01	--
	.5	78.13	60.43	53.64	21.36	24.38	11.36	

[1]Concentration is estimated because recovery is less than 60 percent or variability is greater than 25 percent RSD.
[2]Concentration is estimated because of unstable instrument response.
[3]Concentration is estimated because the reference standard is from a technical mixture.
*Percent recovery corrected for background concentration in the unspiked sample.

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 spike level so that the compound would be detected in each of the replicate reagent-water samples. Initial MDLs that were calculated by using fortified concentrations higher than the approved spike amount have been defined as estimated MDLs, and have been footnoted as such in table 5. Initial MDLs that were calculated from this procedure for single-component compounds (excluding hormones and sterols) ranged from 0.03 to 0.48 µg/L and averaged 0.15 µg/L. Initial MDLs for the sterols, hormones, and multicomponent *para*-NP compounds are greater than 0.15 µg/L.

The initial minimum reporting levels (MRLs) have been set higher (two to five times for most compounds) than the calculated initial MDLs (table 5). This precaution reduces the risk of reporting that a compound is undetected (less than the MRL), when it is actually in the sample near the MDL concentration (Childress and others, 1999). All qualitatively identified compounds detected less than the MRL are reported as estimated, regardless of the established MRL, because the wastewater method is classified as an "information-rich" method, as are other mass spctrometric methods (Childress and others, 1999).

Calculation of the MDL over a long time (6 to 12 months), including results from 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 1 µg/L will be used routinely throughout the year to calculate LT–MDLs for the wastewater method. The initial MDLs and initial MRLs will be updated

Table 5. Wastewater method initial detection limits calculated from the recovery variability data reported in table 4 using the eight replicate reagent-water samples with compound concentrations that range from 0.5 to 80 micrograms per liter

[All concentrations in micrograms per liter; RSD, relative standard deviation; MDL, method detection limit; MRL, minimum reporting level]

Compound name	Spike amount	Mean recovery	RSD	Initial MDL	Initial MRL
1-Methylnaphthalene	0.5	0.291	0.044	0.13	0.5
2,6-Dimethylnaphthalene	.5	.272	.032	.10	.5
2-Methylnaphthalene	.5	.277	.042	.13	.5
3*beta*-Coprostanol	2.0	1.640	.173	.52	2.0
3-Methyl-1H-indole (skatol)	.5	.252	.100	.30	1.0
4-Cumylphenol	.5	.294	.122	.37	1.0
4-*n*-Octylphenol	.5	.192	.110	.33	1.0
4-*tert*-Octylphenol	.5	.413	.123	.37	1.0
5-Methyl-1H-benzotriazle[1]	16.0	15.848	.307	.92	2.0
Acetophenone[1]	.5	.367	.030	.09	.5
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) [1]	.5	.380	.041	.12	.5
Anthracene	.5	.365	.035	.11	.5
Anthraquinone	.5	.474	.036	.11	.5
Benzo[*a*]pyrene[1]	.5	.325	.025	.08	.5
Benzophenone	.5	.479	.039	.12	.5
beta-Sitosterol	2.0	1.851	.199	.60	2.0
beta-Stigmastanol	2.0	2.028	.241	.72	2.0
Bisphenol A[1]	4.0	2.970	.127	.38	1.0
Bromacil	.5	.596	.032	.10	.5
Caffeine[1]	.5	.450	.031	.09	.5
Camphor[1]	.5	.400	.028	.09	.5
Carbazole	.5	.469	.037	.11	.5
Chlorpyrifos[1]	.5	.460	.025	.08	.5
Cholesterol	2.0	.550	.237	.71	2.0
Cotinine	.5	.329	.111	.33	1.0
Diazinon[1]	.5	.464	.022	.07	.5
Ethynyl estradiol[1]	16.0	1.736	.693	2.08	5.0
Fluoranthene[1]	.5	.412	.250	.08	.5
Hexahydrohexamethyl-cyclo-pentabenzopyran (HHCB)	.5	.388	.027	.08	.5
Indole	.5	.369	.045	.14	.5
Isoborneol	.5	.441	.036	.11	.5
Isophorone	.5	.215	.063	.19	.5
Isoquinoline	.5	.422	.035	.11	.5
Menthol[1]	.5	.434	.025	.08	.5
Metalaxyl[1]	.5	.240	.025	.08	.5
Methyl salicylate[1]	.5	.438	.025	.08	.5

Table 5. Wastewater method initial detection limits calculated from the recovery variability data reported in table 4 using the eight replicate reagent-water samples with compound concentrations that range from 0.5 to 80 micrograms per liter—Continued

Compound name	Spike amount	Mean recovery	RSD	Initial MDL	Initial MRL
Metolachlor[1]	0.5	0.457	0.025	0.08	0.5
N,N-diethyl-*meta*-toluamide (Deet)	.5	.510	.048	.14	.5
Naphthalene	.5	.281	.049	.15	.5
para-Cresol	.5	.179	.092	.27	1.0
Phenanthrene[1]	.5	.399	.026	.08	.5
Phenol	.5	.463	.036	.11	.5
Prometon	.5	.505	.039	.12	.5
Pyrene[1]	.5	.406	.025	.08	.5
Tri(2-chloroethyl) phosphate[1]	.5	.516	.030	.08	.5
Tri(dichloroisopropyl) phosphate[1]	.5	.482	.027	.08	.5
Tributyl phosphat	.5	.562	.033	.10	.5
Triclosan[1]	4.0	3.380	.159	.48	1.0
Triethyl citrate (ethyl citrate) [1]	.5	.491	.028	.09	.5
Triphenyl phosphate[1]	.5	.450	.020	.06	.5
Tri(2-butoxyethyl) phosphate	.5	.517	.067	.20	.5
1,4-Dichlorobenzene	.5	.150	.093	.28	.5
Compounds with low recovery, high variable recovery (RSD), unstable instrument response, or from a technical mixture to be reported with an "E" code (estimated concentration)					
17*beta*-Estradiol[1]	16.0	12.000	.547	1.64	5.0
3-*tert*-Butyl-4-hydroxyanisole (BHA)	4.0	2.057	1.020	3.06	5.0
Bromoform	.5	.273	.059	.18	.5
Carbaryl	.5	.806	.147	.44	.5
Dichlorvos	.5	.071	.032	.10	1.0
d-Limonene[1]	.5	.093	.017	.05	.5
Equilenin	4.0	2.321	.598	1.80	5.0
Estrone	.5	.106	.373	1.12	5.0
Isopropylbenzene (cumene)[1]	.5	.103	.013	.04	.5
Nonylphenol, diethoxy-(total, NPEO2)	8.0	6.695	.840	2.52	5.0
Octylphenol, diethoxy-(OPEO2)[1]	.8	.981	.014	.04	1.0
Octylphenol, monoethoxy-(OPEO1)[1]	16.0	12.050	.096	.29	1.0
para-Nonylphenol (total)	10.0	3.678	2.133	6.40	5.0
Pentachlorophenol[1]	4.0	3.220	.128	.39	2.0
Tetrachloroethylene[1]	.5	.092	.010	.03	.5

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

annually by using data acquired from the NWQL (Childress and others, 1999).

SAMPLE PRESERVATION AND HOLDING TIMES

Whole-water samples are preserved from biodegradation (Ogawa and others, 1981) in the field by filtering them through a 0.7-µm nominal pore diameter, glass-fiber filter. Removing suspended sediment also is required for processing samples by SPE. When the sample is received at the laboratory, 60 g of NaCl is added prior to refrigeration at 4ºC, further augmenting sample preservation. It might be possible to add NaCl to samples in the field, thus improving the timeliness of sample preservation, as well as extending time requirements for shipping samples to the laboratory. After these considerations for sample preservation have been evaluated more thoroughly, a holding-time study is planned to calculate a statistically acceptable holding time. Until then, to ensure that samples are processed in a timely manner, the holding time for the wastewater method has been set at 14 days from the date of sample collection.

SUMMARY

The U.S. Geological Survey (USGS) National Water Quality Laboratory and National Research Program have developed an analytical method for the determination of 67 compounds typically found in domestic and industrial wastewater. The wastewater 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. Water samples are filtered and the compounds are isolated by solid-phase extraction and determined by capillary-column gas chromatography/mass spectrometry. The method focuses on the determination of compounds that are an indicator of wastewater and compounds that have been chosen on the basis of their endocrine-disrupting potential or toxicity. 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, flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, polycyclicaromatic hydrocarbons, and high-use domestic pesticides.

Average recovery of all method compounds for short-term single-operator results in reagent-water samples fortified at 4 micrograms per liter was 74 ± 7 percent relative standard deviation. Initial method detection limits for single-component compounds (excluding hormones and sterols) averaged 0.15 microgram per liter.

The high frequency of compounds that were detected at environmentally significant concentrations for 3 years with the continuous liquid-liquid extraction wastewater method demonstrates the capability of identifying anthropogenic contaminants over a wide range of sample matrices. Many compounds are recognized endocrine-system disrupters (alkylphenols, alkylphenol polyethoxylates, and bisphenol A, for example), whereas others, such as caffeine, musk fragrances, and fecal sterols, are excellent indicators of wastewater. Even though the method is not particularly sensitive for the underivatized fecal sterols or hormones, it has proven to be effective for identifying their presence in wastewater.

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