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Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment

Mark R. Burkhardt*, Rhiannon C. ReVello, Steven G. Smith, Steven D. Zaugg

U.S. Geological Survey, Box 25046, MS 407, Denver, CO 80225-0046, USA

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Abstract

A broad range of organic compounds is recognized as environmentally relevant for their potential adverse effects on human and ecosystem health. This method was developed to better determine the distribution of 61 compounds that are typically associated with industrial and household waste as well as some that are toxic and known (or suspected) for endocrine-disrupting potential extracted from environmental sediment samples. Pressurized liquid extraction (PLE) coupled with solid-phase extraction (SPE) was used to reduce sample preparation time, reduce solvent consumption to one-fifth of that required using dichloromethane-based Soxhlet extraction, and to minimize background interferences for full scan GC/MS analysis. Recoveries from spiked Ottawa sand, commercially available topsoil, and environmental stream sediment, fortified at 4–720 μg per compound, averaged 76 ± 13%. Initial method detection limits for single-component compounds ranged from 12.5 to 520 μg/kg, based on 25 g samples. Results from 103 environmental sediment samples show that 36 out of 61 compounds (59%) were detected in at least one sample with concentrations ranging from 20 to 100,000 μg/kg. The most frequently detected compound, beta-sitosterol, a plant sterol, was detected in 87 of the 103 (84.5%) environmental samples with a concentration range 360–100,000 μg/kg. Results for a standard reference material using dichloromethane Soxhlet-based extraction are also compared.

Keywords: Pressurized liquid extraction; Solid-phase extraction; Sediment

1. Introduction

Industrial and domestic waste needs to be managed effectively to meet the challenges of increasing population, stringent regulatory requirements, and aging wastewater-treatment facilities in the United States. In 2002, the U.S. Geological Survey (USGS) reported results for a broad range of emerging organic wastewater compounds (pharmaceuticals, hormones, antibiotics, and other indicators of industrial and household waste) in a reconnaissance of streams throughout the United States [1]. One of the five analytical methods developed to support this study [2] uses gas chromatography/mass spectrometry (GC/MS) for determining less-polar compounds (not antibiotics or pharmaceuticals) in water samples. This paper describes the development of an analogous analytical sediment method needed to further understanding of the occurrence, fate, and transport of wastewater compounds at significant concentrations in environmental sediment samples.

The U.S. Environmental Protection Agency (USEPA) regulates many compounds, and appropriate analytical methods generally are available [3] to monitor them in industrial wastes or in discharge from wastewater-treatment facilities. However, because of the complexity of sample matrices (soils, sediments, suspended sediments), specific analytical methods are required to determine polar and nonpolar organic compounds that might affect water quality. Other compounds known to be toxic to aquatic life are currently (2004) unregulated even though some, such as nonylphenol

* Corresponding author. Tel.: +1 303 236 3250; fax: +1 303 236 3499.
E-mail address: mrburk@usgs.gov (M.R. Burkhardt).

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Table 1
Waste indicator sediment method compound names, endocrine-disrupting potential, and possible compound uses

Compound name	HSA[a]	CAS number	Possible compound uses or sources[b]
1,4-Dichlorobenzene	–	106-46-7	Moth repellant, fumigant, deodorant
1-Methylnaphthalene	–	90-12-0	2–5% of gasoline, diesel fuel, or crude oil
2,6-Dimethylnaphthalene	–	581-42-0	Present in diesel/kerosene (trace in gasoline)
2-Methylnaphthalene	–	91-57-6	2–5% of gasoline, diesel fuel, or crude oil
3,4-Dichlorophenyl isocyanate	–	102-36-3	Degradate of diuron, a noncrop herbicide
3beta-Coprostanol	–	360-68-9	Carnivore fecal indicator
3-Methyl-1*H*-indole (skatol)	–	83-34-1	Fragrance and stench in feces and coal tar
3-*tert*-Butyl-4-hydroxyanisole (BHA)	E	25013-16-5	Antioxidant, general preservative
4-Cumylphenol	–	599-64-4	Nonionic detergent metabolite
4-*n*-Octylphenol	E	1806-26-4	Nonionic detergent metabolite
4-*tert*-Octylphenol	E	140-66-9	Nonionic detergent metabolite
Acetophenone	–	98-86-2	Fragrance in detergent and tobacco, flavor in beverages
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN, tonalide)	–	21145-77-7	Musk fragrance (widespread use) persistent in groundwater
Anthracene	–	120-12-7	Wood preservative, component of tar, diesel, or crude oil, CP
Anthraquinone	–	84-65-1	Manuf. dye/textiles, seed treatment, bird repellant
Atrazine	E	1912-24-9	Selective triazine herbicide
Benzo[*a*]pyrene	A	50-32-8	Regulated PAH, used in cancer research, CP
Benzophenone	E	119-61-9	Fixative for perfumes and soaps
beta-Sitosterol	–	83-46-5	Plant sterol
beta-Stigmastanol	–	19466-47-8	Plant sterol
Bisphenol A	E	80-05-7	Manuf. polycarbonate resins, antioxidant, FR
Bromacil	–	314-40-9	H (GUP), >80% noncrop usage on grass/brush
Camphor	–	76-22-2	Flavor, odorant, ointments
Carbazole	–	86-74-8	I, Manuf. dyes, explosives, and lubricants
Chlorpyrifos	–	2921-88-2	I, domestic pest and termite control (domestic use restricted as of 2001)
Cholesterol	–	57-88-5	Often a fecal indicator, also a plant sterol
Diazinon	–	333-41-5	I, >40% nonagricultural usage, ants, flies
Diethyl phthalate	–	84-66-2	Plasticizer for polymers and resins
Diethylhexyl phthalate	E	117-81-7	Plasticizer for polymers and resins, pesticides
d-Limonene	–	5989-27-5	F, antimicrobial, antiviral, fragrance in aerosols
Fluoranthene	–	206-44-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB, galaxolide)	–	1222-05-5	Musk fragrance (widespread use) persistent in groundwater
Indole	–	120-72-9	Pesticide inert ingredient, fragrance in coffee
Isoborneol	–	124-76-5	Fragrance in perfumery, in disinfectants
Isophorone	–	78-59-1	Solvent for lacquer, plastic, oil, silicon, resin
Isopropylbenzene (cumene)	–	98-82-8	Manuf. phenol/acetone, fuels and paint thinner
Isoquinoline	–	119-65-3	Flavors and fragrances
Menthol	–	89-78-1	Cigarettes, cough drops, liniment, mouthwash
Metalaxyl	–	57837-19-1	H, F (GUP), mildew, blight, pathogens, golf/turf
Methyl salicylate	–	119-36-8	Liniment, food, beverage, UV-absorbing lotion
Metolachlor	–	51218-45-2	H (GUP), indicator of agricultural drainage
N,*N*-Diethyl-*meta*-toluamide (Deet)	–	134-62-3	I, urban uses, mosquito repellent
Naphthalene	–	91-20-3	Fumigant, moth repellent, major component (about 10%) of gasoline
Nonylphenol, diethoxy- (total, NPEO2)	E	26027-38-3	Nonionic detergent metabolite
Nonylphenol, monoethoxy- (total, NPOE1)	E	NA	Nonionic detergent metabolite
Octylphenol, diethoxy- (OPEO2)	E	26636-32-8	Nonionic detergent metabolite
Octylphenol, monoethoxy- (OPEO1)	E	26636-32-8	Nonionic detergent metabolite
para-Cresol	–	106-44-5	Wood preservative
para-Nonylphenol (total)	E	84852-15-3	Nonionic detergent metabolite
Pentachlorophenol	T	87-86-5	H, F, wood preservative, termite control
Phenanthrene	–	85-01-8	Manuf. explosives, component of tar, diesel fuel, or crude oil, CP
Phenol	–	108-95-2	Disinfectant, manuf. several products, leachate
Prometon	–	1610-18-0	H (noncrop only), applied prior to blacktop
Pyrene	–	129-00-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP
Tetrabromodiphenyl ether	–	40088-47-9	Fire retardant
Tri(2-butoxyethyl)phosphate	–	78-51-3	Flame retardant
Tri(2-chloroethyl)phosphate	–	115-96-8	Plasticizer, flame retardant
Tri(dichloroisopropyl)phosphate	–	13674-87-8	Flame retardant
Tributyl phosphate	–	126-73-8	Antifoaming agent, flame retardant
Triclosan	–	3380-34-5	Disinfectant, antimicrobial (concern for acquired microbial resistance)
Triphenyl phosphate	–	115-86-6	Plasticizer, resin, wax, finish, roofing paper, FR

HSA, hormone system affected; A, androgen; E, estrogen/testosterone; T, thyroid; CAS, Chemical Abstract Service; F, fungicide; H, herbicide; I, insecticide; GUP, general use pesticide; FR, flame retardant; WW, wastewater; Manuf., manufactured; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; UV, ultraviolet; NA, not applicable; –, no data.

[a] http://www.ourstolenfuture.org/Basics/chemlist.html, 2003.

[b] ChemFinder Webserver, 2001, http://chemfinder.camsoft.com; National Toxicology Program, 2001, http://ntpserver.niehs.nih.gov/Main_Pages/Chem-HS.html; National Institute of Standards and Technology, 2001; Spectrum Laboratories, Inc., 2001, http://www.speclab.com/compound/chemabc.htm; Health-Central.com, 2001, http://www.rxlist.com; EXtension TOXicology NETwork, 2001, http://ace.orst.edu/info/extoxnet.

ethoxylates (NPEOs), are on the USEPA Toxic Substance Control Act Priority Testing List [4]. To meet some of the challenges of assessing the effect of wastewater discharge on water quality, the U.S. Geological Survey's (USGS) National Water Quality Laboratory (NWQL) developed an analytical method that measures representative wastewater compounds from various chemical classes in environmental sediment samples.

Traditional methods for determining organic compounds in environmental sediment or soil samples generally are optimized for one or two classes of compounds and use organic solvent extraction followed by analysis with gas chromatography (GC) with various detectors or MS detection [5,6]. These hydrophobic organic compounds, including the alkylphenol ethoxylate nonionic surfactants and their degradates [7–11], food additives [12], fragrances [13–16], flame retardants [17–19], plasticizers [20], industrial solvents [20], disinfectants [18,21], fecal sterols [22], polycyclic aromatic hydrocarbons (PAH) [23], and high-use domestic pesticides [24], may be associated with particulates or sediments, or both, in the environment [19,20,23–28]. Environmental sediment samples containing these compounds generally require extensive extract cleanup procedures to provide the low matrix background extract that can be analyzed routinely in a production laboratory and yet retain most of the compounds of interest. Because most existing environmental sediment methods generally use labor-intensive Soxhlet extraction and require extensive extract cleanup steps, it has become imperative to implement more efficient, environmental-friendly methods. Analytical methods that use SPE as an alternative to liquid–liquid extraction have been implemented for the determination of pesticides and wastewater compounds in water [5,29–34]. These SPE methods are attractive because they are rapid, efficient, use much less solvent than liquid–liquid extraction, and, consequently, are more affordable and produce less toxic waste. Coupling SPE and PLE allows for complex matrices to be extracted, matrix interferences minimized, and full-scan GC/MS analysis to be performed.

This paper describes a method coupling pressurized liquid extraction (PLE) with SPE for analysis of wastewater compounds in sediment. PLE has demonstrated advantages for automation, reduced extraction time, and lower solvent use than conventional Soxhlet extraction. Recently, PLE with subcritical heated water (PLEHW) has been used for extracting polar to moderately polar organic compounds from sediment samples. At temperatures above 250 °C, extraction of nonpolar high-molecular-weight compounds, such as PAHs [35,36], PCBs [37], and brominated flame retardants [38] have been reported. The solubility of solutes in subcritical water increases dramatically [39] with increasing temperature and is largely a function of the decreasing dielectric constant (ϵ) of water. For example, the solubilities of triazine herbicides increase about three-fold with every 25 °C increase in temperature [40]. The addition of a cosolvent has a similar effect on solubility as increasing the temperature and made it possible quantitatively to extract atrazine from beef kidney at a moderately low temperature of 100 °C with an ethanol concentration of 30% [40]. The pressure required for PLEHW must be high enough to maintain water in the liquid state, but otherwise has little effect on ϵ or solubility [41]. The PLEHW of sediments provides more selectivity for compounds than conventional Soxhlet extraction using organic solvents as evidenced by a dramatic reduction in the extraction of the bulk organic nonpolar matrix [36]. Although it is still possible to gain some degree of selectivity using modified PLEHW by varying the modifier concentration, the use of organic cosolvents produces dirtier extracts, which often require cleanup prior to analysis. In a production laboratory where stable reproducible instrument response with minimum maintenance is desirable, extract quality (low matrix background, greater than 60% analyte recovery) is important. PLEHW field extraction of petroleum-contaminated sediment samples with simultaneous absorption onto SPE disks has been reported to produce clean extracts [23]. However, in a laboratory setting, more options are possible for washing, adjusting the pH, and eluting SPE cartridges if the SPE is cleaned up off-line.

The ASE^{TM} 200 is a commercially available PLE instrument produced by Dionex (Sunnyvale, CA, USA), and the process, which also has been termed "accelerated solvent extraction" (ASE), generally uses conventional organic solvents at a temperature of about 100 °C. The upper operating temperature limit of 200 °C for the ASE^{TM} 200 is too low to extract effectively nonpolar high-molecular-weight organic compounds, such as PAHs (about molecular weight 202 or higher) using subcritical water, without the addition of a cosolvent.

The scope of the study described in this paper includes determination of method performance in Ottawa reagent-sand, in stream-sediment samples collected from Cherry Creek near Garland Park, Denver, CO, USA, and in topsoil from a commercially available mixture. Table 1 lists the compounds of interest, endocrine disruption potential, and historical uses. Method performance was determined at two concentrations for each compound (4 and 40 μg spikes for most compounds) in each sediment type. Initial method detection limits (MDL) were determined according to an accepted statistical procedure outlined by the USEPA [42]. The method was also tested on a set of 103 environmental soil, sediment, and suspended-sediment samples collected throughout the United States.

2. Experimental

2.1. Chemicals and reagents

Dichloromethane (DCM), diethyl ether (DEE), acetone, isopropyl alcohol (IPA), and pentane were all pesticide grade or better (B&J Brand, Muskegon, MI, USA). Reagent water, for the dilution buffer and pressurized liquid extraction, was in-house deionized water polished through a Solution

2000 purification system (Solution Consultants, Inc., Jasper, GA, USA). Sodium sulfate, dipotassium hydrogen phosphate, and potassium dihydrogen phosphate were purchased from Fisher Scientific (Fairlawn, NJ, USA). The extraction SPE cartridges (20 ml barrel, packed with 1 g of PSDVB; Oasis polystyrene-divinylbenzene packing material) were purchased from Waters Corp. (Milford, MA, USA), and the Florisil cartridges (6 ml barrel, packed with 1 g of Florisil) were purchased from International Sorbent Technologies (IST, Mid Glamorgan, UK). Internal standards (acenapthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, phenanthrene-d_{10}, perylene-d_{12}) were purchased as a mixture from Supelco (Bellefonte, PA, USA). Surrogate compounds (bisphenol A-d_3, caffeine-$^{13}C_3$ decafluorobiphenyl, fluoranthene-d_{10}) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The sodium sulfate was heated to 450 °C for 4 h before use. All other reagents were used as received.

2.2. Sediment samples

Ottawa reagent-sand (Fisher Scientific, Fairlawn, NJ, USA), stream sediment samples collected from Cherry Creek near Garland Park, Denver, CO, USA, and soil samples from commercially available topsoil mixture were used to describe method performance. Sets of the subsamples were fortified at a lower concentration (4–72 μg) of each compound, and at a higher concentration (40–720 μg) of each compound. In addition, the three sample matrices were extracted and analyzed (unfortified) to determine the background presence of any method compounds. The sediment samples are stored at −20 °C or less to inhibit biological activity until the samples are extracted.

2.3. Pressurized liquid extraction

All samples were extracted using a Dionex (Sunnyvale, CA, USA) ASE 200 accelerated solvent extraction system. Stainless steel extraction cells (22 ml) were used for all extractions. The use of PLE with hot water/IPA to extract wet-sediment samples avoids the need for sample pretreatment (mixing with drying agents and grinding) required when extracting with organic solvent. The use of hot water/IPA also makes it possible to avoid using a separate aliquot of the sample to obtain a dry weight for moisture corrections, because the dry sample weight was obtained after extraction at 200 °C. A glass fiber extraction thimble (79 mm × 19 mm ID × 1.5 mm thick, Whatmann International, Inc., Maidstone, UK) was placed in a 22-ml cell prior to loading with 15–30 g of wet sediment. If the amount of sediment was insufficient to fill the cell, the dead volume was filled with pre-conditioned Ottawa sand (heated to 450 °C for 4 h) to provide consistent extract volumes. The use of filter papers at the bottom of the extraction cell was not required because the glass fiber thimble provided the necessary filtration capacity.

Three milliliters of pentane was added to each 200 °C collection vial to provide a cooling effect and an upper organic barrier to help prevent sample compound volatilization losses. Pentane also had the added advantage of providing a solvent for the hydrophobic compounds to deter their mixing into the coextracted matrix material. It also was essential to use an appropriate volume of pentane (3 ml) so that it would be completely evaporated and the extract would be amenable to SPE cleanup.

Extraction was first performed at 120 °C with water/IPA (50:50, v/v) to obtain the major portion of polar and heat-susceptible compounds, because it is generally recognized that a moderate temperature is needed to avoid hydrolysis and thermal degradation in wet sediment matrices [43]. The same cell then was extracted with water/IPA (20:80, v/v) at 200 °C to obtain the more hydrophobic compounds, such as PAHs (pyrene and higher molecular weight), which are generally more thermally stable. The use of two separate extractions also exhaustively extracts the sediment samples under controlled conditions. All extractions were at 13,800 kPa and each extraction was carried out three times (three 10-min static extraction steps per temperature). Extracts for each temperature were collected in separate 60 ml collection vials. The 60-ml collection vials contained about 40 ml of the sample extract. With concern for possible compound carryover, especially at 200 °C, a series of alternating high matrix spikes and rinses separated by blank sand samples indicated that an additional rinse with dichloromethane between samples was necessary to clean the extraction system. Also, frequent replacement of extraction cell cap seals, O-rings, and frits were important for avoiding leaks and contamination.

2.4. Solid-phase extraction

Dilution of water/IPA extracts, prior to SPE, with phosphate buffer (pH 7) was required to minimize polar compound breakthrough. To facilitate dilution, disposable polypropylene reservoirs (150 ml, Macherey-Nagel GMBH and Co.) are attached to 20 ml SPE cartridges containing 1 g modified polystyrene-divinylbenzene (PSDVB) phase via a Teflon control valve. The SPE cartridge and reservoir are precleaned with 25 ml of the DCM/DEE elution solvent. The Teflon valve is closed and the 200 °C extract is added first to the reservoir. The 60-ml extract collection vial then is rinsed two times with 50 ml of the phosphate buffer. Each rinse is added to the reservoir. The ASE extracts are loaded onto the SPE cartridge at about 20 ml/min by vacuum. After the 200 °C extract is loaded, the 120 °C extract is loaded in a similar manner. The loaded SPE cartridges then are washed with 10 ml reagent water to remove inorganic salts, residual IPA, and interferences. The bulk of the water is removed from the SPE phase by continuing to apply vacuum for 1 min after extract loading has been completed. The SPE cartridge then is dried for an additional 15 min using 2 l/min nitrogen.

About 4 g of sodium sulfate is placed in the 6 ml barrel of a 1-g Florisil SPE cartridge. This sodium sulfate/Florisil

Table 2
Method compound, surrogate, and internal standard retention times, quantitation ions, and confirmation ions

Compound name	Retention time (min)	Quantitation ion (*m*/*z*)	Confirmation ion (*m*/*z*)	Confirmation ion (*m*/*z*)
Isopropylbenzene (cumene)	11.507	105	120	–
Phenol	13.651	94	66	65
1,4-Dichlorobenzene	15.212	146	148	111
d-Limonene	15.819	93	136	121
Acetophenone	17.234	105	120	77
para-Cresol	17.460	107	108	77
Isophorone	19.298	82	138	–
Camphor	20.135	90	105	152
Isoborneol	20.582	95	136	140
Menthol	20.921	95	123	138
Naphthalene	21.123	128	127	102
Methyl salicylate	21.269	120	152	92
Isoquinoline	22.834	129	102	–
Indole	23.418	117	89	–
Diethyl phthalate	23.500	149	177	–
2-Methylnaphthalene	23.568	142	141	115
3,4-Dichlorophenyl isocyanate	23.639	187	189	124
1-Methylnaphthalene	23.869	142	141	115
3-Methyl-1*H*-indole (skatol)	25.120	130	131	–
2,6-Dimethylnaphthalene	25.519	156	141	–
Atrazine	26.550	200	215	202
3-*tert*-Butyl-4-hydroxyanisole (BHA)	26.606	180	165	137
N,*N*-Diethyl-*meta*-toluamide (Deet)	27.983	119	190	91
4-*tert*-Octylphenol	28.320	135	206	107
Nonylphenol, monoethoxy- (total, NPEO1)	28.5–29.5	179	193	207
Benzophenone	28.806	182	105	77
Tributyl phosphate	28.830	99	155	211
para-Nonylphenol (total)	29.7–30.6	135	220	107
Prometon	30.099	210	225	168
Tri(2-chloroethyl)phosphate	30.311	249	251	205
Pentachlorophenol	30.394	266	264	268
4-*n*-Octylphenol	30.448	107	206	–
Diazinon	30.673	304	179	199
Phenanthrene	30.903	178	176	89
Octylphenol, monoethoxy- (OPEO1)	30.903	135	107	179
Anthracene	31.044	178	176	89
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	31.468	243	258	213
Carbazole	31.524	167	139	166
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	31.538	243	258	197
4-Cumylphenol	31.576	197	212	–
Metalaxyl	32.135	206	220	249
Bromacil	32.587	205	207	–
Metolachlor	32.850	162	138	240
Chlorpyrifos	32.878	314	316	197
Anthraquinone	33.095	208	180	152
Fluoranthene	34.134	202	101	203
Triclosan	34.378	288	290	218
Diethylhexyl phthalate	34.700	149	167	279
Pyrene	34.731	202	101	203
Bisphenol A	34.994	213	228	119
Octylphenol, diethoxy- (OPEO2)	35.168	223	135	294
Nonylphenol, diethoxy- (total, NPEO2)	35.7–36.5	237	223	279
Tetrabromodiphenyl ether	35.7	328	326	324
Tri(dichloroisopropyl)phosphate	36.400	379	383	381
Tri(2-butoxyethyl)phosphate	37.054	299	199	125
Triphenyl phosphate	37.176	326	325	215
Benzo[*a*]pyrene	41.431	252	250	126
3beta-Coprostanol	42.927	373	355	388
Cholesterol	43.209	386	301	275
beta-Sitosterol	45.038	414	396	381
beta-Stigmastanol	45.193	416	401	233

Table 2 (*Continued*)

Compound name	Retention time (min)	Quantitation ion (*m*/*z*)	Confirmation ion (*m*/*z*)	Confirmation ion (*m*/*z*)
Surrogates				
Decafluorobiphenyl	18.786	334	265	–
Fluoranthene-d_{10}	34.087	212	106	–
Bisphenol A-d_3	34.947	216	234	–
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	–

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

cartridge is attached below the dried, loaded SPE extraction cartridge prior to elution. The sodium sulfate/Florisil SPE cartridge is used to remove water and matrix-interfering compounds. The combined SPE stack then is eluted with three 10-ml aliquots of DCM/DEE (80:20). The collected elution solvent then is evaporated by using a gentle stream of nitrogen to a final volume of 1 ml. Internal standards are added prior to transferring the extract to an autosampler vial. Compounds then are determined by GC/MS.

2.5. Gas chromatography/mass spectrometry

All sample extracts were analyzed on an Agilent Technologies, Model 5973 gas chromatograph/mass spectrometer. Separations were performed using a 30 m × 0.25 mm inside diameter fused-silica capillary column coated with a 0.50-μm bonded film of 5% polyphenylmethylsilicone (J&W Scientific). A 1 μl volume was injected in a splitless mode (30 s) with an injection port temperature of 290 °C. The oven temperature was programmed as follows: 40 °C (hold 3 min), then ramped at 4 °C/min to 100 °C, and 9 °C/min to 320 °C; with electronic pressure control set for a constant flow of helium carrier gas of 1 mL/min. The MS was set as follows: 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 eV), and full-scan mode from 45 to 450 atomic mass units (amu) for 30 min. Scan 45–550 amu for the last 10 min to detect the brominated flame retardants. Table 2 lists method compound, surrogate, and internal standards retention times, quantification ions, and confirmation ions.

3. Results and discussion

3.1. Development of the method

Conditions for extracting the waste indicator compounds from sediment with pressurized water/IPA were optimized (extraction temperature, extraction cosolvent concentrations, compound recovery). The conditions that allowed the largest set of compounds to be recovered with the highest efficiency, while minimizing the matrix effects, were used for this study.

Because PAHs include a wide range of vapor pressures and solubilities, they are expected to demonstrate a wide range of extraction behavior. If the PAH is completely soluble in the 200 °C water/IPA mixture (up to about chrysene), the high extraction efficiency is likely explained by the extraction mixture interacting with interstitial water, thus causing particles to swell much more than typical solvent extraction. Consequently, the portion of PAH molecules that are highly sequestered in pores are more available than with other solvents that cause less swelling. Another advantage of subcritical water is that the same extraction technique is possible for suspended sediments without drying or fragmenting the filter material, which is usually necessary to obtain acceptable extractions using conventional organic solvents. This advantage of using water over conventional solvents allows suspended material to be processed and extracted in a routine manner without compromising sample integrity by attempting to remove small quantities of sample from the filter, by cutting up the filter material, or by minimizing volatile compound losses caused by excess drying.

Extractions using only water at 120 or 200 °C required the addition of a cosolvent to efficiently extract the high molecular weight nonpolar compounds. Isopropanol was found to be an effective cosolvent (over ethanol or methanol) for extracting selected compounds while minimizing the extraction of natural organic matter (NOM). The use of 80% isopropanol at 200 °C increased the solvating power of the extraction fluid and allowed for efficient extraction of the high-molecular-weight nonpolar compounds.

The use of a two-step, two-temperature extraction on the ASE-200 greatly decreased extract condensation and collection difficulties observed if extractions were carried out at only 200 °C. The use of two extractions allowed for the thermally sensitive compounds, such as phenol, isopropylbenzene, diazinon, chlorpyrifos, and menthol, to be extracted at a lower temperature, thereby increasing the recovery of these compounds from the sediment sample. Using the

two-temperature extraction followed by SPE cleanup also minimized GC/MS maintenance and reproducibility problems caused by dirty (i.e., natural organic matter-rich) extracts.

3.2. Method validation

Reagent-sand samples, stream-sediment samples collected from Cherry Creek near Garland Park, Denver, CO, and soil samples collected from commercially available topsoil mix were used to test method performance. One set of the subsamples was fortified at concentrations ranging from 4 to 72 μg for each compound, and the other set was fortified at concentrations ranging from 40 to 720 μg for each compound. The samples were spiked at the time the samples were placed in the ASE extraction cells. The samples were spiked with analytes of interest and extracted from 1 to 24 h from the time of spiking. This time frame was used to minimize concern about the difference between extracting the samples immediately and letting the samples age. The use of a standard reference material (SRM) was also used to determine the potential of lower recovery using aged samples. The SRM samples have been characterized and aged for greater than 5 years. The recoveries from the presented aged materials show that even for aged samples, the method does perform well. In addition, the three sample matrices were extracted and analyzed unfortified to determine the background presence of any method compounds.

The detection of 15 compounds (anthracene, benzophenone, cholesterol, *para*-cresol, 2,6-dimethylnaphthalene, diethyl phthalate, diethylhexyl phthalate, fluoranthene, indole, isophorone, menthol, naphthalene, OPOE1, phenol, tri(2-chloroethyl)phosphate) in the reagent-sand blank at or less than half the method detection limits emphasizes the ubiquitous nature of several of the method compounds, as well as the importance of avoiding contamination throughout sample collection, preparation, and analysis. Phthalates and preservatives (BHT and related compounds) in the SPE cartridge material and housing often contribute to low-concentration contamination. SPE reservoirs may also contribute phthalate plasticizer compounds and unresolved high-molecular-weight hydrocarbons. Other hydrocarbons and hydrocarbon degradation products can also cause interferences. These potential sources of interference may not introduce method compounds, but may introduce nontarget compounds that are present in the background. For this reason, the analyses of laboratory reagent blanks are particularly important to provide information about the presence of contaminants (most of which are not method compounds). Comparison of the sample with the laboratory reagent blanks is especially important if nontarget compounds are to be identified in full-scan (FS) spectra. If interferences are identified in laboratory blanks (particularly method compounds), cleaning or replacement of parts are necessary to remove interferences. Some individual sample results are qualified because of measured blank contamination. Fortified samples were extracted and analyzed on different days, so comparisons of different matrices and concentrations include day-to-day variation. Mean bias and precision data from the analyses are listed in Table 3. Recovery was corrected for concentration of selected compounds found in the unspiked matrices. The matrix samples were spiked with a known concentration (in micrograms) and recoveries are calculated based on micrograms. The sample concentrations were not converted to microgram per kilogram because of the variable sample size in loading the ASE extraction cells. Environmental sediment samples are weighed, and the results are reported in micrograms per kilogram. Sample showing recovery results less than 60% or precision greater than 25% R.S.D. are qualified because of the low recovery and or large R.S.D. These qualified results can be caused by instrumental or extraction difficulties. Other sample results are also qualified as because the reference standard is from a technical mixture. Percent recoveries were corrected for background analyte concentrations in the unspiked samples.

The median recoveries for all selected compounds in the sand, sediment, and topsoil matrices at the lower spiking range (4–72 μg) were very similar. The selected compound median recovery in the sand was 78.4%, in sediment it was 78.9%, and in topsoil it was 77.2%. Statistical paired means testing demonstrated that the mean recoveries were not statistically different between matrices at the 95% confidence level. The average standard deviations for the corresponding recoveries, however, were statistically different at the 95% confidence level. The average standard deviation in the sand matrix was 12.2%, in sediment it was 20.7%, and in topsoil it was 16.5%. These differences in standard deviations are related to the varying amount of NOM in the matrices used in the validation.

Six compounds were also investigated in the development of this method but were excluded in the final analysis of environmental samples because of high or low extraction recovery, relative standard deviations greater than 30%, or low SPE recovery. These compounds were 5-methyl-1*H*-benzotriazole, caffeine, carbaryl, cotinine, dichlorvos, and triethyl citrate (ethyl citrate). The variable recoveries and standard deviations are thought to be related to the polarity of these compounds and breakthrough on the PSDVB SPE cartridge with the use of greater than 10% organic phase throughout the procedure.

3.3. Method detection limits

Initial MDLs were determined according to the procedure outlined by the U.S. Environmental Protection Agency [34] assuming a 25-g sample size. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the compound concentration is greater than zero. According to the USEPA procedure, at least seven replicate samples are fortified with compounds at concentrations of 2–5 times the calculated MDL. This concentration range was used to calculate initial MDLs for most

Table 3
Wastewater method mean bias and precision of spike recovery data for seven or eight replicates with compounds spiked at two concentrations ranging from 4 to 720 μg per sample in reagent-sand (including calculated method detection limits), stream-sediment, and topsoil samples

Compound name	Spike amount (μg)	Mean % recovery			% R.S.D.			Initial MDL (μg/kg)
		Sand	Stream-sediment	Topsoil	Sand	Stream-sediment	Topsoil	
1,4-Dichlorobenzene	4	70.1	45.4	67.2	7.0	14.0	5.0	27.6
	40	64.6	51.6	64.4	8.6	16.9	10.8	
1-Methylnaphthalene	4	76.7	77.5	77.2	6.5	13.5	3.8	27.8
	40	78.5	78.1	82.6	5.2	8.3	1.0	
2,6-Dimethylnaphthalene	4	75.7	77.0	75.6	5.9	12.1	4.8	24.8
	40	78.5	77.4	82.3	4.6	7.9	1.7	
2-Methylnaphthalene	4	76.7	77.5	77.2	6.5	13.5	3.8	27.8
	40	78.5	78.1	82.6	5.2	8.3	1.0	
3,4-Dichlorophenyl isocyanate[a]	4	43.3	36.3	36.4	24.9	18.0	28.0	60.4
	40	24.9	26.1	31.8	74.3	26.7	28.8	
3beta-Coprostanol	16	105.7	73.2	93.1	15.2	31.7	23.4	360
	160	92.6	77.3	70.2	14.6	12.8	8.3	
3-Methyl-1*H*-indole (skatol)	4	83.1	99.9	78.9	6.7	11.9	8.4	30.9
	40	84.7	106.6	80.2	2.5	10.6	4.0	
3-*tert*-Butyl-4-hydroxyanisole (BHA)[a]	4	79.0	40.6	93.6	22.9	26.9	8.5	101
	40	66.0	38.1	80.5	17.7	45.5	9.5	
4-Cumylphenol	4	85.9	79.6	84.0	7.0	10.6	4.8	33.7
	40	92.9	96.5	92.0	4.8	4.69	6.8	
4-*n*-Octylphenol	4	82.3	77.1	82.5	8.0	10.1	5.2	36.8
	40	89.3	90.5	88.5	5.2	6.34	9.8	
4-*tert*-Octylphenol	4	85.3	82.9	86.7	4.8	10.5	5.1	22.9
	40	87.4	88.5	89.0	3.1	4.73	2.6	
Acetophenone[a]	4	45.0	26.7	28.9	40.0	49.5	67.5	101
	40	53.6	42.2	39.6	13.7	9.35	7.8	
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	4	78.0	79.0	80.4	2.9	10.0	6.1	12.5
	40	83.7	77.4	83.6	3.9	6.11	5.3	
Anthracene	4	78.1	80.3	75.7	4.5	10.9	7.1	19.8
	40	84.2	83.1	79.4	2.9	5.16	2.2	
Anthraquinone	4	84.3	87.0	84.3	5.2	6.22	4.7	24.3
	40	84.4	74.7	85.6	2.7	39.5	2.4	
Atrazine	4	78.7	70.0	66.0	13.4	16.9	15.4	58.9
	40	99.7	92.1	86.6	5.0	7.1	6.9	
Benzo[*a*]pyrene	4	77.8	84.7	75.8	5.6	22.2	7.1	24.6
	40	81.7	79.2	76.9	3.8	5.2	9.5	
Benzophenone	4	88.8	87.9	96.1[b]	6.4	7.8	5.5	31.8
	40	87.5	86.4	95.8[b]	0.9	3.8	3.0	
beta-Sitosterol	16	97.4	123	199	16.7	25.7	28.6	363
	160	82.1	66.8	83.8	10.9	12.9	12.1	
beta-Stigmastanol	16	96.1	73.2	92.8	17.1	27.2	31.4	367
	160	79.8	63.8	72.2	9.7	9.4	9.1	
Bisphenol A[a]	4	64.5	53.2	58.0	8.7	18.1	15.6	31.6
	40	53.5	44.4	59.6	13.5	5.6	8.0	
Bromacil[a]	14	62.8	43.9	48.9	20.7	36.0	39.8	254
	140	78.3	63.6	52.7	5.1	8.1	11.1	
Camphor	4	79.1	70.6	67.6	6.1	12.8	17.1	27.0
	40	87.3	84.6	84.4	1.9	5.9	6.5	
Carbazole	4	82.9	82.0	79.7	4.8	7.5	4.8	22.4
	40	93.2	91.5	91.4	1.3	4.0	4.1	
Chlorpyrifos	4	60.4	62.2	68.3	9.9	29.1	18.9	33.6
	40	92.0	92.3	86.4	7.6	5.7	5.4	
Cholesterol	16	99.3	125	92.4	7.6	19.2	16.9	168
	160	92.3	77.3	70.2	14.6	19.1	12.1	
Diazinon	4	75.8	75.5	76.0	11.5	28.2	13.1	48.7
	40	76.9	70.8	80.2	5.0	10.4	4.5	
Diethyl phthalate[c]	4	58.2	58.3	61.0	14.3	5.7	7.9	46.7
	40	70.3	74.8	82.6	5.6	9.1	9.8	
Diethylhexyl phthalate[c]	4	153	147	129	16.1	25.2	20.6	138
	40	82.9	75.4	58.2	11.2	13.0	5.5	

Table 3 (*Continued*)

Compound name	Spike amount (μg)	Mean % recovery			% R.S.D.			Initial MDL (μg/kg)
		Sand	Stream-sediment	Topsoil	Sand	Stream-sediment	Topsoil	
d-Limonene[a]	4	65.7	29.0	64.2	6.4	20.6	5.1	23.7
	40	65.1	48.0	64.8	10.5	21.3	12.1	
Fluoranthene	4	81.0	102	82.0	5.1	38.0	4.2	23.2
	40	84.7	85.1	85.6	2.8	5.3	3.2	
Hexahydrohexamethyl-cyclo-pentabenzopyran (HHCB)	4	76.8	76.6	78.4	3.8	14.2	6.3	16.5
	40	82.7	78.2	82.2	4.0	6.3	7.8	
Indole	4	82.0	89.4	74.6	11.7	18.0	19.5	53.5
	40	83.3	71.8	65.0	3.4	6.9	19.4	
Isoborneol	4	86.5	78.8	85.0	8.1	20.3	9.0	39.3
	40	86.9	76.2	87.6	5.1	8.8	2.7	
Isophorone[a]	4	12.1	4.5	5.5	64.1	45.9	56.8	43.4
	40	46.3	33.0	32.8	12.3	11.9	20.2	
Isopropylbenzene (cumene)[a]	4	54.4	15.1	52.8	28.4	41.0	10.5	86.6
	40	61.0	37.1	59.1	9.6	28.8	15.0	
Isoquinoline[a]	4	59.5	46.3	37.3	25.0	31.8	50.0	83.1
	40	65.6	49.7	42.8	11.2	15.1	4.6	
Menthol	4	88.4	84.2	82.9	8.5	12.8	18.0	42.0
	40	86.9	70.8	94.2	16.3	9.8	12.9	
Metalaxyl[a]	4	57.7	37.6	41.3	20.7	43.4	61.8	53.4
	40	79.7	53.2	53.6	5.9	24.0	16.1	
Methyl salicylate[a]	4	13.4	12.3	35.4	47.7	156	77.9	35.8
	40	22.7	14.4	46.4	42.7	51.9	36.9	
Metolachlor	4	83.9	85.7	81.2	7.9	10.5	4.8	37.2
	40	92.0	92.3	86.4	7.6	5.7	5.4	
N,*N*-Diethyl-*meta*-toluamide (Deet)[a]	4	76.3	58.7	56.7	13.2	27.5	35.8	56.2
	40	75.5	62.4	58.0	10.2	14.1	7.5	
Naphthalene	4	75.7	71.2	76.6	5.6	8.4	3.4	23.5
	40	78.9	73.6	81.6	3.7	11.2	3.3	
Nonylphenol, diethoxy- (total, NPEO2)[a]	64	106	106	113	8.9	20.6	6.8	852
	640	98.6	93.6	99.4	2.9	4.0	6.4	
Nonylphenol, monoethoxy- (total,NPEO1)[d]	32	93.7	90.6	96.2	8.0	20.8	4.8	336
	320	93.1	89.2	93.8	3.5	6.6	7.2	
Octylphenol, diethoxy- (OPEO2)[d]	2.8	103	98.3	109	9.6	24.3	8.6	38.5
	28	99.1	94.2	98.4	1.4	3.2	1.9	
Octylphenol, monoethoxy- (OPEO1)[d]	28	86.6	83.9	85.3	6.5	17.0	6.3	219
	280	92.3	93.3	91.4	3.3	5.5	5.3	
para-Cresol	4	85.4	124	76.9	33.6	45.0	11.2	161
	40	74.2	115	67.6	5.1	14.9	5.1	
para-Nonylphenol (total)[d]	72	79.4	79.9	83.7	6.2	11.5	10.2	499
	720	86.5	86.0	86.3	7.4	5.5	7.2	
Pentachlorophenol[a]	16	52.7	45.2	54.2	44.1	35.1	19.8	520
	160	35.2	40.3	40.5	28.0	24.3	26.4	
Phenanthrene[c]	4	78.2	84.9	80.8	4.7	10.0	3.9	20.7
	40	85.4	86.0	88.0	2.6	5.1	2.2	
Phenol[a]	4	20.9	20.8	87.5	32.8	37.8	76.4	38.2
	40	41.9	47.0	39.8	16.3	6.2	13.3	
Prometon	4	74.7	79.9	66.6	10.6	16.9	10.7	44.2
	40	88.6	74.4	73.3	5.1	10.2	6.7	
Pyrene	4	73.3	91.6	73.2	5.0	36.9	7.2	20.6
	40	82.7	80.9	83.2	2.1	5.6	3.1	
Tetrabromodiphenyl ether	4	79.6	79.0	83.5	4.3	9.9	6.6	19.1
	40	84.4	87.6	67.0	5.8	8.8	19.3	
Tri(2-butoxyethyl)phosphate	4	101	97.7	102	17.5	32.6	9.2	98.5
	40	87.9	87.8	89.3	2.4	3.7	1.0	
Tri(2-chloroethyl)phosphate[a]	4	49.4	39.3	39.3	25.4	20.8	59.7	70.3
	40	66.7	48.0	39.8	13.0	16.6	9.4	
Tri(dichloroisopropyl)phosphate[a]	4	47.0	48.1	66.6	27.8	22.3	30.6	73.0
	40	46.3	49.8	63.9	24.1	18.1	21.8	

Table 3 (*Continued*)

Compound name	Spike amount (μg)	Mean % recovery			% R.S.D.			Initial MDL (μg/kg)
		Sand	Stream-sediment	Topsoil	Sand	Stream-sediment	Topsoil	
Tributyl phosphate	4	86.5	84.7	85.7	8.1	18.3	7.0	39.6
	40	86.9	91.0	87.9	3.6	4.1	4.5	
Triclosan	4	82.9	70.9	86.6	10.7	12.2	13.1	49.6
	40	82.4	74.8	85.3	6.4	3.6	3.1	
Triphenyl phosphate[a]	4	47.8	47.9	61.4	17.2	29.3	29.0	46.0
	40	49.0	49.0	64.6	18.4	16.5	16.1	
Surrogate compounds								
Fluoranthene-d_{10}	8	83.4	92.5	85.0	4.4	6.0	3.8	
	8	84.1	74.6	81.6	11.4	21.4	6.2	
Bisphenol A-d_3	8	68.2	70.5	64.1	9.4	12.0	18.9	
	8	56.8	44.1	60.7	7.4	9.7	6.7	
Decafluorobiphenyl	8	56.7	55.2	62.5	12.3	11.6	14.1	
	8	65.7	44.8	66.6	11.7	9.8	11.4	

[a] Sample results reported will be qualified as estimates because recovery is less than 60% or precision is greater than 25% R.S.D. This can be caused by instrumental or extraction difficulties.
[b] Percent recovery corrected for background concentration in the unspiked sample.
[c] Sample results reported will be qualified as estimates because of potential blank contamination unless concentration is greater than 10 times the 95th percentile of all blank concentrations.
[d] Sample results reported will be qualified as estimates because the reference standard is from a technical mixture.

of the compounds. However, initial MDLs for some method compounds were calculated by using concentrations higher than the desired spiking level so that the compound would be detected in each of the replicate reagent-sand samples. Initial MDLs that were calculated from this procedure for single-component compounds ranged from 12.5 to 520 μg/kg and are listed in Table 3.

3.4. Performance data using standard reference material (SRM) 1944

SRM 1944 is natural marine sediment that contains specific PAH concentrations certified by the United States National Institute for Standards and Technology (NIST). Nine SRM 1944 samples were extracted and analyzed by this ASE method during a 2-month period and results were compared with 36 h Soxhlet extraction results with dichloromethane for common PAH compounds (Table 4). The NIST certified results for SRM 1944 were obtained also by 36 h Soxhlet extraction with DCM and GC/MS analysis. There is no certified standard reference materials that contain the diverse list of compounds analyzed for in the presented method. The PAHs in the SRM were used as representative hydrophobic compounds to demonstrate the ability of this method to extract hydrophobic compounds from environmental sediment samples. The use of these compounds as representative compounds has been demonstrated before. It has been suggested (19) that water-based extraction solvents cause clay particles to swell much more than typical organic solvents. Consequently, the part of PAH molecules that is highly sequestered in clay pores is more available to subcritical water. As the solubility of higher molecular weight PAH compounds decreases in the hot IPA/water mixture, ASE recoveries generally are comparable to Soxhlet extraction with DCM. Hawthorne et al. [23] also observed this same trend for subcritical water extraction of SRM 1944 at 250 °C. The recovery results (Table 4) for the common PAH compounds (anthracene, benzo[*a*]pyrene, fluoranthene, naphthalene, phenanthrene, and pyrene) was greater by 10–20% using this ASE method compared to certified values obtained by DCM-based Soxhlet extraction. Method precision for the certified PAH compounds using this method was 9–16% R.S.D. and was not statistically different than the Soxhlet results.

3.5. Reconnaissance study

Fig. 1 shows the results from analysis by the described method of 103 environmental sediment samples collected

Table 4
Concentrations certified by the National Institute of Standards and Technology for Standard Reference Material 1944 determined by Soxhlet and this method

Compound name	NIST certified (μg/kg)	Mean SOX (μg/kg)	Mean ASE (μg/kg)	SOX recovery (%)	ASE recovery (%)	SOX R.S.D. (%)	ASE R.S.D. (%)
Anthracene	1770	1440	1877	81.3	106.0	7.79	10.26
Benzo[*a*]pyrene	4300	3170	3363	73.6	78.2	7.61	12.08
Fluoranthene	8920	6670	8970	74.8	100.5	6.07	10.69
Naphthalene	1650	820	1980	49.3	120.0	10.5	15.70
Phenanthrene	5270	3970	5723	75.3	108.6	6.36	8.76
Pyrene	9700	6580	9397	67.8	96.8	5.53	9.32

SOX, Soxhlet; ASE, accelerated solvent extraction; R.S.D., relative standard deviation; *n*, number of samples: $n = 7$ by Soxhlet, $n = 9$ by ASE.

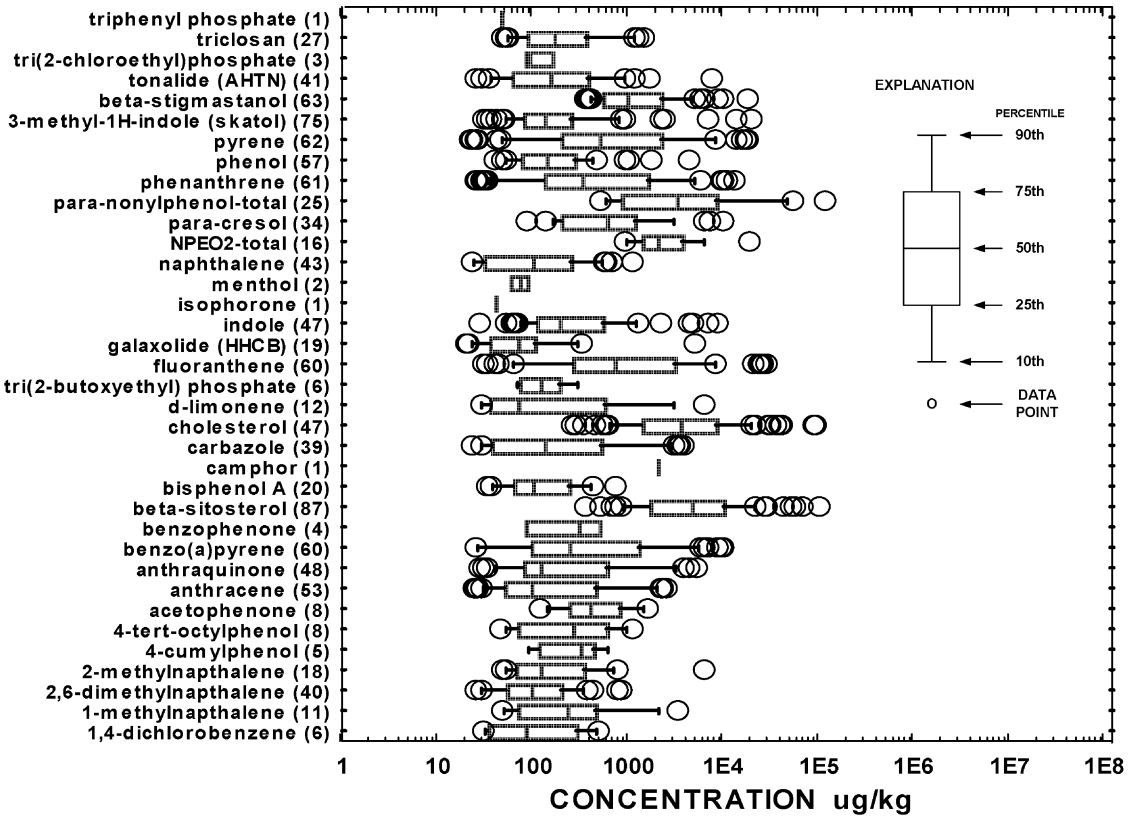

Fig. 1. Analysis of 103 environmental soil, sediment, and suspended-sediment samples. The concentration axis is in log scale to accommodate the large concentration ranges for the compounds of interest. The number of compound detections is listed after each compound name.

throughout the United States. The samples are a mixture of soils, stream sediments, and suspended sediments, the majority from urban sampling sites. The data are reported using a log scale to accommodate the large concentration ranges for each compound. Thirty-six out of 61 compounds (59%) were detected in at least one sample with concentrations ranging from 20 to 100,000 μg/kg. The most frequently detected compound, beta-sitosterol, a plant sterol, was detected in 87 of the 103 (84.5%) environmental samples with a concentration range of 360–100,000 μg/kg. As a group, PAH accounted for 428 of the 1110 (56.8%) detections. The fragrances accounted for 203 of the 1110 (18.3%) detections. The three compounds with the highest measured average concentration were beta-sitosterol, cholesterol, and the total *para*-nonylphenols. Their concentrations ranged from 300 to 100,000 μg/kg with an average about 5000 μg/kg. The results (concentration ranges and detection frequencies) demonstrate the ability of the described method to determine the compound classes of interest in various sediment and soil types.

4. Conclusion

This ASE method has advantages over conventional Soxhlet extraction in sample automation, reduced extraction time, and reduced solvent volume. Sample preparation also is simplified considerably over Soxhlet extraction with DCM because the ASE water/isopropyl alcohol extract is well suited for reverse-phase SPE extract cleanup. Coupling pressurized liquid extraction with solid-phase extraction provides a rapid, economical, and simple method for the determination of semivolatile organic compounds, polycyclic aromatic hydrocarbons, and other anthropogenic compounds in sediment samples. Data demonstrating the method bias, precision, and sensitivity, demonstrate method suitability for routine monitoring of the compounds of interest in samples of soil, sediment, and suspended sediment.

Pressurized liquid extraction, coupled with SPE columns, provides clean sample extracts allowing the use of full-scan GC/MS. Full-scan GC/MS allows for the compounds of interest to be identified in the presence of potential matrix interferences. It also allows for the tentative identification of compounds that are extracted and isolated using this method, even though they are not on the list of selected compounds. These tentatively identified compounds may be of environmental significance and serve as a starting point for additional research regarding their presence, fate, temporal and spatial distribution, and transport in the environment.

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