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Methods of Analysis—Determination of Pesticides in Sediment Using Gas Chromatography/Mass Spectrometry

Techniques and Methods 5–C3

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

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By Michelle L. Hladik and Megan M. McWayne

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
micrometer (µm)	3.937×10^{-5}	inch (in)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Volume	
liter (L)	0.2642	gallon (gal)
microliter (µL)	2.642×10^{-7}	gallon (gal)
milliliter (mL)	0.000264	gallon (gal)
mL/min	0.0338	ounce per minute
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)
microgram (µg)	3.527×10^{-8}	ounce, avoirdupois (oz)
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois (oz)
nanogram (ng)	3.527×10^{-11}	ounce, avoirdupois (oz)

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

$$°F=(1.8\times°C)+32$$

Conversion Factors—Continued

Abbreviated units of measurement used in this report:

Å	angstrom
amu	atomic mass unit
cm	centimeter
g	gram
i.d.	inner diameter
L	liter
m	meter
mg	milligram
min	minute
mL	milliliter
mL/min	milliliter per minute
mm	millimeter
m/z	mass-to-charge ratio
ng	nanogram
ng/µL	nanogram per microliter
nm	nanometer
psi	pound per square inch
µg/kg	microgram per gram
µg/mL	microgram per milliliter
µL	microliter
µm	micrometer (micron)

Conversion Factors—Continued

Other abbreviations used in this report
(additional information or clarification given in parentheses)

ACS	American Chemical Society
ASE®	accelerated solvent extraction
ASTM	American Society for Testing and Materials
C	sample concentration (equations 1, 2, 4 and 5)
CAS	Chemical Abstracts Service (American Chemical Society)
CCV	continuing calibration verification
DCM	dichloromethane
E	extract concentration (equation 3)
EI	electron ionization
EtOAc	ethyl acetate
GC	gas chromatograph
GC/MS	gas chromatography with mass spectrometry
GF/F	glass-fiber filter (grade GF/F)
GPC	gel-permeation chromatography
HPLC	high-performance liquid chromatograph
ISTD	internal standard
MDL	method detection limit (text and equation 6)
MS	mass spectrometer
NAWQA	National Water Quality Assessment (USGS)
PAH	polycyclic aromatic hydrocarbon
PFTBA	perfluorotributylamine
PPE	personal protective equipment
QA	quality assurance
QA/QC	quality assurance and quality control
QC	quality control
RF	response factor (equation 2)
RPD	relative percent difference
RSD	relative standard deviation
SIM	selected ion monitoring
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV-Vis	ultraviolet and visible light
v/v	volume-to-volume
Wd	dry weight of sediment extracted (equation 3)
Ww	wet weight of sediment extracted (equation 34)

Methods of Analysis—Determination of Pesticides in Sediment By Using Gas Chromatography/ Mass Spectrometry

By Michelle L. Hladik and Megan M. McWayne

Abstract

A method for the determination of 119 pesticides in environmental sediment samples is described. The method was developed by the U.S. Geological Survey (USGS) in support of the National Water Quality Assessment (NAWQA) Program. The pesticides included in this method were chosen through prior prioritization. Herbicides, insecticides, and fungicides along with degradates are included in this method and span a variety of chemical classes including, but not limited to, chloroacetanilides, organochlorines, organophosphates, pyrethroids, triazines, and triazoles.

Sediment samples are extracted by using an accelerated solvent extraction system (ASE®), and the compounds of interest are separated from co-extracted matrix interferences (including sulfur) by passing the extracts through high performance liquid chromatography (HPLC) with gel-permeation chromatography (GPC) along with the use of either stacked graphitized carbon and alumina solid-phase extraction (SPE) cartridges or packed Florisil®. Chromatographic separation, detection, and quantification of the pesticides from the sediment-sample extracts are done by using gas chromatography with mass spectrometry (GC/MS).

Recoveries in test sediment samples fortified at 10 micrograms per kilogram (µg/kg) dry weight ranged from 75 to 102 percent; relative standard deviations ranged from 3 to 13 percent. Method detection limits (MDLs), calculated by using U.S. Environmental Protection Agency procedures (40 CFR 136, Appendix B), ranged from 0.6 to 3.4 µg/kg dry weight.

Introduction

Pesticides are of environmental concern in streams in both the water column and sediment. Those pesticides that are more hydrophobic tend to be detected more frequently in sediment; thus, measuring pesticides in sediment is important for tracking their fate in the environment and evaluating for potential toxicity. Determining priority pesticides for analysis in water and sediment has been undertaken by the U.S. Geological Survey (USGS) by using a broad approach to address multiple USGS program goals, including the upcoming third decade (Cycle 3) of sampling for the National Water Quality Assessment (NAWQA) Program (Norman and others, 2012).

Multiple methods exist to measure pesticides at environmentally relevant concentrations, including one method already developed by the USGS Organic Chemistry Laboratory in Sacramento, Calif. (Sacramento Laboratory) for sediment (Smalling and Kuivila, 2008; Hladik and others, 2009c). The previously developed Sacramento Laboratory sediment method (with slight modifications made over the years) has been robust across many types of sediments (bed and suspended sediment; varying percent organic carbon), with matrix-spike recoveries greater than 70 percent and with values of relative percent difference (RPD) between replicate samples of less than 25 percent (Orlando and others, 2008; Smalling and Kuivila, 2008; Hladik and others, 2009a; Smalling and Orlando, 2011; Orlando and others, U.S. Geological Survey, written commun., 2012; Smalling and others, 2012). The most recent version of the Sacramento Laboratory sediment method (Orlando and others, U.S. Geological Survey, written commun., 2012; Smalling and others, 2012) uses gas chromatography with mass spectrometry (GC/MS), and included 91 pesticides and pesticide degradates with method detections levels (MDLs) from 1 to 4 µg/kg.

As the NAWQA Program prepares for Cycle 3, additional pesticides have been prioritized as those of interest for future studies (Norman and others, 2012). The Sacramento Laboratory is updating the current sediment method to include many of these prioritized pesticides. Because the current method has been shown to perform well across a wide range of percent sediment organic carbon concentrations (up to 36 percent), the method itself is not being modified; rather, additional compounds of interest to NAWQA Cycle 3 (that is, those classified as Tier 1 in the pesticide prioritization; Norman and others, 2012) and the Sacramento Laboratory are being added to the existing method. Additional compounds of interest were tested and dropped from the method if they were not amenable to analysis via GC/MS or if initial recoveries were not greater than 70 percent. The updated method will evaluate sediment samples for 119 pesticides and pesticide degradates.

Purpose and Scope

This report describes a method for the extraction and quantification of 119 pesticides from sediment samples by using GC/MS. The method described in this report was developed by the USGS Sacramento Laboratory to support the broad-spectrum analysis of pesticides in sediment by the NAWQA Program. This method expands the previously published method (original method: Smalling and Kuivila, 2008; most recent analyte list: Smalling and others, 2012) and increases the number of target analytes from 91 to 119. The 28 new target analytes include high-priority pesticides from Norman and others (2012) that are amenable to analysis by GC/MS and met performance criteria. Sediment samples were extracted by using the accelerated solvent extraction system (ASE®), followed by high performance liquid chromatography (HPLC) with gel-permeation chromatography (GPC) for sulfur removal, with additional cleanup of the matrix interferences that occur in sediment extracts performed with the use of either carbon/alumina solid-phase extraction (SPE) or Florisil®. Pesticides were quantified by GC/MS. This report also provides extraction recoveries along with the analytical precision (expressed as relative standard deviation(RSD)) and MDLs.

The method of analysis described in this report is assigned USGS method numbers O-6144-12 (bed sediment) and O-7144-12 (suspended sediment), USGS method codes GM031 (suspended sediment) and GM032 (bed sediment), and Sacramento Laboratory code NAWQA3. These unique codes represent the type of analysis described in the report, which can be used to identify the method. This procedure provides an effective option to environmental scientists seeking pesticide analyses in sediment samples, with minimal contamination bias, relatively low MDLs, good recoveries, and excellent precision. The method will contribute to the improved understanding of the occurrence, fate, and transport of pesticides in the environment.

Analytical Method

Organic Compounds and Parameter Codes: Pesticides in bed sediment or suspended sediment using ASE®, HPLC-GPC, SPE/Florisil®, and GC/MS—USGS method numbers O-6144-12 (bed sediment) and O-7133-12 (suspended sediment), USGS method codes GM031 (suspended sediment) and GM032 (bed sediment), and Sacramento Laboratory code NAWQA3.

1. Scope and Application

This method is suitable for determining the pesticides listed in table 1, at microgram-per-kilogram concentrations in sediment samples. The compound names, Chemical Abstracts Service (CAS) numbers, chemical classes, pesticide types, molecular weights, and USGS parameter codes are listed in table 1. Compounds that are being added to the existing method in this update are identified with an asterisk next to the compound name. These are the compounds that met the recovery and detection-level criteria for inclusion. An additional 64 compounds were considered for the new method; 7 of the compounds (mostly degradates) did not have standards available, 44 compounds were not amenable to GC analysis, and 13 compounds were not able to be recovered at levels greater than 70 percent through the sediment extraction and cleanup.

Table 1. CAS Registry number, chemical class, type of pesticide, molecular weight and USGS parameter codes for each pesticide.

[Compounds noted with an asterisk have not been reported in a previous method. This report contains Chemical Abstracts Service Registry Numbers (CASRN), which is a Registered Trademark of the American Chemical Society. Chemical Abstracts Service (CAS) recommends the verification of the CASRNs through CAS Client Services. The five-digit parameter codes are used by the U.S. Geological Survey to uniquely identify a specific constituent or property in the National Water Information System (NWIS) database. **Abbreviations/Acronyms:** amu, atomic mass unit; NA, not available]

Compound	CASRN	Chemical class	Pesticide type	Molecular weight (amu)	Bed-sediment parameter code	Suspended-sediment parameter code
2-Chloro-2,6-Diethylacetanilide*	6967-29-9	Chloroacetanilide	Degradate	225.7	68876	68875
3,4-Dichloroaniline	95-76-1	Aniline	Degradate	162.0	66585	63400
3,5-Dichloroaniline	626-43-7	Aniline	Degradate	162.0	67538	67537
Alachlor	15972-60-8	Chloroacetanilide	Herbicide	269.8	04006	04021
Allethrin	584-79-2	Pyrethroid	Insecticide	302.4	66588	66587
Atrazine	1912-24-9	Triazine	Herbicide	215.7	39631	04017
Azinphos-methyl*	86-50-0	Organophosphate	Insecticide	317.3	64150	65115
Azoxystrobin	131860-33-8	Strobilurin	Fungicide	403.4	66591	66590
Benfluralin (Benefin)*	1861-40-1	Dinitroaniline	Herbicide	335.3	68878	68877
Bifenthrin	82657-04-3	Pyrethroid	Insecticide	422.9	64151	63415
Boscalid	188425-85-6	Pyridine	Fungicide	343.2	67552	67551
Butralin*	33629-47-9	Dinitroaniline	Herbicide	295.3	68880	68879
Butylate	2008-41-5	Thiocarbamate	Herbicide	217.4	64152	65116
Captan*	133-06-2	Phthalimide	Fungicide	300.6	68324	68323
Carbaryl	63-25-2	Carbamate	Insecticide	201.2	64153	65117
Carbofuran	1563-66-2	Carbamate	Insecticide	221.3	64154	65118
Chlorothalonil	1897-45-6	Chloronitrile	Fungicide	265.9	62904	65119
Chlorpyrifos	2921-88-2	Organophosphate	Insecticide	350.6	81404	65120
Clomazone	81777-89-1	Isoxazlidinone	Herbicide	239.7	67564	67563
Coumaphos*	56-72-4	Organophosphate	Insecticide	362.8	68882	68881
Cyhalofop-butyl*	122008-85-9	Aryloxyphenoxypropionate	Herbicide	357.4	68884	68883
Cycloate	1134-23-2	Thiocarbamate	Herbicide	215.4	64155	65121
Cyfluthrin	68359-37-5	Pyrethroid	Insecticide	434.3	65109	65122
Cyhalothrin	68085-85-8	Pyrethroid	Insecticide	449.9	68356	68355
Cypermethrin	52315-07-8	Pyrethroid	Insecticide	416.3	64156	65123
Cyproconazole	94361-06-5	Triazole	Fungicide	391.8	66595	66594
Cyprodinil	121522-61-2	Pyrimidine	Fungicide	225.3	67576	67575
DCPA (Dacthal)	1861-32-1	Benzenedicarboxylic acid	Herbicide	332.0	62905	65124
Deltamethrin	52918-63-5	Pyrethroid	Insecticide	505.2	65110	65125
Diazinon	333-41-5	Organophosphate	Insecticide	304.4	39571	65126
Difenoconazole	119446-68-3	Triazole	Fungicide	406.3	67584	67853
Dimethomorph	110488-70-5	Morpholine	Fungicide	388.0	68375	68374
Dithiopyr *	97886-45-8	Pyridine	Herbicide	401.4	68886	68885
EPTC	759-94-4	Thiocarbamate	Herbicide	189.3	64158	65128
Esfenvalerate	66230-04-4	Pyrethroid	Insecticide	419.9	64159	65129
Ethalfluralin	55283-68-6	Aniline	Herbicide	333.3	64160	65130
Etofenprox	80844-07-1	Pyrethroid	Insecticide	376.5	67606	67605
Famoxadone	131807-57-3	Oxazole	Fungicide	374.4	67611	67610
Fenarimol	60168-88-9	Pyrimidine	Fungicide	331.2	67615	67614
Fenbuconazole	114369-43-6	Triazole	Fungicide	336.8	67620	67619
Fenhexamide	126833-17-8	Anilide	Fungicide	302.2	67624	67622
Fenpropathrin	39515-41-8	Pyrethroid	Insecticide	349.4	65111	65131
Fenpyroximate*	134098-61-6	Pyrazole	Insecticide	421.5	68888	68887
Fenthion*	55-38-9	Organophosphate	Insecticide	278.3	62046	68889
Fipronil	120068-37-3	Phenylpyrazole	Insecticide	437.2	66606	66605
Fipronil desulfinyl	NA	Phenylpyrazole	Insecticide	389.1	66609	66608
Fipronil desulfinyl amide (Desulfinylfipronil amide)*	NA	Phenylpyrazole	Insecticide	421.1	68891	68890

Table 1. CAS Registry number, chemical class, type of pesticide, molecular weight and USGS parameter codes for each pesticide. Compounds noted with an asterisk have not been reported in a previous method.—Continued

[Compounds noted with an asterisk have not been reported in a previous method. This report contains Chemical Abstracts Service Registry Numbers (CASRN), which is a Registered Trademark of the American Chemical Society. Chemical Abstracts Service (CAS) recommends the verification of the CASRNs through CAS Client Services. The five-digit parameter codes are used by the U.S. Geological Survey to uniquely identify a specific constituent or property in the National Water Information System (NWIS) database. **Abbreviations/Acronyms:** amu, atomic mass unit; NA, not available]

Compound	CASRN	Chemical class	Pesticide type	Molecular weight (amu)	Bed-sediment parameter code	Suspended-sediment parameter code
Fipronil sulfide	120067-83-6	Phenylpyrazole	Insecticide	421.2	66612	66611
Fipronil sulfone	120068-36-2	Phenylpyrazole	Insecticide	453.2	66615	66614
Fluazinam	79622-59-6	Pyridine	Fungicide	465.2	67638	67637
Fludioxinil	131341-86-1	Pyrrole	Fungicide	248.2	67642	67641
Flufenacet*	142459-58-3	Anilide	Herbicide	363.3	68893	68892
Flumetralin*	62924-70-3	Dinitroaniline	Plant growth regulator	421.7	68895	68894
Fluoxastrobin	361377-29-9	Strobilurin	Fungicide	458.8	67647	67646
Flusilazole	85509-19-9	Triazole	Fungicide	315.4	67651	67650
Flutolanil*	66332-96-5	Anilide	Fungicide	323.3	68897	68896
Flutriafol	76674-21-0	Triazole	Fungicide	301.3	67655	67654
Hexazinone	51235-04-2	Triazone	Herbicide	252.3	64161	65133
Imazalil	35554-44-0	Triazole	Fungicide	297.2	67664	67663
Indoxacarb*	173584-44-6	Oxadiazine	Insecticide	527.9	68899	68898
Iprodione	36734-19-7	Dicarboxamide	Fungicide	330.2	66618	63457
Kresoxim-methyl	143390-89-0	Strobilurin	Fungicide	313.4	67672	67671
Malathion	121-75-5	Organophosphate	Insecticide	330.4	35931	65135
Metalaxyl*	57837-19-1	Phenylamide	Fungicide	279.3	68439	68438
Metconazole	125116-23-6	Azole	Fungicide	319.8	66622	66621
Methidathion	950-37-8	Organophosphate	Insecticide	302.3	62047	65136
Methoprene	40596-69-8	Terpene	Insecticide	310.5	66625	66624
Methyl parathion	298-00-0	Organophosphate	Insecticide	263.2	39601	65137
Metolachlor	51218-45-2	Chloroacetanilide	Herbicide	283.8	04005	04020
Molinate	2212-67-1	Thiocarbamate	Herbicide	187.3	64163	65138
Myclobutanil	88671-89-0	Triazole	Fungicide	288.8	66634	66633
Napropamide	15299-99-7	Amide	Herbicide	271.4	64164	65139
Novaluron*	116714-46-6	Benzoylurea	Herbicide	492.7	68901	68900
Oxadiazon*	19666-30-9	Oxadiazolone	Herbicide	345.2	68903	68902
Oxyflurofen	42874-03-3	Nitrophenyl ether	Herbicide	361.7	64165	63468
p,p'-DDD	72-54-8	Organochlorine	Degradate	320.0	39311	63124
p,p'-DDE	72-55-9	Organochlorine	Degradate	318.0	39321	63125
p,p'-DDT	50-29-3	Organochlorine	Insecticide	354.5	39301	63126
Pebulate	1114-71-2	Thiocarbamate	Herbicide	203.4	64166	65141
Pendimethalin	40487-42-1	Aniline	Herbicide	281.3	64167	65142
Pentachloroanisole	1825-21-4	Organochlorine	Insecticide	280.4	49460	66638
Pentachloronitrobenzene	82-68-8	Organochlorine	Fungicide	361.7	49446	66640
Permethrin	52645-53-1	Pyrethroid	Insecticide	391.3	64168	65143
Phenothrin	26002-80-2	Pyrethroid	Insecticide	350.5	65112	65144

Table 1. CAS Registry number, chemical class, type of pesticide, molecular weight and USGS parameter codes for each pesticide. Compounds noted with an asterisk have not been reported in a previous method.—Continued

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Compound	CASRN	Chemical class	Pesticide type	Molecular weight (amu)	Bed-sediment parameter code	Suspended-sediment parameter code
Phosmet	732-11-6	Organophosphate	Insecticide	317.3	64169	65145
Piperonyl butoxide	51-03-6	Unclassified	Synergist	338.4	64170	65146
Prodiamine*	29091-21-2	Dinitroaniline	Herbicide	350.3	68905	68904
Prometon	1610-18-0	Triazine	Herbicide	225.3	82402	04011
Prometryn	7287-19-6	Triazine	Herbicide	241.4	78688	04010
Pronamide (Propyzamide)*	23950-58-5	Amide	Herbicide	256.1	67708	67707
Propanil	218.08	Anilide	Herbicide	218.1	66642	63481
Propargite*	2312-35-8	Sulfite ester	Insecticide	350.5	68907	68906
Propiconazole	60207-90-1	Azole	Fungicide	342.2	66645	66644
Propyzamide	23950-58-5	Benzamide	Herbicide	256.1	67708	67707
Pyraclostrobin	175013-18-0	Strobilurin	Fungicide	387.8	66648	66647
Pyridaben*	96489-71-3	Pyridazinone	Insecticide	364.9	68909	68908
Pyrimethanil	53112-28-0	Pyrmidine	Fungicide	199.1	67719	67718
Resemethrin	10453-86-8	Pyrethroid	Insecticide	338.4	65113	65147
Simazine	122-34-9	Triazine	Herbicide	201.7	39046	04008
tau-Fluvalinate	69409-94-5	Pyrethroid	Insecticide	502.9	65114	65148
Tebuconazole	107534-96-3	Azole	Fungicide	307.8	66650	67728
Tebupirimfos oxon (Tebupirimfos oxygen analog)*	NA	Organophosphate	Degradate	302.4	68911	68910
Tebupirimfos*	96182-53-5	Organophosphate	Insecticide	318.4	68913	68912
Tefluthrin	79538-32-2	Pyrethroid	Insecticide	418.7	67733	67732
Tetraconazole	112281-77-3	Azole	Fungicide	372.2	66656	66655
Tetradifon*	116-29-0	Bridged diphenyl	Insecticide	356.0	68915	68914
Tetramethrin	7696-12-0	Pyrethroid	Insecticide	331.4	66659	66658
Thiazopyr*	117718-60-2	Pyridine	Herbicide	396.4	68917	68916
Thiobencarb	28249-77-6	Thiocarbamate	Herbicide	257.8	64171	65149
Triadimefon	43121-43-3	Triazole	Fungicide	293.8	67743	67742
Triadimenol	55219-65-3	Triazole	Fungicide	295.8	67748	67746
Triallate*	2303-17-5	Carbamate	Herbicide	304.7	68919	68918
Tribuphos*	78-48-8	Organophosphate	Herbicide	314.5	39050	68920
Trifloxystrobin	141517-21-7	Strobilurin	Fungicide	408.4	66662	66661
Triflumizole	68694-11-1	Azole	Fungicide	345.6	67755	67754
Trifluralin	1582-09-8	Aniline	Herbicide	335.5	62902	04019
Triticonazole	131983-72-7	Azole	Fungicide	317.8	67760	67759
Vinclozolin	50471-44-8	Oxazole	Fungicide	286.1	67765	67764
Zoxamide	156052-68-5	Benzamide	Fungicide	336.6	67770	67769

2. Method Summary

Sediment samples are collected in the field by using methods such as those outlined by Radtke (2005), and were typically collected in 500-mL amber glass jars. Samples are chilled immediately, shipped to the Sacramento Laboratory, and frozen at –20°C until analysis (within 6 months). For extraction, the samples are thawed, and the percentage moisture is calculated. The samples (~10 g dry weight) are extracted with an ASE® using dichloromethane (DCM). The extract is reduced under nitrogen to 0.5 mL using a TurboVap® system and exchanged into ethyl acetate (EtOAc). Removal of sulfur is achieved by HPLC-GPC of the extract. The GPC eluent is evaporated in a hood using a gentle stream of nitrogen to a volume of 2.0 mL, and then split equally into two 1.0 mL aliquots for either herbicide/insecticide analysis via stacked carbon/alumina SPE or fungicide analysis (which also includes one each of an herbicide, insecticide, and degradate) via Florisil® clean-up.

The herbicide/insecticide fraction (78 target compounds) is exchanged into DCM to undergo additional cleanup on stacked graphitized carbon and alumina SPE cartridges. The compounds of interest are eluted from the SPE cartridge with DCM and then additionally from the alumina cartridge with 50:50 DCM:EtOAc v/v. The eluents are combined and exchanged into EtOAc. The fungicide fraction (41 target compounds) is exchanged into hexane and put through packed Florisil® (6 percent deactivated) as an additional cleanup step. Compounds are eluted from the Florisil® with 20 percent DCM in hexane followed by 50 percent EtOAc in hexane.

Following either the carbon/alumina or Florisil® procedures, eluents are separately reduced to ~0.2 mL under a gentle steam of nitrogen and exchanged to EtOAc. Deuterated polycyclic aromatic hydrocarbon (PAH) internal standards are added prior to analysis. The concentrations of the pesticides in the two extracts are determined by GC/MS.

3. Safety Precautions and Waste Disposal

The following safety precautions are followed:

3.1 All steps that use organic solvents are performed in a well-vented fume hood.

3.2 The ASE® exhaust and TurboVap® exhaust must be vented to a fume hood. The HPLC-GPC is contained in a fume hood.

3.3 Appropriate personal protective equipment (PPE) (eyewear, gloves, etc.) is used during the handling of reagents and chemicals. Disposable nitrile gloves do not provide adequate protection from DCM. Polyvinyl acetate gloves will provide adequate protection. Alternatively, the analyst may wear double nitrile gloves, but if DCM comes in contact with the nitrile gloves, the gloves must be removed immediately.

3.4 Precautions are taken when handling the gas chromatograph (GC) injector or working with the mass spectrometer (MS), because temperatures in their heated zones can be near 300°C. These areas must be allowed to cool before touching them. Laboratory staff will have received training in the Occupational Safety and Health Administration (OSHA) Hazard Communication standard and will be familiar with the properties of the reagents and target compounds prior to using this method.

3.5 All liquid waste produced during the extraction is considered "organic waste" and must be placed in thick-walled carboys and disposed of according to local regulations. The solid-waste stream produced during sample analysis comprises SPE cartridges, extracted sediment or soil, sodium sulfate, and assorted disposable glassware (such as glass pipettes and GC vials). Once the solid-waste items have been dried in a hood (that is, until no organic solvent remains), they can be disposed of according to local policy.

4. Interferences

Compounds that compete with or co-elute with the compounds of interest from the SPE cartridge materials or the Florisil® might cause interferences or low method recoveries. In addition, humic and fulvic acids might also cause interferences or reduce extraction efficiency, thus lowering pesticide recoveries. Possible interferences are addressed with matrix-spiked samples and surrogate compounds.

The purpose of representative sampling is to characterize the true concentration of pesticides in environmental samples. Field and laboratory personnel should be aware that many of the compounds included in this study are common ingredients in household pesticide products, and exposure to these products should be limited prior to sample collection or sample handling. The potential for contamination bias during sample collection or handling is monitored by the use of field blanks and laboratory blanks.

5. Apparatus and Instrumentation

The following apparatus and instrumentation are used:

5.1 *Analytical Balances*—Balances for sediment samples capable of accurately weighing 5.00 g ± 0.01 g. Balance for standard preparation accurately weighs 5.000 mg ± 0.001 mg.

5.2 *Accelerated Solvent Extraction System*—Thermo Fisher Scientific® Dionex (Sunnyvale, Calif.) ASE® 350 including precleaned stainless-steel extraction vessels and glass collection vials.

5.3 *TurboVap®*—Zymark Corporation (Hopkinton, Mass.) TurboVap® II Concentration Evaporation Workstation, including precleaned glass tubes (0.2 to 1.0 mL graduated).

5.4 *N-evap*—Organomation Associates, Inc. (Berlin, Mass.) N-EVAP Nitrogen Evaporator and 12-mL glass concentrator tubes.

5.5 *SPE vacuum manifold*—Includes vial rack to hold 15-mL glass concentrator tubes.

5.6 *SPE cartridges*—CarboPrep® 90 graphitized carbon cartridges (6 cc, 500 mg, Restek, Bellefonte, Pa.) stacked on top of Sep-Pak Alumina A cartridges (500 mg, Waters, Milford, Mass.).

5.7 *Cleanup columns*—Fisher Scientific (Fair Lawn, N.J.) 60-100 mesh Florisil® activated magnesium sulfate and precleaned 200 mL glass columns 400 mm L × 10 mm i.d.

5.8 *HPLC-GPC bench-top system*—Scientific Systems Inc. (State College, Pa.) Series I isocratic HPLC pump and ultraviolet-visible (UV-Vis) detector (set to 254 nm) with a PL-gel guard column (10 µm, 50 × 7.5 mm; Agilent Technologies, Santa Clara, Calif.) and PL-gel analytical column (10 µm, 50 Å, 300 × 7.5 mm; Agilent Technologies, Santa Clara, Calif.).

5.9 *GC/MS bench-top system*—Agilent Technologies 7890A GS coupled to an Agilent 5975C Inert XL EI/CI MS with Chemstation software *v 2008* and a Leap Technologies (Carrboro, N.C.) CTC Combi PAL autosampler.

5.10 *GC/MS analytical* column—DB-5ms (30 m × 0.25 mm × 0.25 µm; Agilent Technologies, Santa Clara, Calif.).

5.11 *Precleaned glassware including pipettes, microsyringes, concentrator tubes, funnels, and graduated cylinders*—Everything but the microsyringes are baked at 450°C for a minimum of 4 hours.

6. Reagents and Consumable Materials

6.1 *Analytical standards*—Neat solutions of pesticides obtained from the U.S. Environmental Protection Agency (USEPA) National Pesticide Standard Repository (Fort Meade, Md.).

6.2 *Internal standards (ISTD)*—Neat solutions of the ISTDs, d_{10}-acenaphthene and d_{10}-pyrene (Cambridge Isotope Laboratories, Andover, Mass.).

6.3 *Surrogate standards*—The surrogates: ring-$^{13}C_{12}$-*p,p'*-DDE and di-*N*-propyl-d_{14}-trifluralin at 100 µg/mL; phenoxy-$^{13}C_6$-*cis*-permethrin at 50 µg/mL (Cambridge Isotope Laboratories, Andover, Mass.).

6.4 *Deionized water*—Generated by purification of tap water to American Society of Testing and Materials (ASTM) Type II water or better (Picosystem® Plus, Hydro Service and Supplies, Inc., Durham, N.C.).

6.5 *Solvents*—Acetone, DCM, hexane, EtOAc; all Fisher Scientific (Fair Lawn, N.J.) Optima grade or better.

6.6 *Sodium sulfate, anhydrous*—Granular, 10-60 mesh, American Chemical Society (ACS)-certified (Thermo Fisher Scientific, Pittsburgh, Pa.), baked at 450°C for a minimum of 4 hours.

6.7 *Glass-fiber syringe filters*—25-mm diameter, 0.7-µm nominal pore size, GF/F-grade glass-fiber filters with GD/X disposable polypropylene housing (Whatman, Piscataway, N.J.).

6.8 *SPE cartridges*—Carboprep 90 graphitized carbon cartridges (6 cc, 500 mg, Restek, Bellefonte, Pa.) stacked on top of Sep-Pak Alumina A cartridges (500 mg, Waters, Milford, Mass.) .

6.9 *Florisil*—Fisher Scientific (Fair Lawn, N.J.) 60-100 Mesh Florisil and precleaned 200 mL glass columns 400 mm L × 10 mm i.d. The Florisil® is previously activated at 550ºC in a muffle furnace for 16 hours and removed at 100ºC. The activated Florisil® is deactivated by adding hexane-washed deionized water, 6 percent by weight; to do this, multiply the mass of activated Florisil® by 0.06 to determine the appropriate amount of water to add. The water is added in 4-5 mL aliquots with 5 minute intervals of shaking between each addition until the calculated amount of water is added. Allow the Florisil® to equilibrate in a tightly closed container overnight in a dessicator.

6.10 *Helium carrier gas (99.999 percent pure)*—GC carrier gas, local supplier.

6.11 *Nitrogen gas (99.999 percent pure)*—For evaporation of organic solvent and extraction gas for ASE®, local supplier.

7. Standards Preparation Procedure

7.1 *Primary standard solutions*—Individual stock solutions of 1,000 ng/µL for each pesticide and ISTD are prepared by accurately weighing, to the nearest 0.01 mg, 4–5 mg of the pure material into a 7-mL amber glass vial. Add 1 mL of acetone (using a microsyringe) per milligram of the weighed compound.

7.2 *Herbicide/insecticide concentrated stock solutions*—Two stock solutions containing 20 ng/µL of each herbicide insecticide are prepared by diluting individual 1,000 ng/µL primary standard solutions (0.5 mL each) into EtOAc in a 25-mL volumetric flask. Half of the herbicide/insecticide compounds go into one stock solution and the other half go into the second stock solution because there are 78 target compounds and they cannot all be added to a single 25-mL volumetric flask.

7.3 *Fungicide concentrated stock solution*— Stock solution containing 20 ng/µL of each fungicide is prepared by diluting individual 1,000-ng/µL primary standard solutions (0.5 mL each) into EtOAc in a 25-mL volumetric flask.

7.4 *ISTD stock solution*—Stock solution containing 10 ng/µL of ISTD is prepared by diluting 1.0 mL of each 1,000-ng/µL ISTD primary standard solution into EtOAc in a 100-mL volumetric flask.

7.5 *Herbicide/insecticide standard solutions*—Two solutions containing 10 ng/µL of pesticides and surrogate are prepared by diluting 5.0 mL of the herbicide/insecticide stock solutions (the two 20 ng/µL solutions from **7.2**) plus 1.0 mL of ITSD stock solution (10 ng/µL from **7.4**) into EtOAc in two separate 10-mL volumetric flasks.

7.6 *Fungicide standard solution*—Solution containing 10 ng/µL of fungicides is prepared by diluting 5 mL of the fungicide stock solution (the 20 ng/µL solution from **7.3**) and 1.0 mL of ITSD stock solution (10 ng/µL from **7.4**) into EtOAc in a 10-mL volumetric flask.

7.7 *Surrogate standard solution*—Solution containing 10 ng/µL of surrogate material is prepared by adding 0.5 or 1.0 mL of the concentrated surrogates (depending on if their initial concentration was 100 or 50 ng/µL, respectively) plus 1 mL of the internal standard stock (10 ng/µL) into EtOAc in a 5-mL volumetric flask.

7.8 *Dilute ISTD solution*—Solution containing 1 ng/µL of ISTD is prepared by diluting 5 mL of 10 ng/µL ISTD stock solution into EtOAc in a 50-mL volumetric flask.

7.9 *Calibration solutions*—In EtOAc, prepare two series, herbicides/insecticides and fungicides, of calibration solutions (no fewer than five concentrations) that contain all the pesticides and the surrogates at concentrations ranging from 0.025 to 2.5 ng/µL, while the internal standard is maintained at a constant concentration of 1 ng/µL. The calibration solutions are made by adding the appropriate amount of standard solution (10 ng/µL) in 5-mL volumetric flasks and bringing to volume with the dilute internal standard solution

7.10 *Matrix-spike solutions*—Two solutions, herbicide/insecticides and fungicides, containing 2 ng/µL of the representative subset of pesticides are prepared by diluting 1 mL of herbicide/insecticide or fungicide stock solutions (20 ng/µL) into EtOAc in a 10 mL volumetric flask.

7.11 *Surrogate-spike solution*—Solution containing 2 ng/µL of surrogate is prepared by adding 0.2 or 0.4 mL of the concentrated surrogates (depending on if their initial concentration was 100 or 50 ng/µL, respectively) into EtOAc in a 10-mL volumetric flask.

8. Sample Preparation Procedure for Sediment Samples

The extraction of pesticides from sediment samples and the subsequent cleanup steps are outlined below:

8.1 *Sediment Sample Extraction*

8.1.1 *Sample collection and storage*—Collect bed-sediment or aqueous suspended-sediment samples by using methods that accurately represent the organic concentrations in the environmental matrix at a given location. Field-sampling procedures need to follow those typically used to collect samples for trace organic compound analyses (Ward and Harr, 1990; Radtke, 2005) and special procedures unique to pyrethroid (Hladik and others, 2009b). Samples are immediately chilled, and at the laboratory, they are stored by freezing to –20°C. A 6-month holding-time limit has been established from the date of sample collection to the date of sample extraction. All samples are thawed before analysis.

8.1.2 *Accelerated Solvent Extraction*—Turn on the ASE® 350; make sure the ASE® exhausts outside the laboratory. Soak the frits from the cap assembly in DCM for several minutes and place in caps. Rinse all stainless-steel vessels and caps with acetone and hexane before use. Place two prebaked GF/F filters in the bottom of each vessel. Start with wet (moist, not dried) sediment; if frozen, thaw the sediment overnight in the refrigerator. Prior to extraction, calculate the percentage moisture of the sediment. Weigh approximately 10.0 g dry weight of homogenized material into a precleaned mortar containing anhydrous sodium sulfate and mix until the sediment is mostly dry. Fill pre-labeled extraction vessel with mixture; add Ottawa sand to fill any dead space in cell. Add 50 µL of 2 ng/µL surrogate solution. For matrix-spike samples, add 100 µL of both 2 ng/µL herbicide/insecticide solutions and the fungicide matrix-spike solution. Cap the ASE® vessels tightly and place into the ASE® sample tray while transferring the label of the vessel to the appropriate glass collection vial in the collection tray. Fill the solvent reservoirs A and B with 100 percent DCM and manually rinse the ASE® three times prior to running. Extract the samples with 100 percent DCM and run the ASE® under the following conditions: pressure at 1,500 psi, temperature 100ºC and heat for 5 minutes, and purge at 60 percent of the volume, for three cycles. For each sample, include a rinse from solvent reservoir B.

Once the ASE® is done running, remove glass collection vials. Set up glass funnels (with glass wool at bottom of funnel) with anhydrous sodium sulfate (about 30 g). Open the extraction vessels and slowly decant the samples over sodium sulfate to remove the water and let the solvent

flow into an appropriate collection vessel. Rinse the sodium sulfate two times with DCM (approximately 5 mL), collecting the DCM in the collection vessel corresponding to the sample. Once rinsed, discard the sodium sulfate. Concentrate extracts under nitrogen to approximately 0.5 mL using the TurboVap®. Filter out any particulates in the extract by transferring it to a concentrator tube through a syringe filter. Use DCM to rinse TurboVap® tube and syringe filter twice to minimize loss of extract. The extract is then exchanged into EtOAc and concentrated under nitrogen to less than 0.5 mL using the N-Evap.

8.2 *Sediment-Sample Removal of Matrix*

8.2.1 *HPLC-GPC*—The first cleanup step, done to primarily remove sulfur, is accomplished with HPLC-GPC. Turn on pump and UV/Vis lamp (254-nm absorbance wavelength) and allow them to warm up for 30 min (flow rate = 1.0 mL/min). Make sure EtOAc reservoir is full. To determine the collection window (time interval), inject 200 µL of each matrix-spike solution (2 ng/µL). Immediately following the injection, start the stopwatch. Once the ultraviolet (UV) absorbance starts to increase, note the time. When the absorbance drops back to approximately zero, note the time again; this will give you a collection window. To make sure all the compounds have had sufficient time to exit the system, give the window a 30-s duration on each side. Usually the collection window ranges from 7–15 min. Rinse the injector loop between samples with EtOAc. After determining the collection window, inject the entire sample onto the GPC. Immediately after the sample is injected, start the stopwatch. Place a 15-mL graduated test tube in the collection beaker; at the start of the collection window, remove the waste hose and place in test tube to collect compounds. At the end of the collection window, re-attach the waste hose and allow solvent to pump through the GPC for another 30–35 min (sulfur should come out ~20 min after the end of your collection window). Reduce the collected sample to 2.0 mL using the N-Evap. Split the samples equally into two 1.0-mL aliquots; half the sample will go through SPE cleanup and the other will go through Florisil® cleanup.

8.2.2 *SPE cleanup (herbicides/insecticides)*—The first step is to exchange the EtOAc fraction into DCM: concentrate this fraction under nitrogen to less than 0.2 mL on the N-Evap, add 1.0 mL of DCM, and shake to mix. Repeat this solvent-exchange again, then concentrate the sample back down to 1.0 mL. Once the fraction is in mostly DCM (DCM is more volatile than EtOAc, so not all the EtOAc can be removed), assemble sets of cartridges with one carbon SPE cartridge stacked onto one alumina SPE cartridge on a vacuum manifold. Clean cartridges with three column volumes of DCM. IMPORTANT: do not allow cartridges to go dry. After the cartridges are cleaned, place 15-mL glass concentrator tubes in the manifold rack. For each of the samples, add the ASE® extract to the top of the carbon cartridge (of the cartridge set) that corresponds to the correctly labeled collection tube and then rinse the concentrator tube with a small volume of DCM (less than 0.5 mL) to remove any remaining extract. Elute a portion of the analytes from the cartridges with 10 mL of DCM at ~1–2 drop/s. Remove the carbon cartridge and elute only the alumina SPE cartridge with 10 mL of 50 percent DCM:EtOAc; collect the eluent from the alumina cartridge in a fresh concentrator tube. Reduce the DCM and DCM:EtOAc fractions using the N-evap to less than 0.5 mL, combine into one fraction and reduce to 0.5 mL, exchange two times to EtOAc. Reduce the resulting sample to 0.2 mL, add 20 µL of dilute ISTD dilute solution (1 ng/µL), and transfer to GC/MS autosampler vials. The sample extracts are stored in a freezer at –20°C until analysis.

8.2.3 *Florisil® cleanup (fungicides)*— Exchange the Florisil® fraction (ASE® extract intended for Florisil cleanup) into hexane by concentrating the previously split fraction (from **8.2.1**) to less than 0.2 mL under nitrogen using the N-Evap, then adding 1.0 mL hexane, and shaking to mix. Repeat this solvent-exchange step, then concentrate the sample back down to 1.0 mL; at this point, the sample extract collected into the concentrator tube will be mostly hexane (because hexane is more volatile than EtOAc, not all the EtOAc can be removed). Prepare Florisil® columns by weighing out 10.0 ± 0.02 g into a precleaned 200 mL glass column equipped with a stopcock and glass wool in the bottom. Add a layer approximately 1-cm thick of sodium sulfate to the top of the Florisil® and rinse with 70 mL of hexane, taking care to close the stopcock when approximately 1 cm of hexane remains above the top of the sodium-sulfate sorbent. Introduce the sample-extract fraction onto the column with a glass pipette; rinse the concentrator tube that contained the extract twice with hexane. The compounds of interest are eluted with 20 mL of 20 percent DCM in hexane followed by 100 mL of 50 percent EtOAc in hexane collected in the same flask. Following Florisil® cleanup, reduce the sample eluents to 0.5 mL, exchange into EtOAc, then further reduce to 0.2 mL, add 20 µL of dilute ISTD, and transfer to GC/MS autosampler vials. The sample extracts are stored in a freezer at –20°C until analysis.

9. Instrument Calibration and Analysis Procedures

Aliquots of the samples are injected and the compounds separated and detected by using an Agilent 7890A GC and detected on a Agilent 5975C Inert XL EI/CI MSD system with a DB-5MS analytical column (30 m × 0.25 mm × 0.25 µm).

9.1 *GC/MS performance evaluation*—Before sample analysis, a new injector insert and septa are installed on the GC, and approximately 3-5 cm is removed from the injector end of the analytical column to maintain column performance with sediment samples. The MS is checked for potential air and water leaks (mass to charge ratio, or *m/z* of 28 and 32, and 18, respectively) prior to beginning the analytical batch. The MS calibration standard, perfluorotributylamine (PFTBA), is used to optimize mass resolution and calibrate representative analyte masses after instrument maintenance. The performance of the GC/MS is evaluated prior to each sample batch by injecting 1 µL of a calibration solution (0.5 ng/µL of either herbicide/insecticide solution or the fungicide solution from **7.9**) and assessing retention times, peak areas, and product ion abundances and ratios (using the conditions described below).

9.2 *GC/MS Injections for Analysis*—The GC/MS conditions for the analysis of pesticides are listed below.

9.2.1 GC conditions: Injections of 1 µL are made with the injector at 275ºC in pulsed splitless mode with a 50 psi pressure pulse for 1 min. The flow of He through a GC column is set at 1.2 mL/min. The herbicide/insecticide oven program is 80ºC for 1.0 min, ramp at 10ºC/min until 120ºC, then ramp at 3ºC/min until 200ºC and hold for 5 minutes, ramp at 3ºC/min until 219ºC, and a final ramp at 10ºC/min until 300ºC and hold for 10 minutes. The fungicide oven program is 80ºC for 0.5 min, ramp at 10ºC/min until 180ºC, then ramp at 5ºC/min until 220ºC and hold for 1 minute, ramp at 4ºC/min until 280ºC and hold for 1 minute, and a final ramp at 10ºC/min until 300ºC and hold for 10 minutes.

9.2.2 MS Conditions: the transfer line from the GC to the MS is set at 280ºC, the quadrupole is at 150ºC, and the MS ion source is set at 230ºC. The MS is operated in electron-ionization (EI) mode. Data is collected in the selected-ion-monitoring (SIM) mode; details of the retention times, quantitation ions, and qualification ions for the SIM windows are given in table 2.

9.3 *Instrument Calibration*—The GC/MS is calibrated with each new sample batch. A minimum of five and up to seven calibration standards are run. The calibration range for GC/MS is 0.025 to 2.5 ng/µL. These calibration standards correspond to environmental sample concentrations of 0.5 to 50 µg/kg for sediment.

9.4 *Data acquisition and processing*—Chemstation *version E.02.00* software is used to acquire data and Agilent Mass Hunter *version B.04.00* software is used to calibrate and quantify the responses of the pesticides. Pesticides with multiple peaks are summed for quantification. Calibration and quantification are described in more detail in section 11.

Table 2. Retention times, quantitation ions and confirmation ions for pesticides analyzed by GC/MS.

[Samples are split into an herbicide/insecticide group (carbon/alumina SPE cleanup) and a fungicide group (Florisil cleanup; the compounds noted with an asterisk are not actually fungicides but work with the Florisil cleanup). **Abbreviations/Acronyms:** GC/MS, gas chromatography with mass spectrometry; m/z, mass-to-charge ratio]

Herbicides/Insecticides	Retention time (minute)	Quantitation ion (m/z)	Confirmation ions (m/z)
EPTC	9.2	128	189,86
3,5-Dichloroaniline	10.4	161	163
Butylate	11.0	146	156
3,4-Dichloroaniline	11.1	161	163
Pebulate	11.9	128	161
Molinate	14.1	126	187,83
Cycloate	17.1	83	154
Ethalfluralin	17.8	276	333,316,292
Trifluralin	18.4	306	316,264
Benfluralin (Benefin)	18.5	292	276,264
2-Chloro-2,6-Diethylacetanilide	19.3	176	225,147
Pentachloroanisole	19.5	265	280,237
Fenpyroximate	20.4	213	198,142
Carbofuran	20.5	164	149
Simazine	20.6	201	186,173
Clomazone	20.9	125	204
Atrazine	21.0	200	215,173
Prometon	21.1	210	225,125
Propyzamide	21.9	173	255,175
Pronamide (Propyzamide)	22.0	173	255,240,145
Diazinon	22.3	179	304,137
Triallate	23.1	169	268,142,128
Tefluthrin	23.4	177	197,141
Tebupirimfos	23.7	261	318,234,152
Propanil	24.9	161	217,163
Methyl parathion	25.2	125	263,109
Alachlor	25.3	160	188,146
Carbaryl	25.6	144	115
Fipronil desulfinyl	25.6	388	390,333

Table 2. Retention times, quantitation ions and confirmation ions for pesticides analyzed by GC/MS.—Continued

[Samples are split into an herbicide/insecticide group (carbon/alumina SPE cleanup) and a fungicide group (Florisil cleanup; the compounds noted with an asterisk are not actually fungicides but work with the Florisil cleanup). **Abbreviations/Acronyms:** GC/MS, gas chromatography with mass spectrometry; m/z, mass-to-charge ratio]

Herbicides/Insecticides	Retention time (minute)	Quantitation ion (m/z)	Confirmation ions (m/z)
Dithiopyr	26.4	354	306,286
Prometryn	26.4	241	226,184
Prodiamine	27.3	321	333,279
Metolachlor	27.6	162	238
Thiazopyr	27.8	60	363,327,306
Chlorpyrifos	27.9	197	314,199
Malathion	27.9	125	173
Thiobencarb	27.9	100	125
DCPA (Dacthal)	28.0	301	332,229
Fenthion	28.2	278	169,125,109
Flufenacet	28.7	151	211,136,123
Butralin	29.1	266	295,224
Pendimethalin	29.9	252	NA
Fipronil sulfide	30.0	351	420,255
Fipronil	30.6	367	369,351
Allethrin	31.2	123	136
Methidathion	31.6	145	85
Methoprene	32.0	73	111
Flumetralin	32.6	143	404,157
Napropamide	33.1	72	128,100
p,p'-DDE	34.2	256	318,316,248
Oxadiazon	34.8	175	344,302,258
Fipronil desulfinyl amide	34.9	406	390,308
Fipronil sulfone	34.9	383	452,255,213
Oxyflurofen	35.4	252	300
p,p'-DDD	37.8	235	237,165
p,p'-DDT	40.9	235	237,165
Hexazinone	41.4	171	NA
Propargite	42.7	135	350,201,173
Piperonyl butoxide	43.4	176	177
Resemethrin	43.7	123	171,143
Phosmet	44.2	160	133,93
Azinphos-methyl	44.2	77	160,132
Bifenthrin	45.0	181	123
Tetramethrin	45.1	164	123
Tetradifon	45.7	159	356,227,111
Phenothrin	46.2	123	183.0
Cyhalofop-butyl	46.8	256	357,229,120
Cyhalothrin	47.1	181	208,197
Fenpropathrin	47.1	181	208
Permethrin	48.3	183	181,163
Coumaphos	48.5	362	226,210,109
Pyridaben	48.5	147	309,132,117
Cyfluthrin	49.2	206	226,165,163
Cypermethrin	49.6	181	208.163
Etofenprox	50.0	163	NA
tau-Fluvalinate	50.9	250	253,181
Esfenvalerate	51.0	125	227,181,167
Deltamethrin	51.6	181	253

Fungicides	Retention time (minute)	Quantitation ion (m/z)	Confirmation ions (m/z)
Novaluron	6.5	168	335,140
Pentachloronitrobenzene	12.7	237	295,214
Tebupirimfos oxon*	13.0	218	302,260,245
Pyrimethanil	13.2	198	199
Chlorothalonil	13.3	266	264
Vinclozolin	14.5	212	198,187
Metalaxyl	14.9	206	220,160,132
Triadimefon	16.2	57	208,128
Tetraconazole	16.2	336	338,101
Fluazinam	16.9	418	372,337
Cyprodinil	16.9	224	225
Captan	17.5	79	149,117
Triadimenol	17.5	112	168,128
Triflumizole	17.6	278	206,179
Flutriafol	18.6	123	219,164
Imazalil	18.7	215	217,173
Flutolanil	18.8	173	323,281,145
Fludioxinil	18.8	248	154,127
Tribuphos*	19.3	169	258.202
Myclobutanil	19.3	179	206,150
Flusilazole	19.3	233	205
Kresoxim-methyl	19.5	116	206,131
Cyproconazole	19.9	222	139,125
Trifloxystrobin	22.0	116	222,131
Fenhexamide	22.2	97	177
Propiconazole	22.2	173	259,175
Tebuconazole	22.8	125	250,127
Zoxamide	24.0	187	258,189
Iprodione	24.0	314	316,187
Metconazole	25.0	125	250
Triticonazole	25.6	235	237,217
Fenarimol	26.8	139	251,107
Fenbuconazole	29.6	129	198
Boscalid	30.5	140	342,112
Pyraclostrobin	32.9	132	164
Difenoconazole	33.8	323	267,265
Indoxacarb*	34.3	150	264,218,203
Azoxystrobin	34.9	344	387,372
Famoxadone	35.3	330	197
Dimethomorph	36.0	301	387,265
Fluoxastrobin	37.9	188	219

10. Quality Assurance and Quality Control

The quality-assurance (QA) and quality-control (QC) program primarily consists of internal checks on precision and accuracy of analytical results. Laboratory QC data from continuous calibration verification (CCV), laboratory-blank and matrix-spiked samples, and internal and surrogate standards are used by the analyst to determine if corrective actions are needed or if sample concentrations are not accurately reported.

10.1 *Field sampling*—Accuracy of sample handling in the field is monitored when field blanks and field replicates are included for analysis by the laboratory. Each environmental sample or QC sample is handled separately for proper data determination by the analyst.

10.2 *Continuous calibration verification (CCV)*—The CCV solutions, which are standard solutions of pesticides prepared in a manner similar to the calibration standards, are used to monitor the method stability in comparison to the initial calibration curve. The CCV control limits are established at ± 25 percent of the expected concentration for each pyrethroid. If a CCV fails the QC criteria, the affected samples are reanalyzed.

10.3 *Internal standards*—Internal standards are added to correct quantitative differences in extract volume as well as to compensate for differences in extract volume injected. Internal standards are also used to monitor instrument conditions, such as extract injection errors, retention time shifts, or instrument abnormalities or malfunctions.

10.4 *Laboratory blank*—A laboratory blank is an aliquot of baked sodium sulfate used to monitor the entire sample preparation and analytical procedure for possible laboratory contamination. The laboratory blank is considered acceptable when a compound is either undetected or is detected at or below one-third of the MDL. Laboratory blanks are analyzed for a minimum of 1 per every 20 samples. If a compound is detected in the laboratory blank above the MDL, no further samples are run until the source of the contamination is identified and eliminated.

10.5 *Laboratory matrix spike*—The laboratory matrix spike is an aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The laboratory matrix spike is analyzed exactly like a regular sample and is used to determine whether the sample matrix contributes bias to the analytical results and, therefore, the degree the method is successful in recovering the target analytes. The background concentration of the analytes in the sample matrix, if any are present, must be determined in a separate aliquot so that the values in the laboratory matrix spike can be corrected for their presence, and the percentage recovery calculated.

10.5.1 *Percent recovery calculation:*

Calculate the percent recovery (*%R*) for each selected compound as follows:

$$\%R = \left[C_{matrix\ spike} - C_{background} \right] / C_{expected} * 100 \text{ percent} \quad (1)$$

where

$C_{matrix\ spike}$ = concentration of the selected compound in the spiked sediment, in nanograms per microliter;

$C_{background}$ = concentration of the selected compounds in the unspiked sediment, in nanograms per microliter; and

$C_{expected}$ = theoretical concentration of the selected compound in the spiked sediment, in nanograms per microliter.

Laboratory matrix spikes are analyzed for a minimum of 1 per every 20 samples, or more frequently if a batch includes new or usual sample matrixes. If a matrix-spike recovery is below 70 percent, the sample set is evaluated for potential issues; if these issues cannot be rectified, the sample-set results are thrown out.

10.6 *Laboratory matrix-spike duplicate*—The laboratory matrix-spike duplicate is prepared and analyzed in the same manner as the laboratory matrix spike and is compared with the laboratory matrix spike to determine method variability. Laboratory matrix-spike duplicates are analyzed for a minimum of 1 per every 30 samples if the study calls for laboratory matrix-spike duplicates. The matrix spike and matrix-spike duplicate must have a RPD less than 25 percent to be considered acceptable.

10.7 *Laboratory replicate*—The laboratory replicate is a sample split into fractions for multiple analyses. Laboratory replicates are analyzed for a minimum of 1 per every 20 samples.

10.8 *Surrogate standards*—Surrogate standards are compounds similar in physical and chemical properties to the target analytes but which are not expected to be present in the environment. Surrogate standards are added to each environmental and quality-assurance/quality-control (QA/QC) sample and are used to monitor matrix effects and overall method performance. Their recoveries are not used to correct compound concentrations in environmental samples. If surrogate recoveries are less than 70 percent or greater than 130 percent, the sample is either thrown out (if there is no more sample material) or re-extracted and analyzed (if more sample material is available).

10.9 *Solvent Blank*—A solvent blank is an injection of solvent (in this case EtOAc) onto the GC/MS to determine if there is carryover of target analytes between sample injections. If analytes are detected in the solvent blank, the source of the carryover is determined, and the sample set is reanalyzed.

10.10 *Instrumental analysis quality control*—An example of a typical analytical sequence used for this method is listed in table 3. Sample extracts (including field blanks, replicates, matrix spikes, and laboratory spikes) are analyzed in an instrument sequence to provide additional information if performance criteria are not met.

Table 3. Example analytical sequence for use in determining pesticides in sediments.

["Samples" listed in column three include environmental samples, blanks (field and laboratory), replicates (field and laboratory), and matrix spikes and matrix-spike duplicates. **Abbreviations/Acronyms:** EtOAc, ethyl acetate; QC, quality control; CCV, continuing calibration verification]

Sample number	Vial number	Sample type
1	1	Solvent blank (EtOAc)
2	2	Calibration standard 1
3	3	Calibration standard 2
4	4	Calibration standard 3
5	5	Calibration standard 4
6	6	Calibration standard 5
7	7	Calibration standard 6
8	8	Calibration standard 7
9	1	Solvent blank (EtOAc)
10	9	Sample 1
11	10	Sample 2
12	11	Sample 3
13	12	Sample 4
14	13	Sample 5
15	14	Sample 6 or QC (lab blank)
16	6	CCV
17	1	Solvent blank (EtOAc)
18	15	Sample 7
19	16	Sample 8
20	17	Sample 9 or QC (matrix spike)
21	18	Sample 10
22	19	Sample 11
23	20	Sample 12
24	6	CCV
25	1	Solvent blank (EtOAc)
26	21	Sample 13
27	22	Sample 14
28	23	Sample 15
29	24	Sample 16
30	25	Sample 17 or QC (replicate)
31	26	Sample18
32	6	CCV
33	1	Solvent blank (EtOAc)

11. Calculation of Results

11.1 *Qualitative identification*— Before quantitative results are reported, each compound first needs to meet qualitative criteria. Identification and quantification of compounds are performed on the raw data files using the Mass Hunter analysis package. A compound is not considered to be identified correctly unless the correct quantitation ion(s) of the peak are detected, the relative ratios of the confirmation ions are within ± 25 percent of the average ratio obtained from the calibration samples, and the relative retention time of the peak is within 5 percent of the expected retention time.

11.2 *Quantification*— Five- to six-point calibration curves are constructed by using linear regression from the calibration standards (which standards are used depends on sample concentrations and instrument performance). Only after the compound has passed qualitative criteria is the concentration calculated according to a calibration curve used to establish the best fit between the calibration points. The correlation coefficient for each standard curve has to be greater than or equal to 0.99 to be accepted. The response factor for each compound is calculated from the calibration curve.

11.2.1 *Response-factor calculation*

Calculate the response factor (*RF*) for each selected compound as follows:

$$RF = \frac{C_c \times A_i}{C_i \times A_c} \quad (2)$$

where

C_c = concentration of the selected compound, in nanograms per microliter;

A_i = area of peak of the quantitation ion for the internal standard;

C_i = concentration of the internal standard, in nanograms per microliter; and

A_c = area of peak of the quantitation ion for the selected compound.

11.3 *Calculations*—If a selected compound has passed the qualitative identification criteria and the area under the peak(s) for the quantitation ion(s) for that compound has been properly integrated, the concentration in the sample is calculated as follows:

11.3.1 *Sediment-Sample Calculations*

Calculate the dry weight of sediment extracted, in grams:

$$W_d = W_w[(100 - \%\,\text{moisture})/100 \quad (3)$$

where

W_d = dry weight of sediment, in grams; and
W_w = wet weight of sediment, in grams.

Calculate sample-extract concentrations, E, for each compound:

$$E = (A_c / A_i) \times (RF) \times C_i \quad (4)$$

where

E = concentration of the selected compound in the sample extract, in nanograms per microliter;
A_c = area of peak of the quantitation ion for the selecetd compound;
A_i = area of peak of the quantitation ion for the internal standard;
RF = response factor calculated in equation 1; and
C_i = concentration of the internal standard, in nanograms per microliter.

Calculate sample concentrations, C_s, in micrograms per kilogram (which is equal to nanograms per gram), for each compound:

$$C_s = (E \times 200\,\mu\text{L}) / W_s \quad (5)$$

where

E = concentration of the selected compound in the sample extract, in nanograms per microliter; and
W_s = dry weight of sediment, in grams.

12. Reporting of Data Results

Pesticides are reported in concentrations from 0.5 to 50 µg/kg for sediment. If the concentration is greater than 50 µg/kg, a portion of the original sample extract is diluted appropriately with EtOAc, prepared with internal standard, and reanalyzed.

13. Method Performance

Initial method performance was evaluated for recovery using sediment collected from a northern California agricultural drain; this drain had a "typical" organic carbon concentration (1.5 percent) and had low background pesticide concentrations. Samples were spiked at 40 µg/kg (dry weight) and all compound recoveries were greater than 70 percent (an unspiked sediment sample was also run to determine if any of the pesticides were natively present in the sediment; data not shown). Additional method-performance metrics, including method recovery, variability, and MDLs, were determined using several samples of two sediments with different levels of percent organic carbon (described below) that had been collected and processed in the same manner as environmental samples.

13.1 *Method recovery and variability*—Pesticide recoveries and analytical variability were determined by comparing seven spiked samples with one another. These recoveries were determined in two different sediments; one from a northern California agricultural creek with 1.5 percent organic carbon and another from a central California estuary with 3.7 percent organic carbon. The northern California agricultural drain had a "typical" organic carbon percentage; the central California estuary had a higher organic carbon percentage to represent a more complex sediment matrix. Pesticides were spiked onto sediment matrices at 10 µg/kg by adding 100 ng of each compound per 10 g (dry weight) of sediment. Corresponding unspiked sediment samples were run to determine if any of the pesticides were present in the sediment before spiking; both sediments had low background pesticide concentrations. The mean recoveries for the two sediment matrixes are shown in table 4; the recoveries for pesticides included in the previous method were similar. The agricultural drain sediment had recoveries ranging from 81 to 101 percent, with relative standard deviations (RSDs) of 2 to 12 percent; the estuary sediment had recoveries of 75 to 102 percent (RSDs of 3 to 13 percent). Recoveries were good for both the "typical" sediment and the sediment with a higher percent organic carbon. Increased organic carbon can interfere with the recoveries of the pesticides of interest, and in sediments with a higher percent organic carbon, additional matrix spikes may be needed to determine the extent of potential interferences.

13.2 *Method detection limit (MDL)*—The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the compound concentration is greater than zero (U.S. Environmental Protection Agency, 1997). Initial MDLs were determined according to the procedure outlined by the USEPA in 40 CFR 136, Appendix B, assuming a 10-g (dry weight) sediment sample size.

The MDL was calculated according to the equation

$$MDL = S \times t_{(n-1,1-\alpha=0.99)} \quad (6)$$

where

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

n = number of replicate analyses; and

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

Following the USEPA procedure, seven replicate samples were fortified with compounds at concentrations two to five times the estimated MDL. This concentration range was used to calculate initial MDLs for the pesticides.

The MDLs for the GC/MS method are 0.6 to 3.1 µg/kg for the agricultural creek sediment and 0.8 to 3.4 µg/kg for the estuary sediment (table 4). The percent organic carbon was higher for the estuary (3.7 percent) than the agricultural drain (1.5 percent), but the MDLs were similar. Higher organic carbon content can lead to more co-extracted matrix interferences that could increase the MDLs, but this method is robust for higher organic carbon concentrations; prior studies have analyzed sediment samples with up to 36 percent organic carbon.

Table 4. Summary of method recovery and variability (expressed as mean percent recovery and relative standard deviation) and method detection limits determined from sets of 7 spiked samples of two different sediment matrixes.

[**Herbicides/Insecticide**s indicates carbon/alumina-SPE cleanup. **Fungicides** indicates Florisil cleanup. Compounds noted with an asterisk are non-fungicides that are amenable to Florisil cleanup. **Abbreviations/Acronyms:** RSD, relative standard deviation; MDL, method detection limit; µg/kg, microgram per kilogram]

Herbicides/Insecticides	Northern California agricultural drain sediment (1.5 percent organic carbon)			Central California estuary sediment (3.7 percent organic carbon)		
	Percent recovery	Percent RSD	MDL (µg/kg)	Percent recovery	Percent RSD	MDL (µg/kg)
2-Chloro-2,6-Diethylacetanilide	96.7	4.2	1.3	88.9	5.2	1.5
3,4-Dichloroaniline	80.5	5.2	1.3	77.3	7.2	1.8
3,5-Dichloroaniline	85.1	5.6	1.5	84.5	6.7	1.8
Alachlor	95.5	1.9	0.6	92.3	3.7	1.1
Allethrin	98.9	5.5	1.7	95.9	6.2	1.9
Atrazine	86.7	5.4	1.5	87.4	6.2	1.7
Azinphos-methyl	94.2	5.7	1.7	93.4	5.8	1.7
Benfluralin (Benefin)	93.7	5.7	1.7	92.6	6.9	2.0
Bifenthrin	99.3	2.0	0.6	96.0	2.6	0.8
Butralin	95.8	5.3	1.6	92.4	5.9	1.7
Butylate	88.2	4.6	1.3	81.5	5.7	1.5
Carbaryl	97.3	3.9	1.2	96.0	5.0	1.5
Carbofuran	88.3	4.4	1.2	93.0	5.2	1.5
Chlorpyrifos	93.0	3.1	0.9	93.0	4.4	1.3
Clomazone	94.9	6.6	2.0	91.2	7.4	2.1
Coumaphos	94.2	4.0	1.2	87.6	5.0	1.4
Cyhalofop-butyl	97.3	2.6	0.8	95.9	3.1	0.9
Cycloate	90.1	2.8	0.8	88.2	4.2	1.2
Cyfluthrin	93.9	4.4	1.3	94.6	4.5	1.3
Cyhalothrin	96.7	2.3	0.7	97.5	2.7	0.8
Cypermethrin	93.9	4.2	1.2	96.5	4.7	1.4
DCPA (Dacthal)	99.5	5.5	1.7	99.3	5.8	1.8
Deltamethrin	94.3	4.2	1.3	97.3	4.4	1.3
Diazinon	86.9	5.8	1.6	87.5	6.9	1.9
Dithiopyr	84.8	4.7	1.3	81.9	5.4	1.4
EPTC	82.2	3.1	0.8	91.8	4.0	1.1
Esfenvalerate	93.0	3.4	1.0	94.0	4.0	1.2
Ethalfluralin	90.5	4.1	1.2	93.0	4.7	1.4
Etofenprox	96.1	3.3	1.0	93.6	4.4	1.3
Fenpropathrin	95.6	3.5	1.0	96.1	4.0	1.2
Fenpyroximate	83.1	7.2	1.9	92.4	7.5	2.2

Table 4. Summary of method recovery and variability (expressed as mean percent recovery and relative standard deviation) and method detection limits determined from sets of 7 spiked samples of two different sediment matrixes.—Continued

[**Herbicides/Insecticide**s indicates carbon/alumina-SPE cleanup. **Fungicides** indicates Florisil cleanup. Compounds noted with an asterisk are non-fungicides that are amenable to Florisil cleanup. **Abbreviations/Acronyms:** RSD, relative standard deviation; MDL, method detection limit; µg/kg, microgram per kilogram]

Herbicides/Insecticides	Northern California agricultural drain sediment (1.5 percent organic carbon)			Central California estuary sediment (3.7 percent organic carbon)		
	Percent recovery	Percent RSD	MDL (µg/kg)	Percent recovery	Percent RSD	MDL (µg/kg)
Fenthion	96.7	6.6	2.0	87.6	8.3	2.3
Fipronil	94.3	5.4	1.6	97.9	5.8	1.8
Fipronil desulfinyl	92.2	6.1	1.8	96.4	7.1	2.1
Fipronil desulfinyl amide	83.4	7.5	2.0	77.9	8.2	2.0
Fipronil sulfide	93.2	5.0	1.5	95.8	5.3	1.6
Fipronil sulfone	98.3	3.1	1.0	98.1	4.0	1.2
Flufenacet	96.0	3.3	1.0	94.1	3.9	1.2
Flumetralin	95.7	4.1	1.2	92.3	5.4	1.6
Hexazinone	94.0	3.1	0.9	86.0	4.6	1.3
Malathion	93.1	3.3	1.0	94.0	4.5	1.3
Methidathion	99.3	5.7	1.8	84.3	6.9	1.8
Methoprene	96.3	5.4	1.6	86.9	6.8	1.9
Methyl parathion	92.4	3.8	1.1	89.9	5.1	1.5
Metolachlor	96.5	2.4	0.7	90.1	4.5	1.3
Molinate	91.1	3.4	1.0	79.7	5.4	1.4
Napropamide	98.5	2.8	0.9	92.2	3.7	1.1
Oxadiazon	99.2	4.4	1.4	91.1	5.3	1.5
Oxyflurofen	100.7	6.0	1.9	96.2	7.5	2.3
p,p'-DDD	95.4	3.3	1.0	97.9	4.2	1.3
p,p'-DDE	99.3	3.1	1.0	96.9	4.1	1.2
p,p'-DDT	93.9	2.8	0.8	96.2	3.7	1.1
Pentachloroanisole	90.4	3.9	1.1	82.2	5.1	1.3
Pebulate	87.7	3.3	0.9	82.2	3.8	1.0
Pendimethalin	94.3	2.7	0.8	95.5	3.7	1.1
Permethrin	94.1	3.1	0.9	97.5	3.5	1.1
Phenothrin	95.5	3.0	0.9	95.9	3.5	1.0
Phosmet	96.5	3.1	0.9	99.6	3.7	1.2
Piperonyl butoxide	94.8	4.1	1.2	90.0	5.7	1.6
Prodiamine	98.5	4.6	1.4	96.0	5.1	1.5
Prometon	89.9	9.5	2.7	87.8	10.2	2.8
Prometryn	85.1	5.0	1.3	84.7	7.8	2.1
Pronamide (Propyzamide)	90.7	6.0	1.7	92.0	6.1	1.8
Propanil	100.5	7.0	2.2	94.4	9.2	2.7
Propargite	94.4	7.4	2.2	91.5	8.3	2.4
Propyzamide	87.3	5.3	1.5	88.5	6.8	1.9
Pyridaben	91.8	4.3	1.2	94.6	4.7	1.4
Resemethrin	95.5	4.4	1.3	96.0	5.0	1.5
Simazine	90.2	4.7	1.3	84.2	5.7	1.5
tau-fluvalinate	92.9	4.0	1.2	94.5	4.3	1.3
Tebupirimfos	95.0	5.1	1.5	88.3	7.2	2.0
Tefluthrin	93.4	2.3	0.7	96.2	2.7	0.8
Tetradifon	96.9	6.4	2.0	93.5	6.0	1.8
Tetramethrin	97.5	3.1	0.9	96.1	4.0	1.2
Thiazopyr	96.0	6.2	1.9	97.8	6.5	2.0
Thiobencarb	95.7	2.0	0.6	94.6	3.6	1.1
Triallate	90.2	4.8	1.4	93.7	4.9	1.5
Trifluralin	91.7	3.0	0.9	88.8	4.3	1.2

Table 4. Summary of method recovery and variability (expressed as mean percent recovery and relative standard deviation) and method detection limits determined from sets of 7 spiked samples of two different sediment matrixes.—Continued

[**Herbicides/Insecticide**s indicates carbon/alumina-SPE cleanup. **Fungicides** indicates Florisil cleanup. Compounds noted with an asterisk are non-fungicides that are amenable to Florisil cleanup. **Abbreviations/Acronyms:** RSD, relative standard deviation; MDL, method detection limit; µg/kg, microgram per kilogram]

Fungicides	Northern California agricultural drain sediment (1.5 percent organic carbon)			Central California estuary sediment (3.7 percent organic carbon)		
	Percent recovery	Percent RSD	MDL (µg/kg)	Percent recovery	Percent RSD	MDL (µg/kg)
Azoxystrobin	97.9	3.0	0.9	102.0	4.1	1.3
Boscalid	96.0	3.9	1.2	100.2	5.8	1.8
Captan	83.9	11.9	3.1	84.1	12.3	3.4
Chlorothalonil	81.4	4.4	1.1	74.8	7.0	1.7
Cyproconazole	98.3	3.2	1.0	93.0	3.9	1.1
Cyprodinil	91.8	5.8	1.7	81.2	8.6	2.2
Difenoconazole	100.0	3.2	1.0	82.8	6.2	1.6
Dimethomorph	87.0	5.3	1.5	93.3	6.2	1.8
Famoxadone	92.8	5.9	1.7	81.3	8.3	2.1
Fenarimol	101.1	4.4	1.4	83.5	7.1	1.8
Fenbuconazole	89.8	6.5	1.8	102.1	6.6	2.1
Fenhexamide	92.8	8.5	2.5	94.0	11.3	3.3
Fluazinam	94.2	6.9	2.1	96.9	8.7	2.6
Fludioxinil	88.8	9.1	2.5	80.3	11.1	2.8
Fluoxastrobin	89.9	4.4	1.2	86.9	6.2	1.7
Flusilazole	92.1	7.4	2.2	92.5	8.6	2.5
Flutolanil	94.9	7.1	2.1	95.9	8.1	2.4
Flutriafol	91.9	3.6	1.1	92.7	4.6	1.4
Imazalil	91.3	6.4	1.8	89.7	7.4	2.1
Indoxacarb*	87.9	8.7	2.4	94.1	9.2	2.7
Iprodione	92.6	3.0	0.9	95.1	4.4	1.3
Kresoxim-methyl	89.2	1.8	0.5	80.1	3.9	0.9
Metalaxyl	86.6	6.9	1.9	87.9	8.4	2.3
Metconazole	95.5	4.1	1.2	90.6	6.7	1.9
Myclobutanil	96.5	5.8	1.7	91.9	7.7	2.2
Novaluron	92.3	3.9	1.1	92.5	4.2	1.2
Pentachloronitrobenzene	84.8	4.1	1.1	81.2	6.1	1.5
Propiconazole	83.5	4.2	1.1	77.5	5.0	1.2
Pyraclostrobin	85.8	4.1	1.1	86.7	5.3	1.4
Pyrimethanil	91.0	3.7	1.1	90.1	4.9	1.4
Tebuconazole	84.3	4.5	1.2	89.8	5.8	1.6
Tebupirimfos oxon*	97.5	6.6	2.0	90.7	8.0	2.3
Tetraconazole	92.6	3.8	1.1	82.1	6.0	1.5
Triadimefon	86.8	5.5	1.5	91.6	6.2	1.8
Triadimenol	92.7	5.3	1.5	83.6	6.5	1.7
Tribuphos*	89.1	7.9	2.2	92.7	8.5	2.5
Trifloxystrobin	96.9	3.4	1.0	94.8	4.1	1.2
Triflumizole	99.0	3.4	1.1	91.9	4.5	1.3
Triticonazole	95.9	5.9	1.8	97.8	6.5	2.0
Vinclozolin	99.3	3.7	1.2	96.9	4.5	1.4
Zoxamide	97.7	3.7	1.1	85.3	7.1	1.9

Summary

This method report provides details for the analysis of 119 pesticides in environmental sediment samples. The pesticides are isolated from sediment samples by accelerated solvent extraction with an organic solvent, sulfur is removed via gel-permeation chromatography, and the co-extracted matrix is removed with either carbon/alumina solid-phase extraction or Florisil®. Chromatographic separation, detection, and quantification are achieved with gas chromatography and mass spectrometry (GC/MS).

The analytical method showed good precision, with greater than 75 percent recovery and standard deviations of less than 13 percent for all compounds; 96 percent of the compounds in the method had recoveries greater than 80 percent and relative standard deviations less than 10 percent. Method detection limits (MDLs) for individual compounds ranged from 0.6 to 3.4 µg/kg for GC/MS for sediment matrices of up to 3.7 percent organic carbon.

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