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Water Resources Mission Area—Water Availability and Use Science Program

Methods of Analysis—Determination of Pesticides in Filtered Water and Suspended Sediment using Liquid Chromatography- and Gas Chromatography-Tandem Mass Spectrometry

Chapter 12 of
Section A, Water Analysis
Book 5, Laboratory Analysis

Techniques and Methods 5–A12

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

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
micrometer (µm)	3.937×10^{-5}	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
centimeter (cm)	0.3937	inch (in.)
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
microliter (µL)	2.642×10^{-7}	gallon (gal)
milliliter (mL)	2.642×10^{-4}	gallon (gal)
liter (L)	0.2642	gallon (gal)
	Flow rate	
milliliter per minute (mL/min)	0.03381	ounce, fluid per minute (fl. oz/min)
	Mass	
nanogram (ng)	3.527×10^{-11}	ounce, avoirdupois (oz)
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)
	Pressure	
millimeters of mercury (mmHg)	0.01934	pounds per square inch (psi)

U.S. customary units to International System of Units

Multiply	By	To obtain
	Pressure	
pound per square inch (psi)	51.7149	millimeters of mercury (mmHg)

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

$$°F = (1.8 \times °C) + 32.$$

Supplemental Information

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L).

Concentration equivalent units (assuming 1 liter equals one kilogram):

parts per thousand: mg/mL

parts per million (ppm): ng/µL

parts per billion (ppb): ng/mL

parts per trillion (ppt): ng/L

megaohm-centimeters (MΩ·cm): resistivity of water, used in the assessment of ultrapure water

volt (V): unit of electric potential difference

Abbreviations

AEI	advanced electron ionization
CCV	continuous calibration verification
EPA	U.S. Environmental Protection Agency
ESI	electrospray ionization
GC	gas chromatography
GC-MS/MS	gas chromatography-tandem mass spectrometry
HLB	hydrophilic-lipophilic balance
LC	liquid chromatography
LC-MS	liquid chromatography-mass spectrometry
LC-MS/MS	liquid chromatography-tandem mass spectrometry
LIMS	laboratory information management system
MDL	method detection limit
OCRL	organic chemistry research laboratory
PTV	programmable temperature vaporizing
QA/QC	quality assurance/quality control
RL	reporting limit
RSD	relative standard deviation
SPE	solid-phase extraction
USGS	U.S. Geological Survey
v:v	volume per volume

Methods of Analysis—Determination of Pesticides in Filtered Water and Suspended Sediment using Liquid Chromatography- and Gas Chromatography-Tandem Mass Spectrometry

By Michael S. Gross, Corey J. Sanders, Matthew D. De Parsia, and Michelle L. Hladik

Abstract

The widespread application of pesticides in agricultural and urban areas leads to their presence in surface waters. Presence of these biologically active chemicals in environmental waters potentially has adverse effects on nontarget organisms. To better understand the environmental fate of these contaminants, a robust method to capture chemicals with wide-ranging physicochemical properties has been developed. The method was developed by the U.S. Geological Survey's Organic Chemistry Research Laboratory to monitor pesticides, pesticide degradates, and other agrochemicals in environmental surface waters throughout the country. The analysis involves a multiresidue method to determine 183 pesticides and pesticide degradates in filtered water samples and 178 pesticides and pesticide degradates in paired suspended sediment samples. After the filtration of whole water, contaminants are individually measured in the filtered water and the collected suspended sediment. Filtered water is extracted via solid-phase extraction, whereas suspended sediment is extracted using an ultrasonication, solid-liquid extraction. Samples are analyzed by liquid chromatography-tandem mass spectrometry using an electrospray ionization source in positive and negative modes and analyzed by gas chromatography-tandem mass spectrometry using an advanced electron ionization source in positive mode. Instrument parameters were optimized for the highest sensitivity, and at least two transitions (quantifier and qualifier) were monitored for each analyte.

Recoveries in test filtered water (n=9; 183 analytes) from the American River, California, and suspended sediment (n=9; 178 analytes) samples fortified at 15 nanograms per liter (ng/L) ranged from 70.1 to 121.0 and 71.1 to 117.0 percent in water and suspended sediment filter samples, respectively. Method detection limits of pesticides and pesticide degradates ranged from 0.5 to 10.6 ng/L in water and 0.7 to 11.8 ng/L in suspended sediment filters. Reporting limits were 1.1–21.1 ng/L and 1.5–23.7 ng/L in water and filter samples, respectively. The developed method is applied to surface-water samples for the analysis of pesticides, pesticide degradates, and other agrochemicals.

Introduction

Pesticide applications can increase crop production, improve crop quality, and reduce proliferation of pest-borne diseases. The United States (U.S.) applies over 450 million kilograms (kg) of pesticides annually, representing 20–25 percent of the world market (Atwood and Paisley-Jones, 2017). Widespread use of pesticides has caused concerns about potential adverse effects because pesticides and their degradates are easily transported into and throughout the environment. Hundreds of synthetic pesticides of wide-ranging physicochemical properties are registered for use in the U.S. with multiple pesticides often being detected in individual surface-water samples (Gilliom and others, 2006; Orlando and others, 2014). The pesticide classes, compounds, and concentrations detected in environmental waters are affected by multiple factors including intensity of use, geographic location, seasonal dependence; and by soil, climate, and hydrologic characteristics (Gilliom and others, 2006). Sensitive (low nanograms per liter [ng/L]) analytical methods that target a diverse array of agrochemicals could improve understanding of the fate and transport of these chemicals in the environment.

The U.S. Geological Survey (USGS) Organic Chemistry Research Laboratory (OCRL) in Sacramento, California, has analyzed pesticides in environmental media since the 1990s. Early methods collected pesticides on octylsilane (C8) solid-phase extraction (SPE) cartridges (Domagalski and Kuivila, 1993; Crepeau and others, 2000). In 2008, SPE was transitioned to hydrophilic-lipophilic balance (HLB) cartridges for the analysis of 62 pesticides and degradates in water (Hladik and others, 2008). Pyrethroids, synthetic organophosphate insecticides, were reported to preferentially adsorb to suspended sediments (Hladik and Kuivila, 2009), highlighting the importance of individually measuring the dissolved and suspended phases of surface-water samples. With the introduction of new pesticides and the acquisition of new instrumentation, the method has been adapted through the years to include additional analytes and improve

sensitivity (Hladik and Calhoun, 2012; Orlando and others, 2013, 2014; Sanders and others, 2018). The most recent report included analysis of 154 pesticides and pesticide degradates in surface water and suspended sediment from the Sacramento–San Joaquin Delta (De Parsia and others, 2019). Methods described in De Parsia and others (2019) have been further updated and validated in this report, with compounds shifted from gas chromatography-tandem mass spectrometry (GC-MS/MS) to liquid chromatography-tandem mass spectrometry (LC-MS/MS) and new analytes added. At the time of this study, water samples are analyzed for 183 analytes and suspended sediments are analyzed for 178 compounds using LC-MS/MS and GC-MS/MS. Support for this report was provided by the California Water Science Center.

Purpose and Scope

The purpose of this report is to describe an analytical procedure for the extraction and quantification of pesticides and pesticide degradates in surface-water samples using LC-MS/MS and GC-MS/MS. Pesticide concentrations are determined individually in filtered water and suspended sediment (project dependent) from a single whole-water sample. The method is an expansion of previous methods (Hladik and others, 2008; Hladik and Calhoun, 2012; Orlando and others, 2013, 2014; Sanders and others, 2018; De Parsia and others, 2019) and increases the total number of target analytes to 183 in water and 178 in suspended sediment. New analytes include pesticide degradates and pesticides that have recently been registered or increasing in application (California Department of Pesticide Regulation, 2023; U.S. Environmental Protection Agency, 2023b). Whole-water samples were collected in 1-liter (L) amber-glass bottles and filtered through a pre-weighed 0.7-micrometer (µm) glass-fiber filter. Filtered water was extracted using SPE and combined with bottle washes that captured chemicals adsorbed to the glass. Suspended sediment samples on filters were air-dried and extracted via sonication. The analytical procedure described will contribute to a better understanding of the occurrence, fate, and transport of pesticides in the environment.

Compound recoveries, analytical precision, method detection limits (MDLs), and reporting limits (RLs) were determined for each analyte from spiked surface water collected from the American River, California. Water from the American River was used in place of laboratory reagent water to better represent environmental media. The American River has low suspended sediment and low dissolved organic carbon (Hladik and Calhoun, 2012). Zero target analytes (pesticides and pesticide degradates) were detected in blank samples during the development of this method. The MDLs were calculated in filtered surface water and suspended sediment samples following the U.S. Environmental Protection Agency (EPA) procedure (U.S. Environmental Protection Agency, 2016). Additional samples were monitored for background concentrations of analytes. Surrogate compounds and internal standards were added to each sample before sample preparation and analysis, respectively, to monitor recoveries, issues with matrix interferences and effects, or method performance. The method is applicable to pesticide analyses of filtered surface water and suspended sediment samples.

Methods of Study

Applications of pesticides in urban and agricultural settings are constantly changing due to changes in regulations, changes in pest pressures, and new chemicals being introduced to the market. As a result, analytical methods must be updated and validated to monitor the presence and fate of these current-use pesticides in surface waters.

Approach

Previous target lists were examined for compounds that could be removed from or added to analysis during updates to the analytical method. Criteria that were monitored when deciding on removing a chemical included (1) current applications of the pesticide, (2) persistence, and (3) toxicity (U.S. Environmental Protection Agency, 2022; California Department of Pesticide Regulation, 2023; Food and Agriculture Organization of the United Nations, 2023). Chemicals that have been registered for use in the U.S. or have seen increased use were added to the method after determining their suitability and applications (California Department of Pesticide Regulation, 2023; U.S. Environmental Protection Agency, 2023b). Analytical standards for pesticides and pesticide degradates were acquired from the EPA National Pesticide Standard Repository (Fort Meade, Maryland; U.S. Environmental Protection Agency, 2023a). If standards were unavailable, they were purchased from Sigma-Aldrich (St. Louis, Missouri), HPC Standards (Atlanta, Georgia), or Accustandard (New Haven, Connecticut). Mass-labeled surrogate and internal standards were purchased from Cambridge Isotope Laboratories (Tewksbury, Massachusetts), Sigma-Aldrich, or HPC.

Standards were individually optimized on LC-MS/MS or GC-MS/MS instrumentation, generating precursor and product ion(s) for each analyte. If necessary, chemicals were optimized in positive and negative mode by LC-MS/MS to choose the ionization mode that provided the best sensitivity. Instrument conditions were further optimized to produce the highest sensitivity for most analytes. The method was validated through different tests including analyte recovery, precision, and MDL.

Previous Studies

The reported method has been adapted from previous studies done by the OCRL (Hladik and others, 2008; Hladik and Kuivila, 2009; Hladik and Calhoun, 2012; Orlando and others, 2013, 2014; Sanders and others, 2018; De Parsia and others, 2019). Extractions with HLB SPE and analyses using GC-MS/MS and LC-MS/MS have provided sufficient sensitivity (low ng/L) and selectivity for the detection and quantification of pesticides and pesticide degradates in filtered water and suspended sediment samples.

Analytical Method

An analytical method is presented for the analysis of 183 pesticides and pesticide degradates in filtered surface waters as well as 178 pesticides and pesticide degradates in paired suspended sediments. Pesticides are analyzed in samples are analyzed by LC-MS/MS and GC-MS/MS. The USGS method number is O-4442-23 and method code is GLC02.

Method Number, Schedule, and Code

The analytical method and validation described in this report were developed by the USGS OCRL. The method was approved as USGS method O-4442-23. Pesticides and pesticide degradates are extracted from filtered water using SPE and analyzed using LC-MS/MS in electrospray ionization (ESI) positive and negative mode and using GC-MS/MS. Suspended sediment is extracted via sonication and analyzed using LC-MS/MS in ESI positive and negative mode and using GC-MS/MS.

Scope and Application

Method O-4442-23 is applied for the determination of 183 agrochemicals in whole-water samples, with individual measurements in filtered water (183 analytes) and suspended sediment (178 analytes). Due to low recoveries (less than 70 percent) in suspended sediment, 5 analytes (bentazon, imazalil, penoxsulam, tebuconazole t-butylhydroxy, and thiamethoxam degradate (NOA-407475) were removed from suspended sediment analyses with the remaining analytes analyzed in both matrices. The method is applicable to surface waters, but the collection and analyses of suspended sediment samples are project dependent. Surface waters with low suspended sediment concentrations may not contain enough suspended sediment in 1 L of water for analysis. Analyses are completed using LC-MS/MS in the ESI positive (n=138) and negative (n=12) modes and using GC-MS/MS (n=33) with advanced electron ionization (AEI). The laboratory method code for this method is GLC02 (U.S. Geological Survey, 2023a).

Analytical parameters, including compound names, retention times, quantifier transitions, and qualifier transitions, are reported in tables 1–3 for each analysis.

Summary of Method

Water samples are collected in the field following methods described in the USGS National Field Manual (U.S. Geological Survey, variously dated), and the samples are typically collected using 1-L pre-cleaned, baked amber-glass bottles. Samples are shipped overnight or transported on ice to the USGS OCRL for processing and analysis. Samples are processed within 7 days of receipt, and final extracts may be stored up to 30 days before analysis.

Samples for pesticide analyses were filtered through pre-weighed, 0.7-µm glass-fiber filters (Whatman Grade GF/F; Piscataway, New Jersey) to remove suspended materials. After filtration, the filter paper containing the suspended sediments was dried in the dark at room temperature overnight and then stored in a freezer at −20 degrees Celsius (°C) until extraction. Before extraction, the filtered water and dried suspended sediment fractions were each spiked with 50 microliters (µL) of a 1 nanogram per microliter (ng/µL) recovery surrogate solution containing atrazine-$^{13}C_3$, fipronil-$^{13}C_4$,$^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, *cis*-permethrin-$^{13}C_6$, *p,p′*-DDE-$^{13}C_{12}$, tebuconazole-$^{13}C_3$, and trifluralin-d_{14}.

Water was loaded under vacuum onto an Oasis HLB (Waters, Milford, Mass.; 6 milliliters [mL], 500 milligrams [mg]) cartridge that had been conditioned before use with one column volume of dichloromethane followed by one column volume of acetone and two column volumes of deionized water. The water samples were pulled through the SPE cartridge under vacuum at a flow rate of approximately 10 milliliters per minute (mL/min). After extraction, the SPE cartridge was dried under vacuum. Analytes were eluted with 10 mL of 1:1 volume per volume (*v:v*) acetone:dichloromethane. The eluent was evaporated to less than 0.5 mL under a gentle stream of dry nitrogen (Organomation N-Evap; Berlin, Mass.) and solvent-exchanged into acetonitrile. The final sample volume was 0.2 mL.

The suspended sediment fraction on the filter paper was extracted twice with 50 mL of dichloromethane via sonication (Fisherbrand 11211; Waltham, Mass.) for 10 minutes. The extract was filtered through sodium sulfate and evaporated under nitrogen using a Turbovap II (Biotage; Uppsala, Sweden) to 0.5 mL. The solvent was exchanged into acetonitrile and further evaporated to less than 0.2 mL using a gentle stream of dry nitrogen. The final sample volume was 0.2 mL.

An internal standard solution containing 2.5 ng/µL of acenaphthene-d_{10}, bifenthrin-d_5, clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 was then added (20 µL) to the extracts of both fractions. Sample extracts were stored in a freezer at −20 °C until analysis, up to 30 days.

Table 1. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) retention times, instrument parameters, and transitions for target compounds in electrospray ionization positive (ESI[+]) mode.

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored.
Abbreviations: min, minute; V, volt; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Fragmentor (V)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transition (CE) (*m/z* → *m/z* [eV])
3,4-Dichloroaniline (3,4-DCA)	7.00	1	123	162 → 127 (20)	162 → 74 (62)
3,5-Dichloroaniline (3,5-DCA)	7.62	1	97	162 → 127 (20)	162 → 74 (50)
Acetamiprid	5.73	1	102	223.1 → 126 (20)	223.1 → 56.1 (12)
Acetochlor	9.39	1	84	270.1 → 224 (4)	270.1 → 59.1 (12)
Atrazine	6.79	1	102	216.1 → 174 (12)	216.1 → 68 (40)
Atrazine-$^{13}C_3$	6.79	1	127	219.1 → 177 (12)	219.1 → 70.1 (32)
Atrazine, desethyl	5.66	1	83	188.1 → 146 (12)	188.1 → 68.1 (28)
Atrazine, desisopropyl	5.31	3	93	174.1 → 68.1 (28)	174.1 → 43.1 (36)
Azoxystrobin	8.25	1	102	404.1 → 372.1 (8)	404.1 → 329 (32)
Benzobicyclon	9.21	1	145	447 → 257 (24)	447 → 349 (36)
Benzovindiflupyr	10.41	1	107	398.1 → 378 (8)	398.1 → 111 (50)
Boscalid	8.48	1	102	343 → 307 (16)	343 → 78 (50)
Boscalid metabolite - M510F01 acetyl	7.96	1	146	401.1 → 140 (20)	401.1 → 112 (50)
Broflanilide	12.66	1	165	663 → 643 (20)	663 → 623 (44)
Bromuconazole	8.32	2	111	376 → 158.9 (28)	376 → 70 (16)
Butralin	13.59	1	68	296.2 → 240 (8)	296.2 → 57.1 (20)
Carbaryl	6.67	1	64	202.1 → 145.1 (4)	202.1 → 115 (36)
Carbendazim	5.01	1	107	192.1 → 160 (12)	192.1 → 105 (40)
Carbofuran	6.52	1	79	222.1 → 123 (16)	222.1 → 165.1 (4)
Chlorantraniliprole	7.40	1	117	482 → 450.9 (12)	482 → 283.9 (8)
Chlorpyrifos	13.38	1	74	349.9 → 197.9 (8)	349.9 → 293.8 (12)
Chlorpyrifos oxon	8.80	1	88	334 → 197.9 (28)	334 → 277.8 (12)
Clomazone	7.42	1	78	240.1 → 125 (16)	240.1 → 99 (50)
Clothianidin	5.58	1	73	250 → 169 (8)	250 → 131.9 (12)
Clothianidin desmethyl	5.43	2	93	236 → 131.9 (8)	236 → 113 (24)
Clothianidin-d_3	5.58	1	63	253 → 172 (8)	253 → 131.9 (12)
Coumaphos	11.51	1	132	363 → 226.9 (24)	363 → 288.9 (24)
Cyantraniliprole	6.82	1	126	473 → 442 (12)	473 → 284 (8)
Cyazofamid	10.26	1	88	325.1 → 108 (8)	325.1 → 44.1 (28)
Cycloate	11.83	1	78	216.1 → 55.1 (28)	216.1 → 72 (16)
Cymoxanil	5.89	1	55	199.1 → 128 (0)	199.1 → 111 (12)
Cyproconazole	7.75	1	98	292.1 → 70 (16)	292.1 → 125 (32)
Cyprodinil	7.70	1	116	226.1 → 93 (40)	226.1 → 77 (48)
DCPMU	6.48	1	106	219 → 126.9 (32)	219 → 161.9 (12)
DCPU	6.15	1	116	205 → 127 (28)	205 → 161.9 (12)
Desthio-prothioconazole	8.16	1	146	312 → 125 (36)	312 → 70.1 (24)
Diazinon	11.14	1	126	305.1 → 169.1 (16)	305.1 → 153.1 (16)
Diazinon oxon	6.85	1	112	289.1 → 153 (16)	289.1 → 84 (40)
Dichlorvos	6.26	1	112	221 → 109 (12)	221 → 94.9 (40)
Difenconazole	10.46	1	141	406.1 → 250.9 (24)	406.1 → 188 (50)
Dimethomorph	7.42	2	111	388.1 → 301.1 (16)	388.1 → 165 (32)
Dinotefuran	5.02	2	45	203.1 → 87 (8)	203.1 → 113 (4)

Table 1. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) retention times, instrument parameters, and transitions for target compounds in electrospray ionization positive (ESI[+]) mode.—Continued

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored.
Abbreviations: min, minute; V, volt; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Fragmentor (V)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transition (CE) (*m/z* → *m/z* [eV])
Diuron	6.85	1	106	233 → 72 (20)	233 → 159.9 (24)
EPTC	9.92	2	79	190.1 → 43.1 (16)	190.1 → 128.1 (8)
Ethaboxam	6.43	1	146	321.1 → 200 (24)	321.1 → 183 (20)
Etoxazole	13.57	1	103	360.2 → 141 (28)	360.2 → 57.1 (28)
Fenamidone	8.31	1	93	312.1 → 236.1 (8)	312.1 → 65.1 (50)
Fenbuconazole	8.92	1	112	337.1 → 70 (16)	337.1 → 125 (32)
Fenhexamid	8.43	1	132	302.1 → 55.1 (40)	302.1 → 97.1 (24)
Fenpyroximate	13.55	1	103	422.2 → 366.1 (8)	422.2 → 138.1 (32)
Flonicamid	5.43	2	131	230.1 → 203 (12)	230.1 → 174 (16)
Florpyrauxifen-benzyl	12.18	1	88	439 → 91 (20)	439 → 65 (50)
Flufenacet	9.49	1	73	364.1 → 152 (12)	364.1 → 194.1 (4)
Fluindapyr	9.54	1	92	352.2 → 256 (28)	352.2 → 312.1 (16)
Flumetralin	13.46	1	69	422.1 → 143 (8)	422.1 → 107 (48)
Fluopicolide	8.77	1	103	383 → 172.9 (20)	383 → 144.9 (50)
Fluopyram	8.83	1	127	397.1 → 207.9 (20)	397.1 → 145 (50)
Fluoxastrobin	9.55	1	103	459.1 → 427 (12)	459.1 → 188 (36)
Flupyradifurone	5.87	1	141	289.1 → 126 (20)	289.1 → 90.1 (48)
Fluridone	7.65	1	170	330 → 309 (36)	330 → 259 (50)
Flutolanil	9.28	1	103	324.1 → 65 (50)	324.1 → 242 (24)
Flutriafol	6.59	1	78	302.1 → 70 (12)	302.1 → 95 (50)
Fluxapyroxad	8.39	1	92	382.1 → 362 (8)	382.1 → 314 (24)
Halauxifen-methyl ester	8.27	1	108	345 → 284.9 (20)	345 → 250 (32)
Hexazinone	6.01	1	73	253.2 → 171 (12)	253.2 → 85.1 (36)
Imazalil	5.87	1	98	297.1 → 41.1 (32)	297.1 → 159 (20)
Imidacloprid	5.66	1	88	256.1 → 175 (12)	256.1 → 209 (12)
Imidacloprid-d_4	5.66	1	91	260.1 → 179 (16)	260.1 → 213 (12)
Imidacloprid desnitro	4.90	1	126	211.1 → 126 (20)	211.1 → 90 (36)
Imidacloprid olefin	5.37	2	59	254.1 → 236 (0)	254.1 → 205 (8)
Imidacloprid urea	5.43	2	112	212.1 → 128 (16)	212.1 → 99 (16)
Imidacloprid, 5-hydroxy	5.44	2	131	272.1 → 225 (12)	272.1 → 191 (12)
Indaziflam	7.08	1	97	302.2 → 158 (12)	302.2 → 145.1 (24)
Indoxacarb	12.57	1	132	528.1 → 56 (32)	528.1 → 150 (20)
Ipconazole	10.37	2	132	334.2 → 125 (40)	334.2 → 70.1 (20)
Iprodione	9.11	1	83	330 → 244.9 (8)	330 → 56 (36)
Isofetamid	10.08	1	79	360.2 → 125 (28)	360.2 → 210 (4)
Kresoxim-methyl	10.36	1	88	314.1 → 267.1 (0)	314.1 → 222.1 (8)
Malathion	9.16	1	84	331.1 → 127 (4)	331.1 → 99 (16)
Malathion oxon	6.40	1	78	315.1 → 99 (20)	315.1 → 127 (4)
Mandestrobin	9.36	1	64	314.2 → 192 (4)	314.2 → 119 (24)
Mandipropamid	8.46	1	97	412.1 → 328.1 (8)	412.1 → 125 (36)
Metalaxyl	6.82	1	98	280.2 → 220.1 (8)	280.2 → 160 (20)
Metalaxyl alanine metabolite	5.82	1	83	296.2 → 278.1 (4)	296.2 → 146.1 (12)

Table 1. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) retention times, instrument parameters, and transitions for target compounds in electrospray ionization positive (ESI[+]) mode.—Continued

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored.
Abbreviations: min, minute; V, volt; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Fragmentor (V)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transition (CE) (*m/z* → *m/z* [eV])
Metconazole	9.10	2	131	320.2 → 125 (40)	320.2 → 70.1 (20)
Methoxyfenozide	8.93	1	92	369.2 → 313.1 (0)	369.2 → 149 (12)
Metolachlor	9.25	1	83	284.1 → 252 (8)	284.1 → 176.1 (24)
Metolachlor-$^{13}C_6$	9.25	1	83	290.1 → 258.1 (8)	290.1 → 182.1 (24)
Myclobutanil	8.16	1	103	289.1 → 70.1 (16)	289.1 → 125 (32)
Myclobutanil-d_4	8.16	1	122	293.1 → 70.1 (16)	293.1 → 129 (32)
Naled (Dibrom)	7.17	1	92	378.8 → 127 (12)	378.8 → 109 (36)
Napropamide	8.72	1	68	272.2 → 58.1 (28)	272.2 → 171 (16)
Oryzalin	9.20	1	132	347.1 → 288 (12)	347.1 → 242.9 (12)
Oxadiazon	13.30	1	88	345.1 → 219.9 (16)	345.1 → 303 (12)
Oxathiapiprolin	9.25	1	150	540.2 → 500 (24)	540.2 → 163 (50)
Oxyfluorfen	13.16	1	88	362 → 316 (8)	362 → 237 (20)
Oxyfluorfen-d_5	13.16	1	79	367 → 237 (24)	367 → 315.9 (8)
Paclobutrazol	7.54	1	83	294.1 → 70.1 (16)	294.1 → 125 (40)
Pendimethalin	13.37	1	64	282.2 → 212 (4)	282.2 → 41.1 (48)
Penoxsulam	7.10	1	155	484.1 → 194.6 (44)	484.1 → 164 (36)
Penthiopyrad	10.52	1	102	360.1 → 276 (8)	360.1 → 177 (36)
Phosmet	8.11	1	64	318 → 160 (12)	318 → 77 (50)
Picarbutrazox	10.55	1	64	410.2 → 310 (8)	410.2 → 107 (24)
Picoxystrobin	10.61	1	74	368.1 → 145 (16)	368.1 → 205 (0)
Piperonyl butoxide	12.98	1	79	356.2 → 177 (4)	356.2 → 119 (36)
Prodiamine	12.99	1	108	351.1 → 250 (24)	351.1 → 43.1 (28)
Prometon	5.78	1	122	226.2 → 142.1 (20)	226.2 → 184.1 (12)
Prometryn	6.74	1	122	242.2 → 158 (20)	242.2 → 200.1 (12)
Propanil	7.49	1	88	218 → 161.9 (12)	218 → 127 (24)
Propargite	13.65	1	78	368.2 → 231.1 (4)	368.2 → 175 (12)
Propiconazole	9.51	1	108	342.1 → 69.1 (16)	342.1 → 158.9 (24)
Propyzamide	8.56	1	73	256 → 172.9 (20)	256 → 44.1 (28)
Pydiflumetofen	11.93	1	87	426 → 192.9 (36)	426 → 406 (8)
Pyraclostrobin	11.42	1	93	388.1 → 194 (4)	388.1 → 163 (20)
Pyridaben	13.93	1	78	365.2 → 147.1 (20)	365.2 → 309.1 (4)
Pyrimethanil	6.72	1	102	200.1 → 107.1 (20)	200.1 → 42.1 (44)
Pyriproxyfen	13.22	1	78	322.2 → 96 (8)	322.2 → 77.7 (50)
Quinoxyfen	12.50	1	170	308 → 162 (50)	308 → 197 (32)
Sedaxane	8.87	2	92	332.2 → 292 (12)	332.2 → 159 (16)
Simazine	6.22	1	87	202.1 → 68 (36)	202.1 → 71.1 (24)
Sulfoxaflor	5.99	1	49	278.1 → 174 (4)	278.1 → 154 (24)
Tebuconazole	8.65	1	92	308.2 → 70.1 (20)	308.2 → 125 (40)
Tebuconazole-$^{13}C_3$	8.65	1	107	311.8 → 70.1 (20)	311.8 → 43.1 (50)
Tebuconazole-t-butylhydroxy	6.82	1	121	324.2 → 70.1 (20)	324.2 → 125 (50)
Tebufenozide	9.97	1	74	353.2 → 133.1 (12)	353.2 → 203.2 (0)
Tebupirimfos	13.33	1	78	319.1 → 277 (8)	319.1 → 153.1 (28)

Table 1. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) retention times, instrument parameters, and transitions for target compounds in electrospray ionization positive (ESI[+]) mode.—Continued

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored. **Abbreviations**: min, minute; V, volt; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Fragmentor (V)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transition (CE) (*m/z* → *m/z* [eV])
Tebupirimfos oxon	8.50	1	83	303.2 → 233 (20)	303.2 → 261 (12)
Tetraconazole	8.56	1	136	372 → 70 (20)	372 → 158.9 (28)
Thiabendazole	5.09	1	151	202 → 175 (24)	202 → 131 (36)
Thiacloprid	5.96	1	45	253 → 126 (16)	253 → 90 (40)
Thiamethoxam	5.40	2	68	292 → 211 (8)	292 → 181 (20)
Thiamethoxam degradate (CGA-355190)	5.64	1	112	248 → 175 (15)	248 → 56 (44)
Thiamethoxam degradate (NOA-407475)	0.75	1	102	247 → 161 (12)	247 → 132 (28)
Thiobencarb	11.47	1	63	258.1 → 125 (12)	258.1 → 100.1 (8)
Tolfenpyrad	12.82	1	175	384.2 → 197.1 (24)	384.2 → 145 (28)
Triadimefon	8.39	1	78	294.1 → 69.1 (16)	294.1 → 197 (12)
Triadimenol	7.57	1	64	296.1 → 70.1 (4)	296.1 → 43.1 (50)
Triallate	13.63	1	88	304 → 86 (12)	304 → 43.1 (24)
Tribufos	14.04	1	92	315.1 → 57.1 (20)	315.1 → 41.1 (50)
Tricyclazole	5.76	1	121	190 → 136 (28)	190 → 163 (20)
Trifloxystrobin	12.63	1	108	409.1 → 206 (8)	409.1 → 186 (12)
Triflumizole	9.37	1	79	346.1 → 278.1 (4)	346.1 → 43.2 (20)
Triticonazole	7.73	1	108	318.1 → 70 (12)	318.1 → 43.1 (50)
Valifenalate	7.99	2	78	399.2 → 155 (36)	399.2 → 116 (16)
Zoxamide	11.05	1	78	336 → 187 (16)	336 → 159 (44)

Table 2. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) retention times, instrument parameters, and transitions for target compounds in electrospray ionization negative (ESI[–]) mode.

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored. **Abbreviations**: min, minute; V, volt; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Fragmentor (V)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transition (CE) (*m/z* → *m/z* [eV])
Bentazon	6.05	1	112	239.1 → 132 (24)	239.1 → 197 (16)
Clothianidin-d_3	4.76	2	69	251 → 58 (8)	251 → 168 (8)
Cyclaniliprole	6.89	1	122	597.9 → 256 (8)	597.9 → 144.9 (32)
Famoxadone	7.04	1	103	373.1 → 282 (12)	373.1 → 77.1 (16)
Fipronil	6.86	1	93	434.9 → 329.9 (8)	434.9 → 183 (40)
Fipronil-$^{13}C_4$,$^{15}N_2$	6.86	1	107	440.9 → 335.9 (8)	440.9 → 251.9 (24)
Fipronil desulfinyl	6.80	1	88	387 → 350.9 (4)	387 → 281.9 (32)
Fipronil desulfinyl amide	6.12	1	68	405 → 328.9 (12)	405 → 368.9 (0)
Fipronil sulfide	6.90	1	83	418.9 → 261.9 (24)	418.9 → 382.9 (4)
Fipronil sulfone	6.96	1	117	450.9 → 414.9 (8)	450.9 → 281.9 (20)
Fluazinam	7.45	1	165	462.9 → 415.9 (12)	462.9 → 397.9 (8)
Flubendiamide	6.89	1	112	681 → 254 (20)	681 → 271.9 (20)
Fludioxinil	6.61	1	141	247 → 180 (28)	247 → 126 (28)
Novaluron	7.19	1	97	491 → 471 (4)	491 → 305 (4)

Table 3. Gas chromatography-tandem mass spectrometry (GC-MS/MS) retention times, instrument parameters, and transitions for target compounds.

[CE represents the collision energy reported in electronvolts (eV) for the fragmentation of precursor to the product for each transition monitored. **Abbreviations**: min, minute; *m/z*, mass-to-charge ratio]

Compound	Retention time (min)	Window (min)	Quantifying transition (CE) (*m/z* → *m/z* [eV])	Qualifying transitions (CE) (*m/z* → *m/z* [eV])
Acenaphthene-d_{10}	8.72	1	164.1 → 162.1 (20)	164.1 → 160.1 (38)
Acibenzolar-S-methyl	11.94	1	182 → 180.9 (6)	134.9 → 106.9 (8)
Allethrin	13.58	2	123.1 → 81 (6)	79.1 → 77 (12) 134.9 → 63 (22)
Benefin (Benfluralin)	9.73	1	292 → 263.9 (6)	292 → 160 (26)
Bifenthrin	18.86	1	181 → 166 (4)	181 → 165.1 (22)
Bifenthrin-d_5	18.83	1	186.1 → 171.1 (16)	186.1 → 170.1 (30)
Chlorfenapyr	15.42	1	59 → 31 (6)	59 → 29 (10)
Chlorothalonil	10.86	1	263.8 → 228.8 (18)	263.8 → 167.9 (30)
Cyfluthrin	23.30	2	163 → 127 (4)	163 → 91 (14)
Cyhalofop-butyl	20.37	1	256 → 120 (10)	357.1 → 256 (8)
Cyhalothrin	20.62	1	208.1 → 181 (6)	197 → 141 (14)
Cypermethrin	23.90	2	163 → 127 (4)	181 → 152 (28)
DCPA	12.64	1	298.9 → 220.9 (32)	300.9 → 272.8 (8)
Deltamethrin	26.49	1	172 → 93 (10)	181 → 152 (26)
Dithiopyr	11.89	1	354 → 306 (6)	306 → 286 (6)
Esfenvalerate	25.64	1	167 → 124.9 (6)	225 → 118.9 (20)
Ethalfluralin	9.61	1	276 → 202 (18)	316.1 → 276 (8)
Etofenprox	24.33	1	162.9 → 134.9 (8)	162.9 → 106.9 (20)
Fenpropathrin	19.18	1	181 → 152.1 (28)	181 → 127 (32)
Methoprene	13.84	1	73 → 43 (18)	69.1 → 41 (8)
Methylparathion	11.70	1	262.9 → 108.9 (12)	125 → 79 (6)
Nitrapyrin	8.41	1	193.9 → 132.9 (18)	193.9 → 111.9 (36)
p,*p*'-DDD	16.22	1	234.9 → 165 (32)	234.9 → 198.9 (16)
p,*p*'-DDE	15.03	1	245.9 → 175.9 (38)	317.9 → 245.9 (28)
p,*p*'-DDE-$^{13}C_{12}$	15.03	1	258 → 188 (38)	330 → 258 (30)
p,*p*'-DDT	17.35	1	234.9 → 164.9 (26)	234.9 → 198.9 (18)
Pentachloroanisole (PCA)	10.26	1	264.8 → 236.8 (12)	279.8 → 264.7 (8)
Pentachloronitrobenzene (PCNB)	10.55	1	248.8 → 213.8 (14)	213.8 → 178.8 (14)
Permethrin	22.22	2	182.9 → 165 (6)	182.9 → 168 (6)
Permethrin-$^{13}C_6$	22.08	1	189 → 174 (6)	189 → 171 (6) 182.9 → 155.1 (5)
Phenothrin	19.86	1	123 → 81 (6)	183 → 165 (6)
Resmethrin	18.02	2	143.1 → 128 (6)	123 → 81 (6)
Tefluthrin	10.85	1	176.9 → 126.9 (18)	197 → 141 (12)
Tetramethrin	18.95	1	163.9 → 107 (14)	163.9 → 135 (6)
t-Fluvalinate	25.58	2	250 → 55 (18)	250 → 200 (22)
Trifluralin	9.70	1	306 → 264 (6)	264 → 206 (6)
Trifluralin-d_{14}	9.64	1	315.1 → 267 (6)	267 → 209 (6)
Vinclozolin	11.62	1	197.9 → 144.9 (18)	212 → 171.9 (16)

Safety Considerations

Appropriate personal protective equipment must always be worn during sample handling and processing, including safety glasses/goggles, nitrile gloves, and laboratory coats. Steps that use organic solvents must be completed in a well-vented fume hood. Proper precautions should be taken when handling heated zones (that is, injector, oven, and MS sources) of the LC-MS/MS and GC-MS/MS instrumentation, which can be upwards of 320 °C. Zones should be given time to cool before instrument maintenance procedures. Laboratory personnel should receive hazardous materials safety training and understand the hazards associated with solvents, target compounds, and reagents related to this method. Liquid waste produced during sample preparation and analysis must be collected in appropriate containers (glass bottles or plastic carboys) for proper disposal.

Interferences

Interferences that cause positive and negative analytical biases potentially lead to inaccurate identification or quantitation of target analytes. Matrix interferences, including additional environmental contaminants, natural organic matter, and salts, may occupy active sites on the SPE stationary phase or coelute with target analytes, causing lower recoveries or matrix effects in instrumental analysis. To address and recognize potential interferences, quality assurance/quality control (QA/QC) samples are necessary, including instrument blanks, laboratory blanks, field blanks, field replicates, matrix spikes, and continuous calibration verification (CCV) samples. Additional QA/QC protocols, such as surrogate and internal standards, will help correct for or interpret these interferences through monitoring recovery and instrument response. Furthermore, because many of these target analytes are used in household pest controls, it is important for field and laboratory personnel to limit contamination concerns related to repellent-treated clothing and contamination from applications of pesticides at home or near the laboratory before sample handling.

Equipment and Supplies

The following equipment and supplies are used for water and suspended sediment method development, sample collection, and sample preparation. If appropriate, equivalent equipment and supplies may be used. All laboratory materials must be properly cleaned before sample preparation to avoid possible contamination. Glassware is washed with Liquinox solution, rinsed with hot tap water, and then rinsed with organic-free water. After washing, glassware is baked at 450 °C in a muffle furnace. Glass-fiber filters, glass wool, and sodium sulfate are all baked at 450 °C in a muffle furnace. Materials that cannot be baked, including stainless-steel spatulas and tweezers, are solvent-rinsed with acetone.

- Analytical balances—An analytical balance capable of weighing to the nearest 0.1 mg is used for weighing filter papers pre- and post-filtering (Sartorius Quintix). An analytical balance capable of weighing to the nearest 0.002 mg is used for weighing and preparing neat standards (Sartorius Cubis II). Analytical balances are internally calibrated before use and externally calibrated yearly. The accuracy is checked as necessary.
- Concentrator tubes—Samples are eluted into, transferred into, and evaporated under nitrogen in 15 mL and 200 mL glass concentrator tubes (DWK Life Sciences Snap Cap Centrifuge Tube and Biotage Evaporation Tube).
- Diaphragm pumps—Diaphragm pumps are used to pump water through filters or to pull water through SPE cartridges (Masterflex L/S with polytetrafluoroethylene [PTFE], Diaphragm Pumphead and a Gast Diaphragm Vacuum/Pressure Pump).
- Electronic pipettes—A 10–100 µL electronic pipette is used to fortify samples with surrogate standard, internal standard, and matrix spike. Additional capacities of electronic pipettes or manual pipettes (0.1–2 µL, 0.5–10 µL, 20–300 µL, 100–1,000 µL, 500–5,000 µL, and 1–10 mL) may be necessary for standard preparation. Appropriate disposable polypropylene tips are used with the pipettes. Electronic and manual pipettes are calibrated yearly, and accuracy is checked as necessary.
- Erlenmeyer flasks—Suspended sediment filter papers are extracted in a 250-mL glass Erlenmeyer flask.
- Filter holder—An aluminum filter holder (Geotech, 142 millimeter [mm]) is used for filtering water samples.
- GC-MS/MS Column—An Agilent Technologies DB-5MS analytical column (30 meter [m]×0.25 mm×0.25 µm) is used for gas chromatography (GC) separation. The column contains a 10-m integrated guard column made from deactivated fused silica tubing at the front of the analytical column.
- Glass bottles—Amber-glass bottles (1 L) are used to collect grab samples in the field.
- Glass-fiber filter—A Whatman Grade GF/F glass-fiber filter (142 mm, 0.7 µm) is used to filter water samples and collect suspended sediment.
- Glass funnels are used in filtering and drying suspended sediment extracts.
- Glass wool is used to plug glass funnels to which sodium sulfate is added, and suspended sediment samples are poured through following extraction.

- Graduated cylinders—Water samples are filtered into 1-L graduated glass cylinders. Additional sizes may be necessary in preparation of mobile phases and organic solvent mixtures.
- LC-MS/MS column—An Agilent Technologies Zorbax Eclipse XDB-C18 column (2.1 mm×150 mm, 3.5 µm) preceded by a Zorbax Eclipse XDB-C8 guard cartridge (2.1 mm×12.5 mm, 5 µm) is used for liquid chromatography (LC) separation.
- Muffle furnace—Glassware is baked at 450 °C for a minimum of 4 hours after washing to remove organic contaminants before use (Thermo Scientific Lindberg Blue M).
- Nitrogen generators produce nitrogen (up to 99.9 percent) for evaporators and LC-MS/MS instrumentation (Claind Nigen LCMS 40-1, FDGSi Maestro 64-1).
- Nitrogen evaporators are used to concentrate samples (Organomation N-Evap, Biotage Horizon XcelVap, and Biotage TurboVap).
- Oasis HLB SPE cartridges—Water samples are extracted with 500 mg, 6 mL Waters Oasis HLB SPE cartridges.
- Pasteur pipettes—Glass Pasteur pipettes are used for the transfer of samples.
- Solvent dispensers—Solvent bottles are equipped with 1–10 mL solvent dispensers (BrandTech Dispensette S) for volumetric additions of solvent to samples.
- A sonicator is used to extract suspended sediment filter samples (Fisherbrand 11211).
- The SPE tube adapters allow SPE cartridges to be eluted in series if one clogs during sample loading.
- The SPE tubing is used to load 1-L samples under vacuum onto SPE cartridges. Tubing is made from PTFE and contains an adapter to fit in the cartridge and a weighted end to sit at the bottom of the sample bottle.
- Vacuum manifold—A vacuum manifold is used for SPE of water samples (Supelco Visiprep 12). The manifold includes a vial rack to hold concentrator tubes.
- Vial inserts—Final sample extracts are placed in 250-µL vial inserts.
- Vials and caps—Amber-glass screw top vials (2 mL) and screw caps are used for final sample extracts. Extracts are placed in a 250 µL vial insert and housed in the screw top vials. Vials must fit in instrument autosampler trays.

Instrumentation

Surface water and suspended sediment sample extracts are analyzed by LC-MS/MS and GC-MS/MS. Instrumentation are described below, including columns for chromatography.

Liquid Chromatography-Tandem Mass Spectrometry

The LC-MS/MS analysis is completed on an Agilent Technologies (Santa Clara, Calif.) 1260 infinity bio-inert high-performance liquid chromatograph coupled to a 6430 triple quadrupole mass spectrometer. The instrumentation is equipped with a 1260 bio-inert high-performance autosampler, a bio-inert quaternary pump, and a 1290 thermostatted column compartment. An Agilent Technologies Zorbax Eclipse XDB-C18 column (2.1 mm×150 mm, 3.5 µm) preceded by a Zorbax Eclipse XDB-C8 guard cartridge (2.1 mm×12.5 mm, 5 µm) is used for separation. Analyses are completed in positive and negative ion modes following an ESI source.

Gas Chromatography-Tandem Mass Spectrometry

The GC-MS/MS analysis is completed on a Trace 1310 gas chromatograph coupled to a TSQ 9000 triple quadrupole mass spectrometer (Thermo Scientific, Waltham, Mass.). The instrument is equipped with a TriPlus RSH autosampler, a programmable temperature vaporizing (PTV) inlet, and an AEI source. An Agilent Technologies DB-5MS analytical column (30 m×0.25 mm×0.25 µm) with a 10-m integrated guard column is used for GC separation.

Analytical Standards and Reagents

Analytical standards and reagents used for method validation, sample preparation, and analyte quantification are described below. Equivalent standards and reagents may be used, but should be validated to ensure no contamination.

Neat Standards, Standard Solutions, and Reagents

- Analyte protectants—Analyte protectants of ethylglycerol, gulonolactone, and sorbitol were purchased from Sigma-Aldrich. Analyte protectants are used to limit matrix effects in GC-MS/MS analysis.
- Analytical standards—Neat analytical standards of pesticides and pesticide degradates were obtained from the EPA National Pesticide Standard Repository (U.S. Environmental Protection Agency, 2023a).

Standards for compounds that were not available at the pesticide repository were purchased from Sigma-Aldrich, HPC Standards, or Accustandard.

- Internal standards—Internal standard compounds of acenaphthene-d_{10}, bifenthrin-d_5, clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 were purchased from Sigma-Aldrich.
- Sodium sulfate—Certified American Chemical Society (ACS) grade, granular, 10–60 mesh purchased from Fisher Scientific.
- Surrogate standards—Surrogate standard compounds of atrazine-$^{13}C_3$, fipronil-$^{13}C_4$,$^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, *cis*-permethrin-$^{13}C_6$, *p,p′*-DDE-$^{13}C_{12}$, and trifluralin-d_{14} were purchased from Cambridge Isotope Laboratories. The compound tebuconazole-$^{13}C_3$ was purchased from Sigma-Aldrich.

Solvents and Gases

- Acetone—Optima grade (Fisher Chemical, A929-4).
- Acetonitrile—OmniSolv liquid chromatography-mass spectrometry (LC-MS) grade (MilliporeSigma, AX0156).
- Compressed gases—Argon (99.999 percent), helium (99.999 percent), and nitrogen (99.999 percent) were purchased from local suppliers. Argon and nitrogen are used as collision gases for the GC-MS/MS and LC-MS/MS, respectively. Helium is used as the GC-MS/MS carrier gas. Nitrogen generators are used to produce nitrogen for the LC-MS/MS ESI source and for evaporation during sample preparation.
- Dichloromethane—GC Resolv grade (Fisher Chemical, D154-4).
- Ethyl acetate—Optima grade (Fisher Chemical, E196-4).
- Formic acid—Optima LC-MS grade (Fisher Chemical, A117-50).
- Isopropanol—Certified ACS grade (Fisher Chemical, A416-4).
- Methanol—Optima grade (Fisher Chemical, A454-4).
- Organic-free water—Generated from purification of house deionized water using a PURELAB flex 2 (ELGA LabWater, Woodridge, Illinois) system. The PURELAB flex 2 delivers ultrapure type I (18.2 megaohm-centimeters [MΩ·cm]) water.

Standards Preparation

1. Primary standard solutions—Individual stock solutions of neat analytical standards are prepared at 1 milligram per milliliter (mg/mL) by accurately weighing, using a calibrated microbalance, 2–5 mg of the neat standard into a 7-mL amber-glass vial. Using appropriate electronic pipettes, add 1 mL of acetone per milligram of the weighed standard. If analyte is not dissolvable in acetone, an appropriate solvent is used, or the standard is prepared at a lower concentration.
2. LC-MS/MS ESI(+) stock solution—A 5-ng/µL stock solution is prepared by adding 125 µL of 1-mg/mL primary standard solutions (138 unlabeled compounds, table 1) to a 25-mL volumetric flask and bringing to volume with acetonitrile. Appropriate volumes are added for primary standard solutions that are less than 1 mg/mL.
3. LC-MS/MS ESI(−) stock solution—A 5-ng/µL stock solution is prepared by adding 125 µL of 1-mg/mL primary standard solutions (12 unlabeled compounds, table 2) to a 25-mL volumetric flask and bringing to volume with acetonitrile. Appropriate volumes are added for primary standard solutions that are less than 1 mg/mL.
4. GC-MS/MS stock solution—A 10-ng/µL stock solution is prepared by adding 250 µL of 1-mg/mL primary standard solutions (33 unlabeled compounds, table 3) to a 25-mL volumetric flask and bringing to volume with acetonitrile. Appropriate volumes are added for primary standard solutions that are less than 1 mg/mL.
5. Intermediate stock solutions—Intermediate stock solutions at concentrations of 2.5 ng/µL for the analytes and surrogates and 0.25 ng/µL for the internal standards are prepared for the LC-MS/MS ESI(+), LC-MS/MS ESI(−), and GC-MS/MS stock solutions. Add 2.5 mL of 5-ng/µL stock or 1.25 mL of 10-ng/µL stock to a 5-mL volumetric flask. Dependent upon analysis, the appropriate surrogates and internal standards are added to each solution. Surrogate volumes are 250 µL for 50-ng/µL solutions, 125 µL for 100-ng/µL solutions, and 12.5 µL for 1-mg/mL solutions. Add 0.5 mL of a 2.5-ng/µL solution of the appropriate internal standards and bring to volume with acetonitrile. The GC-MS/MS intermediate solution also contains 0.5 mL of the analyte protectant stock.
6. Analyte protectant stock solution—An analyte protectant stock solution is prepared by adding 2.5-g (in grams) ethylglycerol, 0.25-g gulonolactone, and 0.25-g sorbitol to a 25-mL volumetric flask. Add 8.75 mL of organic-free water and bring to volume with acetonitrile. Final concentrations are 100-mg/mL ethylglycerol and 10-mg/mL gulonolactone and sorbitol.

7. Internal standard stock solution—A 25-ng/µL stock solution is prepared by adding 125 µL of 1-mg/mL acenaphthene-d_{10}, bifenthrin-d_5, clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 to a 5-mL volumetric flask and bringing to volume with acetonitrile.

8. Internal standard spike solution—A 2.5-ng/µL stock solution is prepared by diluting 500 µL of the 25-ng/µL stock solution to 5 mL in a volumetric flask by bringing to volume with the analyte protectant stock solution.

9. Calibration internal standard solutions—A 2.5-ng/µL internal standard solution is made for the LC-MS/MS ESI(+), LC-MS/MS ESI(−), and GC-MS/MS calibration curves. For LC-MS/MS ESI(+), 62.5 µL of 1-mg/mL clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 are added to a 25-mL volumetric flask and brought to volume with acetonitrile. For LC-MS/MS ESI(−), 62.5 µL of 1-mg/mL clothianidin-d_3 are added to a 25-mL volumetric flask and brought to volume with acetonitrile. Lastly, for GC-MS/MS, 62.5 µL of 1-mg/mL acenaphthene-d_{10} and bifenthrin-d_5 are added to a 25-mL volumetric flask and brought to volume with acetonitrile.

10. Dilute calibration internal standard solutions—A 0.25-ng/µL dilute calibration internal standard solution is made for the LC-MS/MS ESI(+), LC-MS/MS ESI(−), and GC-MS/MS calibration curves. For the LC-MS/MS ESI(+) and ESI(−) solutions, add 5 mL of the 2.5-ng/µL calibration internal standard solution to a 50-mL volumetric flask and bring to volume with acetonitrile. For the GC-MS/MS solution, add 5 mL of the 2.5-ng/µL calibration internal standard solution to a 50-mL volumetric flask, add 5 mL of the analyte protectant stock solution, and bring to volume with acetonitrile.

11. Surrogate standard stock solution—A 10-ng/µL stock solution is prepared by adding 1,000 µL of 50-ng/µL *cis*-permethrin-$^{13}C_6$, 500 µL of 100-ng/µL atrazine-$^{13}C_3$, fipronil-$^{13}C_4$,$^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, *p,p'*-DDE-$^{13}C_{12}$, and trifluralin-d_{14}, and by adding 50 µL of 1-mg/mL tebuconazole-$^{13}C_3$ to a 5-mL volumetric flask and bringing to volume in acetone.

12. Surrogate standard spike solution—A 1-ng/µL stock solution is prepared by diluting 500 µL of the 10-ng/µL stock solution to 5 mL in a volumetric flask by bringing to volume with acetone.

13. Matrix spike solution—A 1-ng/µL matrix-spike solution is prepared by adding 1 mL of the 5-ng/µL LC-MS/MS ESI(+) and LC-MS/MS ESI(−) stock solutions and 500 µL of the 10-ng/µL GC-MS/MS stock solution to a 5-mL volumetric flask and by bringing to volume with acetone.

14. Calibration solutions—Calibration solutions are prepared for LC-MS/MS ESI(+), LC-MS/MS ESI(−), and GC-MS/MS analyses. Calibration solutions contain all pesticides and surrogates at nine concentrations (0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1.0 ng/µL). Internal standards are maintained at the same concentration (0.25 ng/µL) in all calibration solutions. The calibration solutions are made by adding the appropriate amount of intermediate stock solutions to 5-mL volumetric flasks and bringing to volume with dilute calibration internal standard solutions. Formic acid (0.1 percent) is added to prevent degradation of base-sensitive analytes in acetonitrile.

Sample Collection, Shipment, and Holding Times

Samples were collected following methods described in the National Field Manual (NFM) for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Dip samples were collected into 1-L, narrow-mouthed, baked, amber-glass bottles. Integrated samples were collected using equipment that was cleaned following methods described in NFM chapter A3 (U.S. Geological Survey, variously dated). Samples were shipped or transported to the USGS OCRL within 24 hours of collection. Samples have a 7-day maximum holding time before processing. Holding-time studies revealed that nearly all pesticides were stable at 14 days in reagent water (Sandstrom and others, 2016). A 7-day holding time was chosen because this interval provided sufficient and reasonable time for sample processing. Specific projects may have shorter or longer holding times as described by internal quality assurance project plans.

Sample Preparation

Steps for the extraction of pesticides and pesticide degradates from filtered water and suspended sediment are outlined below. All laboratory materials must be properly cleaned (as described in the "Equipment and Supplies" section) before sample preparation to avoid contamination.

Filtered Water Extraction

1. Log project and sample information, including site, sampling date, sampling time, and QC are entered into a laboratory notebook or laboratory information management system (LIMS) database. Label each sample with a unique identifier. Throughout the sample preparation procedure, record any important comments, such as "added surrogate twice or lost x mL of sample when extracting" in the notebook or database.

2. If suspended sediment is being analyzed, before filtering, weigh a 142-mm, 0.7-µm pore size glass-fiber filter in a piece of clean foil large enough to envelop the filter for storage, and record the weight (in grams, g) of the foil + filter. If suspended sediment is not being analyzed, the filter does not need to be weighed.

3. Filter the sample through a 142-mm, 0.7-µm glass-fiber filter into a 1-L graduated cylinder using a diaphragm pump and a filter manifold.

    a. For each water sample, record the extraction procedure (SPE[HLB] + bottle wash [BW]), extraction date, and volume (to the nearest hundredth of a L).

    b. After filtration, the water sample will be transferred from the graduated cylinder back into its original sample bottle. If analyzing suspended sediment, carefully transfer the filter back to the pre-weighed foil in which the filter was originally weighed using stainless-steel tweezers or a spatula. Allow the filter to air-dry overnight by folding the foil over the filter to cover, but not touch, the collected sediment. Suspended sediment may need to be air-dried further if it is still wet upon return. If suspended sediment is not being analyzed, the filters may be discarded.

    c. Once the suspended sediment is dried, weigh the filters in their foil and record the weight (in g) of the foil + filter + dry sediment. Calculate the total dry weight of suspended sediment (g) by subtracting the original foil + filter weight (g) from the new foil + filter + dry sediment weight (g). After the weight is recorded, store the filters in their original foil and place them in a −20 °C freezer until extraction.

    d. Continue onward for the water-extraction procedure or proceed to step 14 for the suspended sediment filter extraction procedure.

4. Before processing the next sample or after the last sample, clean the tubing and filter manifold by pumping through 25–50 mL of methanol followed by 200–500 mL of organic-free water. Once the filter manifold is cleaned, continue with filtering the next water sample or leave the manifold open on a clean total wipe to dry for storage.

5. Remove the surrogate standard spike solution from the freezer and bring it to room temperature on the laboratory bench. The surrogate standard spike solution contains 1 ng/µL of atrazine-$^{13}C_3$, fipronil-$^{13}C_4$,$^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, *cis*-permethrin-$^{13}C_6$, *p,p′*-DDE-$^{13}C_{12}$, tebuconazole-$^{13}C_3$, and trifluralin-d_{14} in acetone. Using the 10–100 µL electronic pipette, add 50 µL of the surrogate solution to each water sample. Shake the sample well following the addition of the surrogate.

6. If the water sample is a matrix spike for quality control, add 50 µL of the matrix spike solution using a 10–100 µL electronic pipette. The matrix spike solution contains 1 ng/µL of all unlabeled analytes (listed in tables 1–3) in ethyl acetate. Samples may be spiked before filtration to meet cooperator requirements for specific projects.

7. Water samples are extracted by SPE using 6 mL, 500-mg Oasis HLB cartridges. Before extraction, condition the SPE cartridges using the manifold by passing through one column volume (approximately 6 mL) of dichloromethane, followed by one column volume (approximately 6 mL) of acetone, and two column volumes (approximately 12 mL) of organic-free water. Leave a few centimeters (cm) of water above the top frit (porous polyethylene disks at the top and bottom of SPE media) in the final conditioning step. Label cartridges with a unique identifier before performing SPE. Connect water samples to their respective cartridges using SPE tubing and perform extraction under vacuum (not to exceed −20 millimeters of mercury [mmHg]), drawing samples through the cartridge at a flow rate of approximately 10 mL/min.

    a. Monitor the SPE cartridge for clogs. If the cartridge becomes clogged and the sample will not pump through, you will need to use another conditioned cartridge for the sample. The new cartridge will be processed in series with the previously clogged cartridge using the same unique identifier.

    b. Once the water sample has passed through the SPE cartridge, the cartridge is either dried under vacuum on the manifold or stored at −20 °C. The SPE cartridges that were stored wet are returned to room temperature on the laboratory bench and placed on the manifold under vacuum until fully dried. Dried SPE cartridges are either immediately eluted or put in a zip-top bag, labelled with the date and project identifier, and stored at −20 °C until elution. Proceed to step 9 for elution procedure.

    c. Empty bottles are retained for a bottle wash to ensure complete recovery of compounds that tend to adsorb to glass. Proceed to step 8 for bottle wash procedure.

    d. Following extraction, SPE tubing must be cleaned by pulling through 10–15 mL of methanol followed by 20–50 mL of organic-free water under vacuum. Discard methanol into the organic solvent waste container before water is pulled through SPE tubing.

8. For bottle wash, add a small amount of sodium sulfate (about 10–20 g) to each bottle and gently shake the bottle to ensure that all water is removed. Using acetone, rinse the bottle three times with about 2–4 mL per rinse, and empty each rinse into one labeled concentrator tube. After all bottle wash rinses, place the tubes on the N-Evap and evaporate down to around 1 mL. The SPE cartridges will be eluted into these tubes in step 9.

9. Before elution, the ports on the vacuum manifold must be cleaned by pulling through a small amount (about 1–3 mL) of dichloromethane and acetone under vacuum. Discard solvents into the organic solvent waste container. Bring dried SPE cartridges to room temperature on the laboratory bench if they were previously stored in the freezer. Place labeled concentrator tubes (from step 8) into the elution rack within the vacuum manifold. Place labeled dry SPE cartridges in ports above their matching concentrator tube. Elute each cartridge with 10 mL of 1:1 (*v:v*) acetone:dichloromethane. If multiple SPE cartridges were used during sample extraction, cartridges are stacked using SPE tube adapters and eluted in series.

10. Following elution, samples must be gently evaporated under nitrogen to approximately 0.5 mL using the N-Evap. Solvent exchange the samples into acetonitrile by adding approximately 1.5-mL acetonitrile to the sample and evaporate to approximately 0.2 mL. Final volume may vary slightly but is corrected through the addition of the internal standard solution.

11. Remove the internal standard spike solution from the freezer and bring to room temperature on the laboratory bench. The internal standard spike solution contains 2.5-ng/µL acenaphthene-d_{10}, bifenthrin-d_5, clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 in a solution of analyte protectants: ethylglycerol (100 mg/mL), gulonolactone (10 mg/mL), and sorbitol (10 mg/mL) dissolved in acetonitrile. Using the 10–100 µL electronic pipette, add 20 µL of the internal standard solution to each sample.

12. Transfer each sample to a 2-mL amber vial containing a 250-µL glass insert and cap. The samples can be stored for up to 30 days before analysis.

13. Analysis of water samples are first completed using the LC-MS/MS in positive (table 1) and negative (table 2) mode. After successful analyses, samples are recapped and analyzed using the GC-MS/MS (table 3). After successful analyses using GC-MS/MS, samples are capped with solid caps and sorted into numerical vial files for long-term storage in a freezer at −20 °C.

Suspended Sediment—Filter Paper Extraction

14. For extraction of suspended sediment on filter papers, fold and insert weighed filter into a 250-mL Erlenmeyer flask.

15. Remove the surrogate standard spike solution from the freezer and bring to room temperature on the laboratory bench. The surrogate standard spike solution contains 1 ng/µL of atrazine-$^{13}C_3$, fipronil-$^{13}C_4$,$^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, *cis*-permethrin-$^{13}C_6$, *p,p′*-DDE-$^{13}C_{12}$, tebuconazole-$^{13}C_3$, and trifluralin-d_{14} in acetone. Using the 10–100 µL electronic pipette, add 50 µL of the surrogate solution to each filter sample.

16. If the filter sample is a matrix spike for quality control, add 50 µL of the matrix spike solution using a 10–100 µL electronic pipette. The matrix spike solution contains 1.0 ng/µL of all unlabeled analytes (listed in tables 1–3) in ethyl acetate. Samples may be spiked before filtration to meet cooperator requirements for specific projects.

17. Filter samples are extracted in dichloromethane using sonication.

    a. Using a solvent dispenser, dispense 10-mL aliquots of dichloromethane into the Erlenmeyer until the filter is submerged (about 50–80 mL) and cover it with foil.

    b. Sonicate for 10 minutes and then decant the solvent into a 200-mL TurboVap tube through a funnel containing about 15–20 g of sodium sulfate held in place by a glass wool plug.

    c. Repeat step 17a and step 17b with fresh dichloromethane and decant the solvent through the same funnel and into the same TurboVap tube.

    d. Rinse the sodium sulfate in the funnel with approximately 3 mL of dichloromethane.

    e. Once the solvent has completely dripped through the funnel, remove the funnel from the TurboVap tube and set it on a large piece of foil in the hood to dry before discarding sodium sulfate and glass wool.

18. After extraction and filtration, the sample is evaporated under nitrogen to about 5–10 mL using a TurboVap tube.

    a. Transfer the sample from the TurboVap tube into a 15-mL concentrator tube and evaporate down under nitrogen to approximately 0.5 mL using the N-Evap. Solvent exchange the samples into acetonitrile by adding approximately 1.5-mL acetonitrile to the sample and evaporate to approximately 0.2 mL. Final volumes may vary slightly but are corrected through the addition of an internal standard solution.

19. Remove the internal standard spike solution from the freezer and bring it to room temperature on the laboratory bench. The internal standard spike solution contains 2.5-ng/µL acenaphthene-d_{10}, bifenthrin-d_5, clothianidin-d_3, myclobutanil-d_4, and oxyfluorfen-d_5 in a solution of analyte protectants: ethylglycerol (100 mg/mL), gulonolactone (10 mg/mL), and sorbitol (10 mg/mL) dissolved in acetonitrile. Using the 10–100 µL electronic pipette, add 20 µL of the internal standard solution to each sample.

a. Transfer each sample to a 2-mL amber vial containing a 250-µL glass insert and cap. The samples can be stored for 30 days before analysis.

20. Analyses of filter samples are first completed using the LC-MS/MS in positive (table 1) and negative (table 2) mode. After successful analyses, samples are recapped and analyzed using the GC-MS/MS (table 3). After successful analyses using GC-MS/MS, samples are capped with solid caps and sorted into numerical vial files for long-term storage in a freezer at −20 °C.

Analysis by Liquid Chromatography-Tandem Mass Spectrometry

The LC-MS/MS must be tuned using LC-MS calibration standard in positive and negative ion modes following ESI if the instrument has not been tuned within the last 30 days. Checktunes must be completed weekly. The tuning solution contains multiple components for tuning throughout a large mass range in both ionization modes. Before analyzing samples using the LC-MS/MS, the following maintenance procedures must be completed to ensure optimal performance:

1. Check mobile phase and needle wash solvent levels and ensure there is enough solvent to complete the worklist run. If solvent is added, set solvent levels in MassHunter acquisition software.
2. Open purge valve and purge solvent lines at 2.5 mL/min for 5 minutes.
3. Rinse ESI spray chamber with isopropanol.
4. Wipe interior surfaces of spray chamber with task wipe and isopropanol.
5. Wipe off spray shield with task wipe and isopropanol. If surface contamination is still visible, remove the spray shield and sand in a figure eight motion with 4,000 grit or higher sandpaper.
6. Open the ballast on the rough pump for 5 minutes if oil is present in oil mist filter.
7. Equilibrate LC-MS/MS system with starting mobile phase composition for 15 minutes.
8. Check solvent waste bottles.

The LC-MS/MS analysis is completed on an Agilent Technologies 1260 infinity bio-inert high-performance liquid chromatograph coupled to a 6430 triple quadrupole mass spectrometer. An Agilent Technologies Zorbax Eclipse XDB-C18 column (2.1 mm×150 mm, 3.5 µm) preceded by a Zorbax Eclipse XDB-C8 guard cartridge (2.1 mm×12.5 mm, 5 µm) is used for separation. Analyses are completed in positive and negative ion modes following ESI. For ESI(+) analysis, the mobile phase consists of (A) 0.1 percent formic acid in water and (B) acetonitrile. The gradient starts at 98 percent A and 2 percent B and is held for 2 minutes before ramping up to 50 percent B in 2 minutes, followed by a 6-minute ramp to 60 percent B, and a final 2-minute ramp up to 100 percent B. The mobile phase is kept at 100 percent B for 2 minutes before being brought back to initial conditions in 1 minute and being given 5 minutes to re-equilibrate (20-minute total run time). For ESI(−) analysis, the mobile phase consists of (A) 0.1 percent formic acid in water and (B) methanol. The gradient starts at 98 percent A and 2 percent B and is held for 2 minutes. The gradient is ramped up to 100 percent B in 3 minutes and is held for 2 minutes before returning to initial conditions in 1 minute and being given 5 minutes to re-equilibrate (13-minute total run time). For all analyses, the injection volume is 10 µL, the column flow rate is 0.6 mL/min, the column temperature is 40 °C, the drying gas temperature is 350 °C, the gas flow is 10 liters per minute (L/min), the nebulizer pressure is 40 pounds per square inch (psi), and the capillary voltage is plus or minus 4,000 volts (V). Data are collected in the multiple reaction monitoring (MRM) mode. Retention times, instrument parameters, and MRM transitions of target compounds for ESI(+) and ESI(−) modes are reported in tables 1 and 2, respectively (Gross and others, 2023).

Analysis by Gas Chromatography-Tandem Mass Spectrometry

The GC-MS/MS must be tuned using calibration compound FC-43 (perfluorotributylamine) in positive mode following AEI if the instrument has not been tuned within the last 30 days. Checktunes must be completed weekly. Fragmentation of perfluorotributylamine in the ion source allows for the instrument to be tuned throughout a large mass range. Before running samples on the GC-MS/MS, the following maintenance procedures must be completed to ensure optimal performance:

1. Check carrier gas (helium) and ensure there is enough to complete the worklist run.
2. If necessary, perform inlet maintenance by changing inlet liner, septum, inlet ferrule, and cutting approximately 10 cm off the injector end of the analytical column.
3. Fill wash solvent vials for GC autosampler syringe.
4. Empty wash solvent waste vial.
5. Check GC autosampler syringe for clogged needle or seized plunger by pulling up solvent from the wash solvent vials. Change syringe if necessary.

The GC-MS/MS analysis is completed on a Trace 1310 gas chromatograph coupled to a TSQ 9000 triple quadrupole mass spectrometer (Thermo Scientific). The instrument is equipped with a programmable temperature vaporizing (PTV) inlet and an AEI source. Sample injection volume is 1 µL. The initial temperature of the PTV is 110 °C, which is increased at a rate of 5 °C per second (°C/s) to 290 °C and held for 3 minutes for transfer. Then, the temperature is increased at a rate of 14.5 °C/s to 320 °C and held for 10 minutes for cleaning. The inlet has a split flow of 50 mL/min and a splitless time of 3 minutes. Separation is performed on a DB-5MS analytical column (30 m×0.25 mm×0.25 µm; Agilent Technologies) with helium as the carrier gas at a flow rate of 1.2 mL/min. The oven is initially held at a temperature of 65 °C for 2 minutes, increased to 150 °C at a rate of 25 °C/minute, held for 1 minute, increased to 215 °C at a rate of 25 °C/minute, held for 2 minutes, increased to 280 °C at a rate of 5 °C/minute, and increased to 300 °C at a rate of 10 °C/minute. The oven is held at 300 °C for 5 minutes (31-minute total run time). The mass transfer line is held at 250 °C, and the ion source is held at 320 °C. Data are collected in the selected reaction monitoring (SRM) mode. Retention times, instrument parameters, and SRM transitions of target compounds are reported in table 3 (Gross and others, 2023).

Quality Assurance and Quality Control Criteria

The instruments are calibrated with each new sample batch by running a nine-point calibration curve (0.0025–1.0 ng/µL) at the beginning and end of the worklist. Sample extracts and QA/QC samples are analyzed in an instrument sequence to provide additional information to facilitate corrective actions that might be required if performance criteria are not met. The QA/QC samples include CCV standards, instrument blanks, laboratory blanks, matrix spikes, field blanks, and field replicates. Additionally, surrogate compounds are added to every sample before extraction, and internal standard compounds are added to every sample before instrumental analysis. Frequency of analysis and acceptance criteria for QA/QC checks are reported in table 4. These checks represent the minimum QA/QC and can be augmented based on project specific needs. Definitions for QA/QC sample types are below:

1. Calibration standards—Calibration standards are solutions of all analytes and surrogates at a range of concentrations (0.0025–1.0 ng/µL) with consistent internal standard concentrations (0.25 ng/µL). Calibration standards are used to calibrate the instrument and quantify results.

2. Continuous calibration verification (CCV)—The CCV solutions (0.05 ng/µL) are standard solutions of the target analytes prepared in a manner similar to the calibration standards. The CCVs are used to monitor the method stability throughout the batch in comparison to the calibration curves.

3. Instrument blanks—Instrument blanks are solvents (acetonitrile) injected onto the instruments to determine if there is carryover of target analytes between sample injections.

4. Laboratory blanks—A laboratory blank is organic-free water (1 L) that is processed through the entire sample preparation and analytical procedure to monitor for possible laboratory contamination.

5. Matrix spikes—A matrix spike is a duplicate environmental sample to which known quantities of the target analytes are spiked before sample processing. The matrix spike is processed exactly like an environmental sample and is used to determine if the sample matrix contributes bias to the analytical results and the degree to which the method is successful in recovering the target analytes. Background concentrations of the analytes are determined from the duplicate environmental sample that is not spiked with method analytes before analysis. Background concentrations are subtracted from spiked concentrations before calculating percentage recoveries.

6. Field blanks—Field blanks are samples of organic-free water (1 L) that are brought into the field and handled following field protocols. Organic-free water is taken from the laboratory to the field and handled in such a way that the water is sampled to monitor for possible contamination during sample collection.

7. Field replicates—A field replicate is a duplicate environmental sample used to monitor method reproducibility. Field replicates are analyzed together to monitor percentage differences in target analytes.

8. Surrogate standards—Surrogate standards are compounds with similar physicochemical properties to the target analytes that are not expected to be present in the environment. These compounds are added to every sample before processing to evaluate overall method performance through their recovery.

9. Internal standards—Internal standards are compounds not expected to be present in the environment that have similar physicochemical properties to the target analytes. Internal standards are added at the same level to every sample before instrumental analysis to correct for quantitative differences in extract volume and to compensate for instrument differences in injection volume. Internal standards are also used to monitor instrument conditions, such as injection errors, retention time shifts, and instrument abnormalities or malfunctions. Internal standard concentrations are the same between calibration standards, CCVs, and samples.

If QA/QC samples fall outside of their respective acceptance criteria reported in table 4, sample handling, instrument performance, and data are reviewed further. Corrective actions are taken depending upon QA/QC type, as listed below:

1. Calibration standards—If calibration standards have a coefficient of determination (R^2) less than 0.99, the data from the analysis will be rejected, and samples must be reanalyzed. If calibration standards continue to fail, instrument maintenance (cleaning, tuning, replacing consumables) or preparation of a new calibration curve may be necessary.

2. Continuous calibration verification (CCV)—If a CCV standard falls outside the accepted percentage recovery range (75 to 125 percent), data will be rejected from the last successful CCV standard forward in the worklist. Samples analyzed after the last successful CCV standard must be reanalyzed and instrument maintenance (cleaning and replacing consumables) may be necessary. Data are only reported when samples fall between two acceptable CCV standards.

3. Instrument blanks—If instrument blanks have concentrations above the RL, data will be rejected from the last successful instrument blank forward in the worklist. Samples ran after the last successful instrument blank must be reanalyzed. Check concentrations of analytes in samples analyzed before the contaminated instrument blank for high values. This sample may need to be diluted to prevent carryover. Ensure that the needle wash solution is filled to prevent carryover and prepare a new instrument blank with fresh solvent.

4. Laboratory blanks—If a laboratory blank has concentrations above the RL, samples will be reanalyzed. Ensure that the needle wash solution is filled to prevent carryover. If the laboratory blank continues to have detections above the RL, samples will be flagged for the analytes detected in the laboratory blank, and potential contamination sources will be examined. Sample processing will halt until the contamination source is discovered and eliminated as determined by a successful laboratory blank.

5. Matrix spikes—If a matrix spike recovery is not within the accepted percent recovery range (70 to 130 percent), the sample will be reanalyzed. Ensure no issues occurred in sample processing and re-extract a new matrix spike sample if errors occurred.

6. Field blanks—If a field blank has concentrations above the RL, samples will be reanalyzed. Ensure that the needle wash solution is filled to prevent carryover. If the field blank continues to have detections above the RL, samples will be flagged for the analytes detected in the field blank, and potential contamination sources will be examined.

Table 4. Quality assurance/quality control (QA/QC) performance checks, frequencies, and acceptance criteria.

[≥, greater than or equal to; ng/µL, nanogram per microliter; %, percent; <, less than; RL, reporting limit]

Laboratory QA/QC sample type	Frequency of analysis	Acceptance criteria
Calibration standards	The calibration curve is run with each batch at the beginning and end of the sequence. Additionally, calibrations are completed following major disruptions or when routine calibration check fall out of specific control limits.	Regression analysis $R^2 \geq 0.99$ using a 9-point calibration curve (of which at least 5 consecutive points must be used) ranging from 0.0025 to 1 ng/µL
Calibration verification	After initial calibration or recalibration. Every 10 samples.	% Recovery=75–125%
Instrument blanks	Before initial calibration. Every 10 samples (including after calibration verification).	Blanks<RL for target analyte
Laboratory blanks	One method blank per 20 samples or one per batch, whichever is more frequent. Laboratory blanks should comprise 10% of all samples per sampling event.	Blanks<RL for target analyte
Matrix spikes	One per 20 samples or minimum of 1 per project.	% Recovery=70–130%
Field blanks	One per 20 samples or minimum of 1 per project.	Blanks<RL for target analyte
Field replicate	Replicates should comprise 5% of total project sample count.	Relative percent difference <25% for replicates
Surrogate standards	Isotopically labeled compounds added to every sample prior to processing.	% Recovery=70–130%
Internal standards	Isotopically labeled compounds added to every sample prior to instrumental analysis.	% Recovery=70–130%

7. Field replicates—If a field replicate is not within the acceptance criteria (relative percent difference [RPD] less than 25 percent), the replicate samples are reanalyzed. Ensure no issues occurred in sample processing, and re-extract new field replicates if errors occurred.

8. Surrogate standards—If surrogate-standard recoveries are outside the accepted percent recovery range (70 to 130 percent), ensure no issues occurred with that sample while processing. Samples must be reanalyzed, and if the surrogate standard is outside the acceptance criteria, the sample will be flagged. Overall surrogate recovery is evaluated for every batch, and if all recoveries are trending low or high, the surrogate will be evaluated to determine if a new solution must be made.

9. Internal standards—If internal standards fall outside the accepted percent recovery range (70 to 130 percent), the samples will be reanalyzed. Overall internal standard peak area is evaluated for every batch, and if the value is trending low or high, the internal standard will be evaluated to determine if a new solution must be made. Internal standard recoveries may fall outside of acceptable range due to variability in final sample volume or matrix effects. Samples may need to be diluted or concentrated to the correct volume. Corrective action may not be necessary if surrogate standards meet QA/QC objectives.

Further training may be necessary if errors occurred in sample preparation protocols. Samples must be reanalyzed if instrument performance was unsatisfactory. Lastly, samples with poor QC performance (surrogate recovery less than 70 percent) will be flagged. For example, in the LIMS database, if data quality objectives are not met upon review, the sample will be flagged. Use of matrix spike, surrogate, and internal standard verification vials will aid in diagnosing QA/QC failures.

Quantitation and Calculation of Results

Identification and quantification of analytes are completed from raw data files using instrument software (Agilent MassHunter v. 10.1 and Thermo TraceFinder v. 4.1). Before quantitative results are reported, each compound first needs to meet qualitative criteria. An analyte is not considered to be identified correctly unless the correct quantitation ion(s) of the peak are detected, the relative area ratios of the confirmation ions are within plus or minus 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.

Samples are quantified using a nine-point external calibration curve (0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1.0 ng/µL), where at least five concentrations must be used in quantitation (which standards are used depends on sample concentrations and instrument performance). Concentrations from the middle of the calibration curve must never be removed during quantification. Only calibration levels at the low or high end of the curve may be removed. Low-end concentrations (0.0025 and 0.005 ng/µL) may be removed if no response is observed for the analyte (the measured concentration is below the instrument detection limit). High-end concentrations (0.5 or 1.0 ng/µL) may be removed if they are outside the linear range for the analyte. Removing these calibration concentrations but maintaining at least five concentration levels will result in more accurate quantitation. The calibration curve is analyzed at the beginning and end of a sample worklist (table 5). The initial calibration curve is used for quantification. Analyzing the calibration curve at the beginning and end of a worklist run provides further confirmation, beyond CCV injections, that instrument performance is satisfactory throughout the range of concentrations. Regression analysis is completed on the calibration curves for each analyte, and the R^2 for each standard curve must be greater than or equal to 0.99 to be accepted. If the R^2 for each standard curve is not acceptable, calibration standard corrective actions may be necessary.

The calibration curve points are plotted as a relative response versus the analyte concentration. The relative response is calculated as follows:

$$Relative\ Response = Area_A/Area_{IS} \quad (1)$$

where

Relative Response is the internal standard normalized peak area,
$Area_A$ is the area of the quantitation ion peak for the specific analyte, and
$Area_{IS}$ is the area of the quantitation ion peak for the internal standard.

Analyte concentrations are known for each level of the standard curve and span 0.0025–1.0 ng/µL. Quantification of analytes in sample extracts are then completed from the curve-fit equations determined following regression analysis for each analyte. As an example, linear regression of the calibration curve results in the following equation:

$$Relative\ Response = mC_E + b \quad (2)$$

where

Relative Response is the internal standard normalized peak area (eq. 1),
m is the slope of the line,
C_E is the analyte concentration (ng/µL) in the sample extract, and
b is the y-intercept.

Table 5. Example analytical sequence for liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-tandem mass spectrometry (GC-MS/MS) analyses.

[Quality assurance/quality control (QA/QC) samples that are not specifically identified in the sequence (for example, laboratory blanks, field blanks, field replicates, and matrix spikes) are represented by samples in the sequence as they are given a unique sample identifier. **Abbreviation**: ng/µL, nanogram per microliter]

Sample number	Vial number	Sample type
1	1	Instrument blank (acetonitrile)
2	2	Calibration standard level 1 (0.0025 ng/µL)
3	3	Calibration standard level 2 (0.005 ng/µL)
4	4	Calibration standard level 3 (0.01 ng/µL)
5	5	Calibration standard level 4 (0.025 ng/µL)
6	6	Calibration standard level 5 (0.05 ng/µL)
7	7	Calibration standard level 6 (0.1 ng/µL)
8	8	Calibration standard level 7 (0.25 ng/µL)
9	9	Calibration standard level 8 (0.5 ng/µL)
10	10	Calibration standard level 9 (1.0 ng/µL)
11	1	Instrument blank (acetonitrile)
12	11	Sample 1
13	12	Sample 2
14	13	Sample 3
15	14	Sample 4
16	15	Sample 5
17	16	Sample 6
18	17	Sample 7
19	18	Sample 8
20	19	Sample 9
21	20	Sample 10
22	36	Continuous calibration verification 1
23	1	Instrument blank (acetonitrile)
24	21	Sample 11
25	22	Sample 12
26	23	Sample 13
27	24	Sample 14
28	25	Sample 15
29	26	Sample 16
30	27	Sample 17
31	28	Sample 18
32	29	Sample 19
33	30	Sample 20

Table 5. Example analytical sequence for liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-tandem mass spectrometry (GC-MS/MS) analyses.—Continued

[Quality assurance/quality control (QA/QC) samples that are not specifically identified in the sequence (for example, laboratory blanks, field blanks, field replicates, and matrix spikes) are represented by samples in the sequence as they are given a unique sample identifier. **Abbreviation**: ng/µL, nanogram per microliter]

Sample number	Vial number	Sample type
34	36	Continuous calibration verification 2
35	1	Instrument blank (acetonitrile)
36	31	Sample 21
37	32	Sample 22
38	33	Sample 23
39	34	Sample 24
40	35	Sample 25
41	1	Instrument blank (acetonitrile)
42	2	Calibration standard level 1 (0.0025 ng/µL)
43	3	Calibration standard level 2 (0.005 ng/µL)
44	4	Calibration standard level 3 (0.01 ng/µL)
45	5	Calibration standard level 4 (0.025 ng/µL)
46	6	Calibration standard level 5 (0.05 ng/µL)
47	7	Calibration standard level 6 (0.1 ng/µL)
48	8	Calibration standard level 7 (0.25 ng/µL)
49	9	Calibration standard level 8 (0.5 ng/µL)
50	10	Calibration standard level 9 (1.0 ng/µL)

The analyte concentration (ng/µL) in the sample extract can then be calculated by rearranging the linear regression equation, as an example:

$$C_E \quad (Relative\ Response - b)/m$$

To calculate the concentration (ng/L) of the analyte in the original water or suspended sediment sample ($C_{S,V}$), the following calculation is necessary:

$$C_{S,V} = (C_E \times V_E)/V_S \tag{3}$$

where

$C_{S,V}$ is the concentration of the analyte in the original water or suspended sediment sample on a volume basis,

C_E is the analyte concentration (ng/µL) in the sample extract,

V_E is the volume of the sample extract (200 µL), and

V_S is the volume (L) of the water sample.

Concentrations are reported from 0.5 to 200 ng/L. If the concentration exceeds 200 ng/L, a part of the sample extract is diluted appropriately with a dilute internal standard solution (0.25 ng/µL) in acetonitrile and reanalyzed.

Concentrations of analytes on suspended sediment samples also can be computed in nanograms per gram (ng/g) dry weight of suspended sediment. The dry weight of the suspended sediment is determined via the following equation:

$$W_S = W_f - W_i \tag{4}$$

where

W_S is the dry weight (g) of the suspended sediment,

W_f is the dry weight (g) of the foil, filter, and dry suspended sediment following filtration, and

W_i is the dry weight (g) of the foil and filter taken before filtration.

The concentration (ng/g dry weight) of the analyte on the suspended sediment ($C_{S,W}$) can then be determined via the following equations:

$$C_{S,W} = (C_E \times V_E)/W_S \text{ or } (C_{S,V} \times V_S)/W_S \quad (5)$$

where

$C_{S,W}$ is the concentration of the analyte in the original suspended sediment sample on a weight basis,
C_E is the analyte concentration (ng/µL) in the sample extract,
V_E is the volume of the sample extract (200 µL),
$C_{S,V}$ is the concentration (ng/L) of analytes on the suspended sediment,
V_S is the volume (L) of the water sample that passed through the filter, and
W_S is the weight (g) of the dried suspended sediment collected on the filter.

Method Performance

Recoveries were calculated from spiked samples (50 ng/L, n=3 and 15 ng/L, n=9) using the following equation:

$$Percent\ Recovery = (C_A - C_B)/C_S \quad (6)$$

where

C_A is the analyzed concentration calculated from the calibration curve following sample preparation and instrumental analysis of a spiked sample,
C_B is the background concentration from an unspiked replicate of the spiked sample, and
C_S is the spiked concentration added to the sample.

Environmental samples (not spiked) were analyzed concurrently with spiked samples to monitor background concentrations of analytes. Initial average recoveries and relative standard deviations (RSDs; 50 ng/L) are reported in table 6. Performance-based MDLs and RLs were determined for each analyte. The MDLs were calculated following procedures similar to the EPA determination of MDLs (U.S. Environmental Protection Agency, 2016). In short, 10 whole-water samples were collected from the American River (near Guy West Bridge). Water from the American River was used in place of laboratory reagent water because this water better represents real-world conditions. The American River carries snowmelt and drainage from the Sierra Nevada, and the water is detained by a series of dams upstream of the collection point, which makes this matrix water consistent in composition (Hladik and Calhoun, 2012). The river has low suspended sediment and low dissolved organic carbon and has not had any pesticide detections of the target compounds in blank samples during the development of this method. Before sample processing, nine water and nine filter samples were individually spiked to a concentration of 15 ng/L of all analytes, while one water and filter sample were left blank to monitor for background concentrations, contamination, or both. Samples were processed following protocols in the standard operating procedure (SOP) and analyzed by LC-MS/MS (ESI[+] and ESI[−]) and GC-MS/MS. Background concentrations or contamination were not detected in blank samples.

The MDLs were computed using the following equation:

$$MDL_S = t_{(n-1,\ 1-\alpha=0.99)} S_s \quad (7)$$

where

MDL_S is the method detection limit of an analyte,
$t_{(n-1,\ 1-\alpha=0.99)}$ is the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with $n-1$ degrees of freedom, and
S_s is the sample standard deviation of the replicate spiked sample analyses.

The Student's t-value for nine replicates is 2.896 (U.S. Environmental Protection Agency, 2016). Reporting limits were calculated using the following equation:

$$RL = 2 \times MDL_S \quad (8)$$

where

RL is the reporting limit of an analyte, and
MDL_S is the method detection limit of an analyte.

For the MDL test (15 ng/L) average recoveries, RSDs, MDLs, and RLs for water and filter fractions are reported in table 7 for all target analytes.

Data Handling

All samples must be tracked using a LIMS or laboratory notebook throughout sample preparation and analysis. Sample collection information, laboratory sample manipulations (filtration, SPE, and addition of solutions), and physical sample measurements are recorded. Once samples are analyzed by the instruments, raw data are checked before quantification. After quantification, the data are reviewed by the project lead, the lead chemist, or both, and any suspected data errors are investigated and resolved or verified. If data quality objectives are not met, sample handling, instrument performance, and data will be further reviewed. Further training may be necessary if errors were observed in sample preparation protocols. Samples must be reanalyzed if instrument performance was unsatisfactory. Lastly, samples with poor QC performance (surrogate recovery less than 70 percent) will be flagged in the LIMS database or final reports if data quality objectives are not met upon further review. Sample analytical results are then uploaded to the USGS National Water Information System (NWIS; U.S. Geological Survey, 2023b) based on project specific needs and timelines.

Table 6. Recoveries and relative standard deviations (RSDs) for target analytes and surrogate compounds from initial recovery study (spiked concentration=50 nanograms per liter; sample size, *n*=3).

[CAS, Chemical Abstract Service; NWIS P code, National Water Information System parameter code; %, percent; LC-MS/MS, liquid chromatography-tandem mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; —, no data]

Compound	CAS number	NWIS P code (water)	Instrument	Recovery (%)	RSD (%)
3,4-Dichloroaniline (3,4-DCA)	95-76-1	66584	LC-MS/MS	73.7	6.9
3,5-Dichloroaniline (3,5-DCA)	626-43-7	67536	LC-MS/MS	77.3	4.4
Acetamiprid	135410-20-7	68302	LC-MS/MS	95.0	5.5
Acetochlor	34256-82-1	68520	LC-MS/MS	91.4	5.7
Acibenzolar-s-methyl	135158-54-2	51849	GC-MS/MS	91.9	5.9
Allethrin	584-79-2	66586	GC-MS/MS	89.9	9.7
Atrazine	1912-24-9	65065	LC-MS/MS	84.3	3.1
Atrazine, desethyl	6190-65-4	68552	LC-MS/MS	103	6
Atrazine, desisopropyl	1007-28-9	68550	LC-MS/MS	98.1	3.3
Azoxystrobin	131860-33-8	66589	LC-MS/MS	93.9	4.7
Benefin (Benfluralin)	1861-40-1	51643	GC-MS/MS	85.1	5.9
Bentazon	25057-89-0	68538	LC-MS/MS	77.9	7.9
Benzobicyclon	156963-66-5	54350	LC-MS/MS	83.5	3.4
Benzovindiflupyr	1072957-71-1	52652	LC-MS/MS	99.0	1.6
Bifenthrin	82657-04-3	65067	GC-MS/MS	93.1	6.8
Boscalid	188425-85-6	67550	LC-MS/MS	82.7	1.1
Boscalid metabolite - M510F01 acetyl	661463-87-2	54349	LC-MS/MS	76.6	4.3
Broflanilide	1207727-04-5	54363	LC-MS/MS	76.5	6.9
Bromuconazole	116255-48-2	68315	LC-MS/MS	88.0	2.6
Butralin	33629-47-9	68545	LC-MS/MS	90.7	5.0
Carbaryl	63-25-2	65069	LC-MS/MS	76.4	5.5
Carbendazim	10605-21-7	68548	LC-MS/MS	103	6
Carbofuran	1563-66-2	65070	LC-MS/MS	77.5	3.3
Chlorantraniliprole	500008-45-7	51856	LC-MS/MS	79.3	4.7
Chlorfenapyr	122453-73-0	53567	GC-MS/MS	98.1	4.4
Chlorothalonil	1897-45-6	65071	GC-MS/MS	84.3	10.7
Chlorpyrifos	2921-88-2	65072	LC-MS/MS	77.7	4.0
Chlorpyrifos oxon	5598-15-2	68216	LC-MS/MS	99.1	4.7
Clomazone	81777-89-1	67562	LC-MS/MS	77.2	3.3
Clothianidin	210880-92-5	68221	LC-MS/MS	92.7	4.2
Clothianidin desmethyl	135018-15-4	52660	LC-MS/MS	90.4	6.9
Coumaphos	56-72-4	51836	LC-MS/MS	86.1	8.0
Cyantraniliprole	736994-63-1	51862	LC-MS/MS	83.3	1.7
Cyazofamid	120116-88-3	51853	LC-MS/MS	90.3	5.6
Cyclaniliprole	1031756-98-5	54355	LC-MS/MS	80.7	4.3
Cycloate	1134-23-2	65073	LC-MS/MS	96.9	6.3
Cyfluthrin	68359-37-5	65074	GC-MS/MS	86.1	7.6
Cyhalofop-butyl	122008-85-9	68360	GC-MS/MS	101	4
Cyhalothrin	68085-85-8	68354	GC-MS/MS	87.9	7.2

Table 6. Recoveries and relative standard deviations (RSDs) for target analytes and surrogate compounds from initial recovery study (spiked concentration=50 nanograms per liter; sample size, *n*=3).—Continued

[CAS, Chemical Abstract Service; NWIS P code, National Water Information System parameter code; %, percent; LC-MS/MS, liquid chromatography-tandem mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; —, no data]

Compound	CAS number	NWIS P code (water)	Instrument	Recovery (%)	RSD (%)
Cymoxanil	57966-95-7	51861	LC-MS/MS	96.3	8.5
Cypermethrin	52315-07-8	65075	GC-MS/MS	89.1	6.5
Cyproconazole	94361-06-5	66593	LC-MS/MS	80.7	4.8
Cyprodinil	121552-61-2	67574	LC-MS/MS	101	6
DCPA	1861-32-1	65076	GC-MS/MS	97.5	2.3
DCPMU	3567-62-2	68231	LC-MS/MS	80.6	2.6
DCPU	2/8/2327	68226	LC-MS/MS	86.9	5.7
Deltamethrin	52918-63-5	65077	GC-MS/MS	88.4	4.8
Desthio-prothioconazole	120983-64-4	51865	LC-MS/MS	89.8	6.1
Diazinon	333-41-5	65078	LC-MS/MS	91.6	4.4
Diazinon oxon	962-58-3	68236	LC-MS/MS	89.1	6.2
Dichlorvos	62-73-7	68572	LC-MS/MS	77.3	6.0
Difenoconazole	119446-68-3	67582	LC-MS/MS	95.4	5.6
Dimethomorph	110488-70-5	68373	LC-MS/MS	80.8	5.0
Dinotefuran	165252-70-0	68379	LC-MS/MS	100	6
Dithiopyr	97886-45-8	51837	GC-MS/MS	99.1	4.0
Diuron	330-54-1	66598	LC-MS/MS	82.5	3.3
EPTC	759-94-4	65080	LC-MS/MS	75.8	4.1
Esfenvalerate	66230-04-4	65081	GC-MS/MS	89.3	6.2
Ethaboxam	162650-77-3	51855	LC-MS/MS	76.9	5.3
Ethalfluralin	55283-68-6	65082	GC-MS/MS	96.5	5.3
Etofenprox	80844-07-1	67604	GC-MS/MS	91.2	4.7
Etoxazole	153233-91-1	68598	LC-MS/MS	83.2	3.3
Famoxadone	131807-57-3	67609	LC-MS/MS	72.8	10.0
Fenamidone	161326-34-7	51848	LC-MS/MS	91.1	6.2
Fenbuconazole	114369-43-6	67618	LC-MS/MS	84.9	4.4
Fenhexamid	126833-17-8	67622	LC-MS/MS	82.9	1.5
Fenpropathrin	39515-41-8	65083	GC-MS/MS	90.3	6.3
Fenpyroximate	134098-61-6	51838	LC-MS/MS	77.9	7.3
Fipronil	120068-37-3	66604	LC-MS/MS	96.1	2.2
Fipronil desulfinyl	205650-65-3	66607	LC-MS/MS	87.4	1.8
Fipronil desulfinyl amide	1115248-09-3	68570	LC-MS/MS	76.3	5.3
Fipronil sulfide	120067-83-6	66610	LC-MS/MS	90.5	3.6
Fipronil sulfone	120068-36-2	66613	LC-MS/MS	86.1	2.1
Flonicamid	158062-67-0	51858	LC-MS/MS	95.9	4.0
Florpyrauxifen-benzyl	1390661-72-9	54356	LC-MS/MS	89.5	5.3
Fluazinam	79622-59-6	67636	LC-MS/MS	82.1	8.5
Flubendiamide	272451-65-7	68606	LC-MS/MS	98.7	3.8
Fludioxonil	131341-86-1	67640	LC-MS/MS	76.0	7.8

Table 6. Recoveries and relative standard deviations (RSDs) for target analytes and surrogate compounds from initial recovery study (spiked concentration=50 nanograms per liter; sample size, *n*=3).—Continued

[CAS, Chemical Abstract Service; NWIS P code, National Water Information System parameter code; %, percent; LC-MS/MS, liquid chromatography-tandem mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; —, no data]

Compound	CAS number	NWIS P code (water)	Instrument	Recovery (%)	RSD (%)
Flufenacet	142459-58-3	51840	LC-MS/MS	87.9	8.3
Fluindapyr	1383809-87-7	54362	LC-MS/MS	89.2	4.0
Flumetralin	62924-70-3	51841	LC-MS/MS	76.7	4.6
Fluopicolide	239110-15-7	51852	LC-MS/MS	89.5	3.5
Fluopyram	658066-35-4	52646	LC-MS/MS	95.1	2.2
Fluoxastrobin	193740-76-0	67645	LC-MS/MS	85.5	5.0
Flupyradifurone	951659-40-8	52764	LC-MS/MS	88.9	4.6
Fluridone	59756-60-4	51864	LC-MS/MS	102	2
Flutolanil	66332-96-5	51842	LC-MS/MS	91.1	5.7
Flutriafol	76674-21-0	67653	LC-MS/MS	78.3	3.2
Fluxapyroxad	907204-31-3	51851	LC-MS/MS	86.3	1.4
Halauxifen-methyl ester	943831-98-9	54361	LC-MS/MS	89.8	5.3
Hexazinone	51235-04-2	65085	LC-MS/MS	89.8	3.7
Imazalil	35554-44-0	67662	LC-MS/MS	103	3
Imidacloprid	138261-41-3	68426	LC-MS/MS	96.3	2.4
Imidacloprid desnitro	127202-53-3	51857	LC-MS/MS	82.9	12.3
Imidacloprid olefin	115086-54-9	52782	LC-MS/MS	59.5	21.2
Imidacloprid urea	120868-66-8	51859	LC-MS/MS	77.9	5.7
Imidacloprid, 5-hydroxy	380912-09-4	54344	LC-MS/MS	101	2
Indaziflam	950782-86-2	53960	LC-MS/MS	82.7	5.2
Indoxacarb	173584-44-6	68627	LC-MS/MS	86.2	7.5
Ipconazole	125225-28-7	52762	LC-MS/MS	87.5	2.6
Iprodione	36734-19-7	66617	LC-MS/MS	94.6	7.7
Isofetamid	875915-78-9	53569	LC-MS/MS	99.5	3.2
Kresoxim-methyl	143390-89-0	67670	LC-MS/MS	103	3
Malathion	121-75-5	65087	LC-MS/MS	90.2	5.0
Malathion oxon	1634-78-2	68240	LC-MS/MS	79.3	3.2
Mandestrobin	173662-97-0	54358	LC-MS/MS	102	3
Mandipropamid	374726-62-2	51854	LC-MS/MS	89.1	5.0
Metalaxyl	57837-19-1	68437	LC-MS/MS	87.6	3.0
Metalaxyl alanine metabolite	85933-49-9	54345	LC-MS/MS	98.7	5.0
Metconazole	125116-23-6	66620	LC-MS/MS	80.8	2.1
Methoprene	40596-69-8	66623	GC-MS/MS	95.1	4.0
Methoxyfenozide	161050-58-4	68647	LC-MS/MS	94.3	1.9
Methylparathion	298-00-0	65089	GC-MS/MS	109	3
Metolachlor	51218-45-2	65090	LC-MS/MS	94.6	5.3
Myclobutanil	88671-89-0	66632	LC-MS/MS	85.1	3.4
Naled (Dibrom)	300-76-5	68654	LC-MS/MS	77.1	7.6

Table 6. Recoveries and relative standard deviations (RSDs) for target analytes and surrogate compounds from initial recovery study (spiked concentration=50 nanograms per liter; sample size, *n*=3).—Continued

[CAS, Chemical Abstract Service; NWIS P code, National Water Information System parameter code; %, percent; LC-MS/MS, liquid chromatography-tandem mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; —, no data]

Compound	CAS number	NWIS P code (water)	Instrument	Recovery (%)	RSD (%)
Napropamide	15299-99-7	65092	LC-MS/MS	100	1
Nitrapyrin	1929-82-4	52763	GC-MS/MS	77.9	3.5
Novaluron	116714-46-6	68655	LC-MS/MS	75.9	6.5
Oryzalin	19044-88-3	68663	LC-MS/MS	96.3	5.1
Oxadiazon	19666-30-9	51843	LC-MS/MS	83.8	6.2
Oxathiapiprolin	1003318-67-9	52766	LC-MS/MS	97.5	5.2
Oxyfluorfen	42874-03-3	65093	LC-MS/MS	81.5	0.4
p,*p*'-DDD	72-54-8	65094	GC-MS/MS	96.7	4.6
p,*p*'-DDE	72-55-9	65095	GC-MS/MS	86.7	4.1
p,*p*'-DDT	50-29-3	65096	GC-MS/MS	97.5	2.4
Paclobutrazol	76738-62-0	51846	LC-MS/MS	86.1	7.2
Pendimethalin	40487-42-1	65098	LC-MS/MS	88.2	4.6
Penoxsulam	219714-96-2	51863	LC-MS/MS	74.9	4.3
Pentachloroanisole (PCA)	1825-21-4	66637	GC-MS/MS	73.9	3.3
Pentachloronitrobenzene (PCNB)	82-68-8	66639	GC-MS/MS	82.9	5.3
Penthiopyrad	183675-82-3	52769	LC-MS/MS	99.3	2.7
Permethrin	52645-53-1	65099	GC-MS/MS	92.0	5.3
Phenothrin	26002-80-2	65100	GC-MS/MS	90.0	7.7
Phosmet	732-11-6	65101	LC-MS/MS	77.2	2.4
Picarbutrazox	500207-04-5	54357	LC-MS/MS	100	3
Picoxystrobin	117428-22-5	51850	LC-MS/MS	101	2
Piperonyl butoxide	51-03-6	65102	LC-MS/MS	97.7	1.5
Prodiamine	29091-21-2	51844	LC-MS/MS	95.2	6.3
Prometon	1610-18-0	67702	LC-MS/MS	94.4	4.6
Prometryn	7287-19-6	65103	LC-MS/MS	85.1	4.5
Propanil	709-98-8	66641	LC-MS/MS	91.0	5.9
Propargite	2312-35-8	68677	LC-MS/MS	86.1	4.4
Propiconazole	60207-90-1	66643	LC-MS/MS	93.9	4.1
Propyzamide	23950-58-5	67706	LC-MS/MS	92.3	1.8
Pydiflumetofen	1228284-64-7	54359	LC-MS/MS	91.3	6.3
Pyraclostrobin	175013-18-0	66646	LC-MS/MS	92.3	5.0
Pyridaben	96489-71-3	68682	LC-MS/MS	92.1	3.7
Pyrimethanil	53112-28-0	67717	LC-MS/MS	92.0	5.6
Pyriproxyfen	95737-68-1	68683	LC-MS/MS	86.1	6.9
Quinoxyfen	124495-18-7	51847	LC-MS/MS	90.2	2.9
Resmethrin	10453-86-8	65104	GC-MS/MS	94.2	4.9
Sedaxane	874967-67-6	52648	LC-MS/MS	89.3	4.8
Simazine	122-34-9	65105	LC-MS/MS	84.0	4.8

Table 6. Recoveries and relative standard deviations (RSDs) for target analytes and surrogate compounds from initial recovery study (spiked concentration=50 nanograms per liter; sample size, *n*=3).—Continued

[CAS, Chemical Abstract Service; NWIS P code, National Water Information System parameter code; %, percent; LC-MS/MS, liquid chromatography-tandem mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; —, no data]

Compound	CAS number	NWIS P code (water)	Instrument	Recovery (%)	RSD (%)
Sulfoxaflor	946578-00-3	52767	LC-MS/MS	100	4
Tebuconazole	107534-96-3	66649	LC-MS/MS	88.9	4.4
Tebuconazole t-butylhydroxy	212267-64-6	54348	LC-MS/MS	79.0	5.4
Tebufenozide	112410-23-8	68692	LC-MS/MS	102	3
Tebupirimfos	96182-53-5	68693	LC-MS/MS	90.9	6.1
Tebupirimfos oxon	1035330-36-9	68694	LC-MS/MS	91.6	2.1
Tefluthrin	79538-32-2	67731	GC-MS/MS	85.2	3.2
Tetraconazole	112281-77-3	66654	LC-MS/MS	94.3	6.1
Tetramethrin	7696-12-0	66657	GC-MS/MS	82.5	5.0
t-Fluvalinate	102851-06-9	65106	GC-MS/MS	102	8
Thiabendazole	148-79-8	67161	LC-MS/MS	84.3	7.6
Thiacloprid	111988-49-9	68485	LC-MS/MS	94.5	5.4
Thiamethoxam	153719-23-4	68245	LC-MS/MS	92.5	3.3
Thiamethoxam degradate (CGA-355190)	902493-06-5	53568	LC-MS/MS	80.5	5.4
Thiamethoxam degradate (NOA-407475)	—	53576	LC-MS/MS	98.1	3.9
Thiobencarb	28249-77-6	65107	LC-MS/MS	89.9	8.1
Tolfenpyrad	129558-76-5	51866	LC-MS/MS	79.8	5.9
Triadimefon	43121-43-3	67741	LC-MS/MS	87.9	1.9
Triadimenol	55219-65-3	67746	LC-MS/MS	84.3	2.7
Triallate	2303-17-5	68710	LC-MS/MS	103	6
Tribufos	78-48-8	68711	LC-MS/MS	81.1	11.0
Tricyclazole	41814-78-2	52768	LC-MS/MS	101	8
Trifloxystrobin	141517-21-7	66660	LC-MS/MS	91.1	7.4
Triflumizole	68694-11-1	67753	LC-MS/MS	93.1	3.8
Trifluralin	1582-09-8	65108	GC-MS/MS	84.8	5.7
Triticonazole	131983-72-7	67758	LC-MS/MS	83.7	4.0
Valifenalate	283159-90-0	54360	LC-MS/MS	81.2	8.2
Vinclozolin	50471-44-8	67763	GC-MS/MS	94.9	3.6
Zoxamide	156052-68-5	67768	LC-MS/MS	95.9	6.2
Surrogate compounds					
Atrazine-$^{13}C_3$	1443685-80-0	90536	LC-MS/MS	87.2	5.0
Fipronil-$^{13}C_4$,$^{15}N_2$	—	90454	LC-MS/MS	90.8	6.7
Imidacloprid-d_4	1015855-75-0	90537	LC-MS/MS	98.6	3.3
Metolachlor-$^{13}C_6$	—	—	LC-MS/MS	100	3
p,*p*'-DDE-$^{13}C_{12}$	201612-50-2	—	GC-MS/MS	91.9	5.0
cis-Permethrin-$^{13}C_6$	—	90558	GC-MS/MS	89.3	2.6
Tebuconazole-$^{13}C_3$	1313734-83-6	—	LC-MS/MS	101	3
Trifluralin-d_{14}	347841-79-6	90557	GC-MS/MS	98.8	4.8

Table 7. Water and filter recoveries, relative standard deviations (RSDs), method detection limits (MDLs), and reporting limits (RLs) for target compounds in MDL spike samples (spiked concentration=15 nanograms per liter; sample size, *n*=9).

[%, percent; NR, not reported]

Compound	Water recovery (%)	Water RSD (%)	Water MDL (ng/L)	Water RL (ng/L)	Filter recovery (%)	Filter RSD (%)	Filter MDL (ng/L)	Filter RL (ng/L)
3,4-Dichloroaniline (3,4-DCA)	83.9	3.2	1.2	2.3	84.0	3.4	1.2	2.5
3,5-Dichloroaniline (3,5-DCA)	71.5	9.1	2.8	5.6	77.9	8.6	3.0	5.9
Acetamiprid	97.2	2.5	1.0	2.1	91.7	5.5	2.2	4.4
Acetochlor	86.9	4.1	1.5	3.1	94.2	4.1	1.7	3.4
Acibenzolar-s-methyl	89.2	13.8	5.3	11	92.1	13.8	5.6	11
Allethrin	85.8	5.0	1.9	3.8	90.2	8.1	3.1	6.2
Atrazine	99.6	2.0	0.9	1.7	89.2	3.5	1.4	2.7
Atrazine, desethyl	101	4	1.6	3.2	87.0	6.0	2.3	4.5
Atrazine, desisopropyl	100	4	1.8	3.7	115	6	2.8	5.6
Azoxystrobin	85.7	2.1	0.8	1.6	97.0	5.1	2.2	4.3
Benefin (Benfluralin)	81.0	5.1	1.8	3.6	90.5	8.8	3.4	6.8
Bentazon	80.5	3.6	1.3	2.5	NR	NR	NR	NR
Benzobicyclon	93.3	2.8	1.2	2.3	90.2	4.4	1.8	3.5
Benzovindiflupyr	88.5	3.0	1.2	2.3	81.5	5.1	1.8	3.6
Bifenthrin	89.9	1.4	0.6	1.1	98.1	1.8	0.8	1.5
Boscalid	93.4	2.5	1.0	2.0	89.8	4.5	1.7	3.5
Boscalid metabolite–M510F01 acetyl	73.2	2.5	0.8	1.6	75.9	5.0	1.7	3.3
Broflanilide	84.2	5.3	1.9	3.9	82.6	5.9	2.1	4.2
Bromuconazole	88.0	2.5	1.0	1.9	73.3	5.9	1.9	3.8
Butralin	85.1	3.3	1.2	2.5	78.1	5.4	1.8	3.6
Carbaryl	70.5	2.7	0.8	1.7	71.3	5.6	1.7	3.5
Carbendazim	92.2	3.1	1.2	2.5	111	5	2.5	4.9
Carbofuran	85.4	1.7	0.6	1.3	82.9	4.3	1.5	3.1
Chlorantraniliprole	84.8	2.0	0.7	1.5	91.1	4.6	1.8	3.7
Chlorfenapyr	78.4	5.2	1.8	3.6	85.5	6.8	2.5	5.0
Chlorothalonil	121	4	1.9	3.9	105	20	9.0	18
Chlorpyrifos	98.0	2.9	1.2	2.4	101	4	1.9	3.9
Chlorpyrifos oxon	91.9	2.6	1.0	2.0	83.5	5.4	2.0	3.9
Clomazone	76.2	3.6	1.2	2.4	74.6	5.6	1.8	3.6
Clothianidin	100	2	1.0	2.0	92.5	7.1	2.8	5.7
Clothianidin desmethyl	80.6	5.2	1.8	3.7	94.0	6.6	2.8	5.6
Coumaphos	85.5	3.1	1.1	2.3	80.2	5.3	1.8	3.7
Cyantraniliprole	92.7	2.7	1.1	2.2	91.0	4.9	2.0	3.9
Cyazofamid	80.1	2.4	0.8	1.7	71.3	5.7	1.8	3.6
Cyclaniliprole	86.0	3.6	1.4	2.7	101	3	1.4	2.9
Cycloate	74.7	2.8	0.9	1.8	78.4	5.1	1.7	3.4
Cyfluthrin	89.6	2.2	0.8	1.7	96.6	2.5	1.0	2.1
Cyhalofop-butyl	78.9	4.4	1.5	3.0	79.5	6.4	2.2	4.4
Cyhalothrin	93.9	1.4	0.6	1.2	96.3	2.3	1.0	1.9

Table 7. Water and filter recoveries, relative standard deviations (RSDs), method detection limits (MDLs), and reporting limits (RLs) for target compounds in MDL spike samples (spiked concentration=15 nanograms per liter; sample size, *n*=9).—Continued

[%, percent; NR, not reported]

Compound	Water recovery (%)	Water RSD (%)	Water MDL (ng/L)	Water RL (ng/L)	Filter recovery (%)	Filter RSD (%)	Filter MDL (ng/L)	Filter RL (ng/L)
Cymoxanil	99.3	5.3	2.3	4.6	82.3	6.1	2.2	4.3
Cypermethrin	102	2	0.9	1.8	105	2	1.1	2.2
Cyproconazole	79.0	4.1	1.4	2.8	77.8	5.6	1.9	3.8
Cyprodinil	72.0	6.8	2.1	4.3	75.3	4.7	1.6	3.2
DCPA	80.2	3.3	1.2	2.3	89.1	3.2	1.2	2.5
DCPMU	70.2	2.4	0.7	1.5	72.9	4.0	1.3	2.6
DCPU	100	2	1.1	2.1	102	4	1.7	3.5
Deltamethrin	82.2	2.0	0.7	1.4	98.4	3.3	1.4	2.8
Desthio-prothioconazole	84.3	1.8	0.7	1.3	79.1	4.0	1.4	2.8
Diazinon	86.3	3.0	1.1	2.3	81.0	4.6	1.6	3.3
Diazinon oxon	72.7	2.4	0.7	1.5	71.4	6.6	2.1	4.1
Dichlorvos	79.4	3.5	1.2	2.4	82.7	2.5	0.9	1.8
Difenoconazole	92.6	3.3	1.3	2.7	74.3	4.4	1.4	2.8
Dimethomorph	84.5	1.9	0.7	1.4	90.3	7.1	2.8	5.5
Dinotefuran	88.4	4.7	1.8	3.6	81.3	10.7	3.6	7.3
Dithiopyr	82.9	3.1	1.1	2.3	87.4	3.4	1.3	2.5
Diuron	88.4	1.8	0.7	1.4	77.5	5.6	1.9	3.8
EPTC	70.5	4.2	1.3	2.6	72.2	4.4	1.4	2.8
Esfenvalerate	87.2	2.0	0.7	1.5	92.7	2.9	1.2	2.4
Ethaboxam	92.7	3.8	1.5	3.0	86.3	4.6	1.7	3.5
Ethalfluralin	97.0	6.4	2.7	5.4	104	7	3.1	6.2
Etofenprox	96.7	4.5	1.9	3.8	109	4	1.7	3.4
Etoxazole	82.1	3.4	1.2	2.4	84.1	5.1	1.9	3.7
Famoxadone	106	15	6.9	14	101	21	9.0	18
Fenamidone	74.2	2.7	0.9	1.7	74.0	3.0	1.0	1.9
Fenbuconazole	85.7	2.4	0.9	1.8	73.1	4.6	1.5	2.9
Fenhexamid	71.8	28.6	8.9	18	71.1	11.3	10	21
Fenpropathrin	93.9	2.0	0.8	1.6	87.3	4.4	1.7	3.3
Fenpyroximate	78.5	4.1	1.4	2.8	76.6	6.5	2.2	4.3
Fipronil	104	2	0.9	1.8	93.5	3.0	1.2	2.4
Fipronil desulfinyl	94.2	2.4	1.0	1.9	80.8	3.0	1.0	2.1
Fipronil desulfinyl amide	79.9	3.0	1.0	2.1	84.4	3.3	1.2	2.4
Fipronil sulfide	94.4	1.8	0.7	1.5	88.7	2.5	1.0	1.9
Fipronil sulfone	96.5	2.1	0.9	1.7	87.0	3.2	1.2	2.4
Flonicamid	96.8	1.8	0.8	1.5	94.1	6.1	2.5	5.0
Florpyrauxifen-benzyl	77.3	4.6	1.5	3.1	76.2	5.0	1.7	3.3

Table 7. Water and filter recoveries, relative standard deviations (RSDs), method detection limits (MDLs), and reporting limits (RLs) for target compounds in MDL spike samples (spiked concentration=15 nanograms per liter; sample size, *n*=9).—Continued

[%, percent; NR, not reported]

Compound	Water recovery (%)	Water RSD (%)	Water MDL (ng/L)	Water RL (ng/L)	Filter recovery (%)	Filter RSD (%)	Filter MDL (ng/L)	Filter RL (ng/L)
Fluazinam	81.0	3.5	1.2	2.4	80.8	4.0	1.4	2.8
Flubendiamide	99.3	3.7	1.6	3.2	117	4	1.9	3.9
Fludioxonil	76.8	3.6	1.2	2.4	72.5	4.2	1.3	2.7
Flufenacet	82.6	5.1	1.8	3.7	77.0	5.6	1.9	3.8
Fluindapyr	90.4	3.4	1.3	2.7	87.1	4.3	1.6	3.2
Flumetralin	86.3	4.6	1.7	3.4	88.8	5.0	1.9	3.8
Fluopicolide	99.8	1.8	0.8	1.6	94.7	4.6	1.9	3.8
Fluopyram	85.9	2.0	0.8	1.5	72.9	5.7	1.8	3.6
Fluoxastrobin	91.0	3.6	1.4	2.8	87.8	4.9	1.9	3.8
Flupyradifurone	79.8	2.0	0.7	1.4	88.9	4.3	1.7	3.3
Fluridone	81.6	4.2	1.5	2.9	72.6	6.7	2.1	4.2
Flutolanil	93.0	3.2	1.3	2.6	89.3	4.9	1.9	3.7
Flutriafol	71.2	4.4	1.4	2.7	74.7	5.8	1.9	3.8
Fluxapyroxad	86.6	1.9	0.7	1.4	87.9	4.4	1.7	3.4
Halauxifen-methyl ester	78.0	2.0	0.7	1.4	78.5	3.2	1.1	2.2
Hexazinone	82.8	1.7	0.6	1.2	85.4	4.5	1.7	3.3
Imazalil	103	3	1.5	3.0	NR	NR	NR	NR
Imidacloprid	97.3	2.4	1.0	2.0	91.8	2.6	1.0	2.1
Imidacloprid desnitro	95.4	8.9	3.7	7.4	92.9	13.6	5.4	11
Imidacloprid olefin	75.5	10.1	3.3	6.6	81.2	15.6	5.5	11
Imidacloprid urea	111	3	1.4	2.8	73.8	6.3	2.0	4.0
Imidacloprid, 5-hydroxy	96.5	4.9	2.0	4.1	98.6	5.1	2.2	4.4
Indaziflam	70.1	4.2	1.3	2.5	77.0	5.9	2.0	4.0
Indoxacarb	86.2	4.2	1.6	3.2	82.7	4.8	1.7	3.5
Ipconazole	86.6	3.1	1.2	2.4	82.1	5.8	2.1	4.1
Iprodione	76.4	3.7	1.2	2.4	79.0	5.6	1.9	3.8
Isofetamid	80.8	4.7	1.7	3.3	76.1	4.6	1.5	3.0
Kresoxim-methyl	86.2	3.0	1.1	2.2	81.0	4.4	1.6	3.1
Malathion	80.3	3.1	1.1	2.2	76.9	6.1	2.0	4.0
Malathion oxon	89.4	1.8	0.7	1.4	72.2	6.1	1.9	3.8
Mandestrobin	84.4	4.4	1.6	3.2	80.9	4.8	1.7	3.3
Mandipropamid	80.6	3.8	1.3	2.6	81.7	6.4	2.3	4.6
Metalaxyl	95.6	1.4	0.6	1.1	95.8	5.3	2.2	4.4
Metalaxyl alanine metabolite	101	3	1.3	2.5	81.0	5.7	2.0	4.0
Metconazole	86.2	2.8	1.0	2.1	88.8	5.3	2.1	4.1
Methoprene	90.4	14.7	5.8	12	99.4	15.4	6.8	13.5

Table 7. Water and filter recoveries, relative standard deviations (RSDs), method detection limits (MDLs), and reporting limits (RLs) for target compounds in MDL spike samples (spiked concentration=15 nanograms per liter; sample size, *n*=9).—Continued

[%, percent; NR, not reported]

Compound	Water recovery (%)	Water RSD (%)	Water MDL (ng/L)	Water RL (ng/L)	Filter recovery (%)	Filter RSD (%)	Filter MDL (ng/L)	Filter RL (ng/L)
Methoxyfenozide	96.7	2.3	1.0	1.9	72.1	4.9	1.5	3.1
Methylparathion	87.2	7.6	2.9	5.8	84.6	12.6	4.7	9.5
Metolachlor	98.4	3.6	1.5	3.1	86.9	4.0	1.5	3.0
Myclobutanil	91.0	1.4	0.6	1.1	91.1	5.3	2.1	4.2
Naled (Dibrom)	75.1	32.4	11	21	79.3	25.2	12	24
Napropamide	87.5	2.6	1.0	2.0	86.1	4.1	1.5	3.0
Nitrapyrin	96.3	2.6	1.1	2.1	85.3	4.4	1.6	3.3
Novaluron	75.7	6.8	2.2	4.5	75.0	6.8	2.2	4.4
Oryzalin	87.9	5.0	1.9	3.8	78.6	4.7	1.6	3.2
Oxadiazon	82.9	2.4	0.9	1.7	97.0	4.6	1.9	3.9
Oxathiapiprolin	96.4	3.2	1.4	2.7	80.6	4.2	1.5	3.0
Oxyfluorfen	85.6	3.7	1.4	2.7	92.1	3.1	1.3	2.5
p,p'-DDD	93.3	3.3	1.3	2.7	103	3	1.1	2.3
p,p'-DDE	81.7	4.2	1.5	3.0	89.0	3.2	1.2	2.5
p,p'-DDT	91.5	3.4	1.3	2.7	101	4	1.8	3.6
Paclobutrazol	72.1	3.6	1.1	2.2	77.1	6.7	2.3	4.5
Pendimethalin	84.9	2.7	1.0	2.0	77.1	5.9	2.0	3.9
Penoxsulam	70.5	7.1	2.2	4.4	NR	NR	NR	NR
Pentachloroanisole (PCA)	90.2	2.9	1.1	2.3	108	5	2.3	4.7
Pentachloronitrobenzene (PCNB)	90.2	3.7	1.4	2.9	91.9	7.3	3.0	6.0
Penthiopyrad	95.0	2.7	1.1	2.2	88.4	5.1	1.9	3.9
Permethrin	96.2	1.7	0.7	1.4	105	2	0.7	1.5
Phenothrin	94.9	2.7	1.1	2.2	105	3	1.3	2.6
Phosmet	71.8	2.2	0.7	1.4	77.1	4.8	1.6	3.3
Picarbutrazox	85.3	3.6	1.3	2.7	79.7	4.7	1.6	3.2
Picoxystrobin	88.8	3.3	1.3	2.6	80.9	5.9	2.0	4.1
Piperonyl butoxide	98.9	2.4	1.0	2.1	85.0	5.8	2.1	4.3
Prodiamine	81.7	3.1	1.1	2.2	72.5	6.3	2.1	4.1
Prometon	97.2	3.4	1.4	2.9	79.4	4.0	1.4	2.8
Prometryn	90.4	1.8	0.7	1.4	83.7	4.5	1.7	3.3
Propanil	87.2	3.2	1.2	2.5	81.3	5.4	1.9	3.8
Propargite	82.1	3.3	1.2	2.4	107	4	1.7	3.4
Propiconazole	93.1	1.8	0.7	1.5	86.7	3.5	1.3	2.6
Propyzamide	90.8	2.6	1.0	2.1	80.6	5.3	1.9	3.7
Pydiflumetofen	85.8	2.8	1.0	2.1	71.2	6.5	2.0	4.1
Pyraclostrobin	89.8	3.8	1.5	2.9	80.4	5.1	1.8	3.6

Table 7. Water and filter recoveries, relative standard deviations (RSDs), method detection limits (MDLs), and reporting limits (RLs) for target compounds in MDL spike samples (spiked concentration=15 nanograms per liter; sample size, *n*=9).—Continued

[%, percent; NR, not reported]

Compound	Water recovery (%)	Water RSD (%)	Water MDL (ng/L)	Water RL (ng/L)	Filter recovery (%)	Filter RSD (%)	Filter MDL (ng/L)	Filter RL (ng/L)
Pyridaben	79.5	3.9	1.4	2.7	98.0	3.1	1.3	2.6
Pyrimethanil	83.8	3.5	1.3	2.6	87.2	2.9	1.1	2.2
Pyriproxyfen	75.6	3.4	1.1	2.3	72.4	5.3	1.7	3.3
Quinoxyfen	78.9	3.3	1.1	2.3	74.1	5.3	1.7	3.4
Resmethrin	92.3	2.3	0.9	1.8	86.3	3.9	1.4	2.9
Sedaxane	90.6	2.3	0.9	1.8	85.8	4.0	1.5	3.0
Simazine	96.6	2.1	0.9	1.7	79.8	3.9	1.4	2.7
Sulfoxaflor	89.2	3.0	1.2	2.4	88.0	6.2	2.4	4.8
Tebuconazole	92.5	1.6	0.6	1.3	89.8	5.9	2.3	4.6
Tebuconazole t-butylhydroxy	79.0	1.9	0.7	1.3	NR	NR	NR	NR
Tebufenozide	83.6	3.3	1.2	2.4	77.1	4.5	1.5	3.0
Tebupirimfos	99.2	2.9	1.3	2.5	88.2	6.0	2.3	4.6
Tebupirimfos oxon	85.7	2.1	0.8	1.5	72.9	4.4	1.4	2.8
Tefluthrin	98.8	1.5	0.7	1.3	94.3	3.0	1.2	2.4
Tetraconazole	92.1	1.5	0.6	1.2	72.3	7.3	2.3	4.6
Tetramethrin	86.7	2.5	0.9	1.9	108	3	1.4	2.7
t-Fluvalinate	98.4	1.9	0.8	1.6	104	2	1.1	2.1
Thiabendazole	76.4	5.2	1.7	3.4	72.3	7.1	2.2	4.5
Thiacloprid	75.9	3.7	1.2	2.5	86.6	5.8	2.2	4.3
Thiamethoxam	82.1	1.5	0.5	1.1	94.4	4.2	1.7	3.5
Thiamethoxam degradate (CGA-355190)	99.3	3.3	1.4	2.9	82.6	7.3	2.6	5.2
Thiamethoxam degradate (NOA-407475)	79.9	7.8	2.7	5.4	NR	NR	NR	NR
Thiobencarb	84.3	3.2	1.2	2.4	79.0	5.8	2.0	4.0
Tolfenpyrad	76.1	5.0	1.6	3.3	81.8	4.9	1.7	3.5
Triadimefon	88.2	2.0	0.8	1.5	78.5	5.0	1.7	3.4
Triadimenol	72.9	3.8	1.2	2.4	71.6	3.5	1.1	2.2
Triallate	80.7	13.5	4.7	9.4	82.0	13.8	4.8	9.6
Tribufos	84.4	3.9	1.4	2.8	82.1	3.1	1.1	2.2
Tricyclazole	89.5	3.9	1.5	3.0	84.3	4.5	1.6	3.3
Trifloxystrobin	82.5	3.6	1.3	2.6	75.7	6.1	2.0	4.0
Triflumizole	71.6	4.1	1.3	2.5	75.0	4.8	1.6	3.1
Trifluralin	78.3	3.9	1.3	2.6	78.7	6.3	2.2	4.3
Triticonazole	80.5	3.7	1.3	2.6	80.5	5.3	1.9	3.7
Valifenalate	87.4	2.6	1.0	2.0	71.4	7.7	2.4	4.8
Vinclozolin	90.4	2.4	0.9	1.9	82.8	6.7	2.4	4.8
Zoxamide	87.0	2.2	0.8	1.7	76.2	5.8	1.9	3.8

Summary

This method provides details for analysis of 183 pesticides and pesticide degradates in whole-water samples, through the analysis of filtered water and suspended sediment (183 analytes in filtered water; 178 analytes in suspended sediment). Following filtration, water is extracted via solid-phase extraction (SPE), combined with bottle washes, and analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-tandem mass spectrometry (GC-MS/MS). Suspended sediment is extracted using an ultrasonication, solid-liquid extraction with organic solvent, passed through sodium sulfate, and analyzed by LC-MS/MS and GC-MS/MS. Recoveries of pesticides and pesticide degradates spiked at 50 nanograms per liter (ng/L) in water collected from the American River, California, ranged from 59.5 to 108.9 percent. Recoveries of pesticides and pesticide degradates in test water (183 analytes) and suspended sediment filters (178 analytes) fortified at 15 ng/L ranged from 70.1 to 121.0 percent and 71.1 and 117.0 percent in water and suspended sediment filter samples, respectively. Method detection limits (MDLs) ranged from 0.5 to 10.6 ng/L in water and 0.7 to 11.8 ng/L in suspended sediment filters. The reporting limits were 1.1–21.1 ng/L and 1.5–23.7 ng/L in water and filter samples, respectively. The developed method is applied to surface-water samples for the analysis of pesticides, pesticide degradates, and other agrochemicals. Support for this report was provided by the California Water Science Center.

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