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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Moderate-Use Pesticides and Selected Degradates in Water by C-18 Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry

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Water-Resources Investigations Report 01-4098

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

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By Mark W. Sandstrom, Max E. Stroppel, William T. Foreman, and Michael P. Schroeder

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 01-4098

U.S. Geological Survey Method O-2002-01
Laboratory Methods (Schedules) 2002 and 2011

Denver, Colorado
2001

U.S. Department of the Interior
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CONVERSION FACTORS

Multiply	By	To obtain
	Length	
centimeter (cm)	3.94×10^{-1}	inch
micrometer (µm)	3.94×10^{-5}	inch
millimeter (mm)	3.94×10^{-2}	inch
meter (m)	3.281	foot
	Mass	
gram (g)	3.53×10^{-2}	ounce
kilogram (kg)	2.205	pound
microgram (µg)	3.53×10^{-8}	ounce
milligram (mg)	3.53×10^{-5}	ounce
nanogram (ng)	3.53×10^{-11}	ounce
	Volume	
liter (L)	2.64×10^{-1}	gallon
liter (L)	33.81	ounce, fliud
microliter (µL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon
milliliter (mL)	1	cubic centimeter
	Pressure	
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
	Area	
hectares (ha) (or) hectometer^2 (hm^2)	2.471	acres
	Concentration, in water	
nanograms per liter (ng/L)	1	parts per trillion (ppt)
micrograms per liter (µg/L)	1	parts per billion (ppb)
milligrams per liter (mg/L)	1	parts per million (ppm)

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

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

ACRONYMS AND ABBREVIATIONS

A	ampere
cm/sec	centimeter per second
dc	direct current
µg/L	microgram per liter
mg/L	milligram per liter
min	minute
mL/min	milliliter per minute
ng/L	nanogram per liter
ng/µL	nanogram per microliter
lb/in^2	pound per square inch
V	volt
±	plus or minus
<	less than
C-18	octadecyl
CCV	continuing calibration verification
ETFE	ethylenetetrafluoroethylene
GC	gas chromatography
GC/MS	gas chromatograph/mass spectrometer
GCC	glass bottle, amber
HPLC	high-performance liquid chromatography
ID	inside diameter
IS	internal standard
LRL	laboratory reporting level
LT–MDL	long-term method detection level
MDL	method detection limit
MS	mass spectrometry
NAWQA	National Water-Quality Assessment program
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OD	outside diameter
PAH	polycyclic aromatic hydrocarbon
PFA	perfluoralkoxy
PFTBA	perfluorotributylamine
LRL	laboratory reporting level
SIM	selected-ion monitoring
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

GLOSSARY

Analyte – The pesticide or pesticide degradate determined in an analysis.

Continuing calibration verification (CCV) – A calibration standard that contains method analytes that is used to measure and control the bias of the existing calibration curve for these analytes. The CCV is an instrumental standard only and is not processed through preparative steps of the method.

Fortified reagent-water-set sample – A quality-control sample prepared by adding a known amount of analytes to a reagent-water sample and analyzed with each set of environmental samples (usually 10). Also known as a "set spike."

Internal standard (IS) – An analyte not expected to be found in any environmental sample that is added to every sample extract in a known amount. The internal standard is used to measure the relative GC/MS responses of other analytes and surrogates in each sample.

Laboratory reporting level (LRL) – The concentration where the false-positive error is minimized to no more than 1 percent and the false-negative error is minimized to no more than 1 percent. The LRL is calculated as 2 times the MDL. An analyte determined to be not identified, confirmed, or measured in a sample is reported as <LRL.

Method detection limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. At this concentration the false positive error is minimized to no more than 1-percent probability (U.S. Environmental Protection Agency, 1997).

Procedural internal standard quantitation – A quantitation method where the internal standard is added to the sample extract prior to evaporation and transfer-to-vial sample processing steps. These final steps in the sample-extract processing are included in the quantitation. Use of the procedural internal-standard quantitation compensates for any bias in the extract evaporation and transfer-to-vial sample processing steps, but not the solid-phase extraction and elution steps of the analytical method.

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

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U.S. Geological Survey Method O-2002-01
Laboratory Methods (Schedules) 2002 and 2011

Abstract

A method for the isolation and analysis of 21 parent pesticides and 20 pesticide degradates in natural-water samples is described. Water samples are filtered to remove suspended particulate matter and then are pumped through disposable solid-phase-extraction columns that contain octadecyl-bonded porous silica to extract the analytes. The columns are dried by using nitrogen gas, and adsorbed analytes are eluted with ethyl acetate. Extracted analytes are determined by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring of three characteristic ions. The upper concentration limit is 2 micrograms per liter (µg/L) for most analytes. Single-operator method detection limits in reagent-water samples range from 0.001 to 0.057 µg/L. Validation data also are presented for 14 parent pesticides and 20 degradates that were determined to have greater bias or variability, or shorter holding times than the other compounds. The estimated maximum holding time for analytes in pesticide-grade water before extraction was 4 days. The estimated maximum holding time for analytes after extraction on the dry solid-phase-extraction columns was 7 days. An optional on-site extraction procedure allows for samples to be collected and processed at remote sites where it is difficult to ship samples to the laboratory within the recommended pre-extraction holding time. The method complements existing U.S. Geological Survey Method O-1126-95 (NWQL Schedules 2001 and 2010) by using identical sample preparation and comparable instrument analytical conditions so that sample extracts can be analyzed by either method to expand the range of analytes determined from one water sample.

INTRODUCTION

Pesticides are widely used in the United States to increase production of agricultural products by controlling weeds, insects, and other pests in a wide variety of settings. More than 450 million kilograms of pesticides, which include insecticides, herbicides, and fungicides, are used each year in the United States. The fate of pesticides after application is important because of the potential adverse effects of pesticides on the environment and human health, especially by movement into the hydrologic system. Small concentrations of pesticides have been widespread in surface- and ground-water samples for several decades (Barbash and Resek, 1996; Gilliom and others, 1999; Larson and others, 1997; Larson and others, 1998).

Pesticides, as is the case for most organic compounds, also are transformed after release to the environment. Both

chemical and biological processes might cause these transformations. The fate of the transformation products, referred to as degradates, in surface and ground water is frequently not known because degradates are not commonly included in monitoring studies. Recent interest in the presence and fate of degradates, however, has increased. Limited studies have indicated that when included in surveys, degradates are frequently detected, often at higher frequencies and concentrations than many parent pesticides. In addition, an understanding of the presence of degradates can help provide an understanding of the overall fate and behavior processes of pesticides.

There are two main reasons why degradates have not been included in previous routine monitoring studies, even after the recognition that their presence might be relevant to evaluate environmental health. First, many degradates are more polar than their parent pesticides because the transformation processes generally add oxygenated or other polar functional groups to the molecule. These more polar degradates are typically more difficult to analyze by common gas chromatography (GC) methods. Second, and more importantly, analytical standards of many potential degradates have not been widely available until recently, so they could not be included in quantitative analytical methods.

The U.S. Geological Survey (USGS) recently developed two analytical methods for the routine determination in water of many of the pesticides used nationally in greatest abundance (Werner and others, 1996; Zaugg and others, 1995). These methods were used in the National Water-Quality Assessment (NAWQA) program as part of a study of the presence and distribution of pesticides in surface- and ground-water samples nationwide (U.S. Geological Survey, 2000). Those methods included only three degradates, and did not include all of the top 120 pesticides used nationally, one of the program goals.

The methods are referred to by laboratory personnel and field teams requesting analytical services by National Water Quality Laboratory (NWQL) schedules. The laboratory schedules are identified for the benefit of readers of this report. NWQL schedules 2001 and 2010 request analyses of 47 pesticides that are isolated from filtered water by C-18 solid-phase extraction (SPE) and identified and quantified by gas chromatography/mass spectrometry (GC/MS) (Zaugg and others, 1995). The pesticide acetochlor was added to the methods in June 1994 (Lindley and others, 1996). NWQL schedules 2050 and 2051 request analyses of 41 pesticides that are isolated from filtered water by Carbopak-B SPE and are identified and quantified by high-performance liquid chromatography (HPLC) with diode-array detection (Werner and others, 1996). Both methods have optional procedures for on-site SPE. Schedules 2010 and 2051 request analyses of pesticides in samples that were extracted from filtered water samples on-site, whereas schedules 2001 and 2050 request analyses for pesticides that were extracted from water samples at the NWQL. For the purposes of this report, schedules 2001 and 2010 will be referred to as method 2001, and schedules 2050 and 2051 will be referred to as method 2050. The new method presented in this report will be referred to as method 2002, even though field teams will need to request either schedules 2002 or 2011.

This report describes a method for determining a broad range of pesticide chemical classes and pesticide degradates in environmental water samples. It was developed by the USGS for use in the NWQL. The method combines octadecyl

(C-18) SPE for pesticide isolation GC/MS operated in the selected-ion monitoring mode (SIM) for selective confirmation and quantitation of the **analytes**.[1] The method was developed to complement method 2001 by using the same sample preparation and analytical steps but adds new analytes. Extracts from method 2001 can be analyzed by the new method 2002 to expand the range of analytes determined from one water sample, because the same sample preparation procedures are followed. The method was implemented in the NWQL in March 1999 for conditional analysis of environmental samples collected as part of the NAWQA program.

This report provides a detailed description of all aspects of the methods, including the equipment, reagents, sampling protocol, instrument calibration, and SPE procedure required for sample analysis. Method performance (bias and variability), holding times in water and after isolation on the SPE column, and estimated **method detection limits** for 75 analytes are presented.

The scope of the report includes determination of method performance in reagent-water samples and in two natural-water types—a ground-water and a surface-water sample from the Denver, Colorado, region. Method performance was determined at two concentration levels—0.1 and 1.0 microgram per liter (µg/L)—in each water type. Method detection limits were estimated according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1997). Holding times of the analytes in water before extraction and on the SPE columns following extraction and column drying were evaluated. An optional laboratory automated procedure is described, and an optional on-site SPE procedure is briefly described in Supplements A and B in this report.

[1]Words in boldface are defined in the Glossary.

INITIAL METHOD DEVELOPMENT

This method was developed to complement the existing method 2001 by adding a new suite of pesticides and pesticide degradates without modifying the analytical procedure. Method development consisted of testing the new analytes by using the 2001 procedure and collecting method validation information on the analytes that were suitable to the GC/MS and SPE conditions used. Initial method development included obtaining analytical standards of the parent pesticides and degradates identified as candidate analytes. The new analytes were tested by GC/MS and deemed acceptable if they provided measurable response and narrow chromatographic peak shapes. The analytes then were combined into mixtures of parent or degradates and added to reagent-water samples to determine initial feasibility of recovery using C-18 SPE. The analytes that were tested initially but subsequently eliminated from the method because of low GC/MS response or C-18 SPE recovery are listed in table 1.

Eight parent pesticides, most of which were selected because of their high national-use rate, had low or no GC/MS response (xgc) and were eliminated from additional testing (table 1). Acephate and methamidophos had low SPE recovery (xspe), and chlorethoxyfos was not obtained in time to include in testing (xor). Likewise, 14 degradates had low or no GC/MS response (xgc), and 9 degradates had low SPE recovery (xspe) during preliminary testing, so the compounds were not included in additional testing. Nine degradates listed in vendors' catalogs were out of stock during testing and therefore could not be considered for method validation (xor).

Table 1. Analytes that were initially considered or tested but subsequently eliminated from complete validation experiments because of problems with ordering, analysis, or recovery

[Analytes separated by parents and degradates, and sorted according to rank. Parent pesticides shown for corresponding degradates. Rank, national pesticide-use rank of analyte; CASRN, Chemical Abstracts Service Registry Number; P-Code, National Water Information System parameter code; xor, problem obtaining chemical standard; xgc, problem with gas chromatograph/mass spectrometer analysis; xspe, problems with solid-phase extraction recovery or instability in water; VOC, volatile organic compound; 2002x, parent pesticide initially tested but eliminated from method; –, no CASRN or parameter code available]

Rank	CASRN	P-Code	Short name	Use	Class	Problem	Parent CASRN	Parent name	Parent class	Parent method
	Parent pesticides									
37	30560-19-1	61579	Acephate	Insecticide	Organo-phosphorus	xspe	–	–	–	–
58	87674-68-8	61588	Dimethenamid	Herbicide	Amide	xgc	–	–	–	–
70	59669-26-0	61608	Thiodicarb	Insecticide	Carbamate	xgc	–	–	–	–
78	133-06-2	61582	Captan	Fungicide	Imide	xgc	–	–	–	–
98	10265-92-6	61597	Methamidophos	Insecticide	Organo-phosphorus	xspe	–	–	–	–
101	115-32-2	61587	Dicofol	Acaricide	Organochlorine	xgc	–	–	–	–
104	76-06-2	61584	Chloropicrin	Fumigant	VOC	xgc	–	–	–	–
153	300-76-5	38856	Naled	Insecticide	Organo-phosphate	xgc	–	–	–	–
155	66841-25-6	61609	Tralomethrin	Insecticide	Pyrethroid	xgc	–	–	–	–
233	95465-99-9	61581	Cadusaphos	Nematocide	Organo-phosphorus	xgc	–	–	–	–
234	54593-83-8	61583	Chlorethoxyfos	Insecticide	Organo-phosphorus	xor	–	–	–	–
	Degradates									
1003	120-83-2	34602	2,4-Dichlorophenol	Degradate	–	xspe	94-75-7	2-4,D	Chlorophenoxy acid	2050
1007	–	61619	2-Chloro-2',6'_alide	Degradate	–	xor	15972-60-8	Alachlor	Acetanilide	2001
1012	6515-38-4	61626	3,5,6-Trichlor_dinol	Degradate	–	xgc	2921-88-2	Chlorpyrifos	Organothio-phosphate	2001
1016	10548-10-4	61675	Terbufos-sulfoxide	Degradate	–	xor	13071-79-9	Terbufos	Organothio-phosphate	2001
1026	–	61658	Metribuzin-des_iketo	Degradate	–	xspe	21087-64-9	Metribuzin	Triazine	2001
1026	–	61657	Metribuzin-desamino	Degradate	–	xspe	21087-64-9	Metribuzin	Triazine	2001
1028	1113-02-6	61639	Omethoate	Degradate	–	xspe	60-51-5	Dimethoate	Organothio-phosphate	2002
1034	2588-04-7	61667	Phorate sulfone	Degradate	–	xspe	298-02-2	Phorate	Organothio-phosphate	2001
1043	–	61622	3-(2,2-Dichlor_ acid	Degradate	–	xgc	52645-53-1	Permethrin	Pyrethroid	2001

Table 1. Analytes that were initially considered or tested but subsequently eliminated from complete validation experiments because of problems with ordering, analysis, or recovery—Continued

Rank	CASRN	P-Code	Short name	Use	Class	Problem	Parent CASRN	Parent name	Parent class	Parent method
1049	100-02-7	34647	4-Nitrophenol	Degradate	–	xspe	56-38-2	Parathion	Organothio-phosphate	2001
1051	2327-02-8	61748	1-(3,4-Dichlor_)urea	Degradate	–	xgc	330-55-2	Linuron	Urea	2001
1060	35884-76-5	61653	Malathion mono_ acid	Degradate	–	xor	121-75-5	Malathion	Organothio-phosphate	2001
1064	65600-62-6	61612	2,3,3-trichlor_ salt	Degradate	–	xgc	2303-17-5	Triallate	Thiocarbamate	2001
1069	3964-56-5	61632	4-Bromo-2-chlo_henol	Degradate	–	xspe	41198-08-7	Profenofos	Organothio-phosphate	2002
1070	16752-77-5	49296	Methomyl	Degradate	–	xgc	59669-26-0	Thiodicarb	Carbamate	2002x
1070	13749-94-5	61655	Methomyl-oxime	Degradate	–	xgc	59669-26-0	Thiodicarb	Carbamate	2002x
1078	–	–	Tetrahydrophthalimide	Degradate	–	xor	133-06-2	Captan	Imide	2002
1084	934-32-7	61616	2-Aminobenzimidazole	Degradate	–	xgc	17804-35-2	Benomyl	Carbamate	9060
1084	10605-21-7	38736	Carbendazim	Degradate	–	xgc	17804-35-2	Benomyl	Carbamate	9060
1086	2814-20-2	61621	2-Isopropyl-6-_dinol	Degradate	–	xspe	333-41-5	Diazinon	Organothio-phosphate	2001
1086	962-58-3	61638	Diazinon, oxyg_nalog	Degradate	–	xgc	333-41-5	Diazinon	Organothio-phosphate	2001
1093	–	61624	3-(3,5-Dichlor_imide	Degradate	–	xor	36734-19-7	Iprodione	Amide	2002
1101	–	61613	2,4'-Dicofol	Byproduct	–	xgc	115-32-2	Dicofol	Organochlorine	2002
1114	3739-38-6	61628	3-Phenoxybenzoic acid	Degradate	–	xgc	52315-07-8	Cypermethrin	Pyrethroid	2002
1124	31110-62-0	61661	O-Ethyl-S-prop_ioate	Degradate	–	xgc	13194-48-4	Ethoprop	Organothio-phosphate	2001
1128	5459-93-8	61659	N-Ethyl cycloh_amine	Degradate	–	xspe	1134-23-2	Cycloate	Thiocarbamate	2002
1129	–	61623	3-(2,2-Dichlor_ylate	Degradate	–	xgc	68359-37-5	Cyfluthrin	Zyrethroid	2002
1134	–	61643	Ethion dioxon	Degradate	–	xor	563-12-2	Ethion	Organothio-phosphate	2002
1227	3761-42-0	61648	Fenthion sulfone	Degradate	–	xor	55-38-9	Fenthion	Organothio-phosphate	2002
1228	–	61651	Isophenphos-de_logue	Degradate	–	xor	25311-71-1	Isofenphos	Organothio-phosphate	2002
1228	–	61650	Isophenphos-de_ropyl	Degradate	–	xor	25311-71-1	Isofenphos	Organothio-phosphate	2002
1232	17210-55-8	61673	Temephos sulfoxide	Degradate	–	xgc	3383-96-8	Temephos	Organothio-phosphate	2002

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Pesticides and degradates, filtered, gas chromatography/mass spectrometry, Laboratory methods (schedules) 2002 and 2011 (U.S. Geological Survey Method O-2002-01)

1. Scope and Application

The method is suitable for the determination of low-level concentrations (1 to 1,000 nanograms per liter) of pesticides and pesticide degradates in filtered natural-water samples. The methods are applicable to pesticides and degradates that are (1) efficiently partitioned from the water phase onto a C-18 organic phase that is chemically bonded to a solid porous silica matrix, and (2) sufficiently volatile and thermally stable for gas chromatography. Suspended particulate matter is removed from the samples by filtration, so this method is suitable for pesticides and degradates in the dissolved phase. The quantity of pesticide dissolved in water in relation to that adsorbed to sediment depends on the physical and chemical properties of the pesticide and the concentration of suspended sediment in the water.

The sample preparation and essential GC/MS operational procedures used for the new method are identical to those in method 2001, which was developed for more abundantly and widely used pesticides (Zaugg and others, 1995). The common preparation and operational procedures will allow analysis of extracts by either method, or analysis of analytes in both methods from one water-sample extract. The 2001 method included an optional on-site extraction procedure, and different laboratory method numbers were used to distinguish laboratory SPE (2001) and on-site SPE (2010). Similarly, the new method numbers distinguish laboratory SPE (2002) and on-site SPE (2011).

The analytes include parent pesticides of national importance based on their use and application or importance to the re-registration monitoring needs of the U.S. Environmental Protection Agency (USEPA) Office of Pesticide Programs, and degradates of pesticides included in NWQL methods 2001, 2050, or the new method 2002 presented in this report (table 2). The USEPA is reviewing older pesticides (those initially registered prior to November 1984) under the Federal Insecticide, Fungicide, and Rodenticide Act to ensure that they meet current scientific and regulatory standards (U.S. Environmental Protection Agency, 2001). Selection of parent pesticides was based on national pesticide-use information from the National Center for Food and Agricultural Policy and the Census of Agriculture (Majewski, 1997). The pesticides were sorted in decreasing order by total mass of active ingredient applied and total treated area. The top 120 were determined by combining the top 100 in total quantity used and the top 100 in total area of land treated (80 are in the top 100 by both criteria). The 120 compounds were considered a high priority for the NAWQA program (Majewski, 1997). Fifty-seven of these compounds were not included in existing NWQL analytical methods. These compounds were classified by physical attributes, such as chemical class, characteristic functional groups, and possible analytical technique. Seventeen pesticides were considered suitable for testing by GC/MS and were initially included in these methods. The USEPA reviewed the resulting list, and set priorities or added pesticides of importance to its pesticide re-registration

process. Selection of pesticide degradates initially was based on whether the parent pesticide was determined by NWQL methods 2001, 2050, or the current method, and whether an analytical standard was readily available. These compounds then were classified by physical attributes, such as chemical class, available functional groups, and whether they would be amenable to the C-18 SPE GC/MS analytical method. Seventy-three degradates initially were considered.

After this selection process, the analytes were obtained and tested in initial and final validation experiments. The analytes that successfully passed the final validation experiments are listed in table 2. The relations of pesticide degradates included in the new method to parent pesticides in U.S. Geological Survey methods 2001, 2050, and 2002 are listed in table 3.

All tables in this report list the average national-use rank of pesticide or pesticide degradate to allow sorting of the analytes and to provide an easy correlation between parent and degradate pesticides. The pesticides sorted in decreasing order in total kilograms of active ingredient applied and total treated hectares were assigned numbers indicating their order (or rank). The arithmetical average of the rank on the basis of total kilograms of active ingredient applied and total treated hectares was calculated and is termed the "rank" in this report. Degradates were arbitrarily assigned a rank of 1000 plus the average rank of the parent pesticide. For example, 2-[2-ethyl-6-methylphenyl)amino]-1-propanol and 2-ethyl-6-methylaniline, both degradates of metolachlor, which has an average rank of 2, are assigned average rank 1002 (table 3). This ranking procedure provides a convenient way to link the degradates and parent pesticides in tables and figures.

Because some degradates potentially can be derived from more than one parent pesticide, some of the degradates in table 2 are listed more than once, in order of the national-use rank of the parent pesticide. In that situation, the degradate was assigned the lowest rank, even though the degradate could have a different rank, depending on which parent it was derived from. For example, 3,4-dichloroaniline is shown in table 2 with rank 1033, even though it could be assigned ranks of 1036, 1051, and 1241, which correspond to the three other potential parent pesticides (linuron, propanil, neburon) of high to moderate national use.

A short, 20-character name was used in the tables to minimize space taken by lengthy chemical names. The short name was defined as the first 14 characters and the last 5 characters of a name, joined by an underscore: "_". Common or chemical names and corresponding short names are listed in table 2.

The calibration range is equivalent to concentrations ranging from 0.001 to 1.0 µg/L for most analytes. The method detection limit (MDL) is not only compound dependent, but also depends on sample matrix, instrument performance, and other operational sources of variation. For all analytes listed in table 2, MDLs in pesticide-grade water vary from 0.001 to 0.7 µg/L. Analytical results are not censored at the MDL; if a pesticide meets the detection criteria (retention time and mass spectra compared to that of a reference standard, as defined later in section 11), the result is calculated and reported with an estimated "E" qualifier.

Table 2. Pesticides and degradates included in new method

[Table sorted by remark code and then by rank. Rank, national rank of pesticide based on application rate. Pesticide degradates were arbitrarily assigned a rank of 1000 plus the average rank of the lowest-ranked parent pesticide; CASRN, Chemical Abstracts Service Registry Number; P-Code, National Water Information System parameter code; I, Insecticide; H, Herbicide; Def, Defoliant; N, Nematocide; F, Fungicide; PGR, Plant Growth Regulator; Deg, Degradate; Fum, Fumigant; IS, Internal Standard; SUR, Surrogate; –, not applicable; E, estimated remark code; --,CASRN not available]

Rank	Name	Short name	CASRN	P-Code	Use	Class	Remark code
	Parent pesticides						
63	Prometryn	Prometryn	7287-19-6	04036	H	Triazine	–
69	Profenofos	Profenofos	41198-08-7	61603	I	Organothiophosphate	–
71	*alpha*-Endosulfan	*alpha*-Endosulfan	959-98-8	34362	I	Organochlorine	–
75	Metalaxyl	Metalaxyl	57837-19-1	61596	F	Amino acid derivative	–
106	Oxyfluorfen	Oxyfluorfen	42874-03-3	61600	H	Diphenyl ether	–
108	*cis*-Propiconazole	*cis*-Propiconazole	*c*-60207-90-1[1]	79846	F	Triazole	–
110	*trans*-Propiconazole	*trans*-Propiconazole	*t*-60207-90-1[1]	79847	F	Triazole	–
121	Myclobutanil	Myclobutanil	88671-89-0	61599	F	Tziazole	–
126	Fenamiphos	Fenamiphos	22224-92-6	61591	N	Organothiophosphate	–
127	Hexazinone	Hexazinone	51235-04-2	04025	H	Triazine	–
128	Cycloate	Cycloate	1134-23-2	04031	H	Thiocarbamate	–
132	Methidathion	Methidathion	950-37-8	61598	I	Organothiophosphate	–
134	Ethion	Ethion	563-12-2	82346	I	Organothiophosphate	–
211	(E)-Dimethomorph	(E)-Dimethomorph	e-110488-70-5[1]	79844	F	Miscellaneous	–
212	(Z)-Dimethomorph	(Z)-Dimethomorph	z-110488-70-5[1]	79845	F	Miscellaneous	–
220	Terbuthylazine	Terbuthylazine	5915-41-3	04022	H	Triazine	–
225	Flumetralin	Flumetralin	62924-70-3	61592	PGR	Dinitroaniline	–
227	Fenthion	Fenthion	55-38-9	38801	I	Organothiophosphate	–
228	Isofenphos	Isofenphos	25311-71-1	61594	I	Organothiophosphate	–
229	Propetamphos	Propetamphos	31218-83-4	61604	I	Organothiophosphate	–
231	Tebupirimphos	Tebupirimphos	96182-53-5	61602	I	Organothiophosphate	–
28	Dimethoate	Dimethoate	60-51-5	82662	I	Organothiophosphate	E
30	Tribuphos	Tribuphos	78-48-8	61610	Def	Organothiophosphate	E
71	*beta*-Endosulfan	*beta*-Endosulfan	33213-65-9	34357	I	Organochlorine	E
76	Tefluthrin	Tefluthrin	79538-32-2	61606	I	Pyrethroid	E
83	Dicrotophos	Dicrotophos	141-66-2	38454	I	Organophosphate	E

Table 2. Pesticides and degradates included in new method—Continued

Rank	Name	Short name	CASRN	P-Code	Use	Class	Remark code
93	Iprodione	Iprodione	36734-19-7	61593	F	Amide	E
102	Cyhalothrin	Cyhalothrin	91465-08-6	61595	I	Pyrethroid	E
114	Cypermethrin	Cypermethrin	52315-07-8	61586	I	Pyrethroid	E
115	Sulprofos	Sulprofos	35400-43-2	38716	I	0rganothiophosphate	E
125	Phosmet	Phosmet	732-11-6	61601	I	Organothiophosphate	E
129	Cyfluthrin	Cyfluthrin	68359-37-5	61585	I	Pyrethroid	E
131	Bifenthrin	Bifenthrin	82657-04-3	61580	I	Pyrethroid	E
230	Sulfotepp	Sulfotepp	3689-24-5	61605	I	Organothiophosphate	E
232	Temephos	Temephos	3383-96-8	61607	I	Organothiophosphate	E
	Degradates						
1002	2-[2-Ethyl-6-methylphenyl)amino]-1-propanol	2-[2-Ethyl-6-m_panol	61520-53-4	61615	Deg	–	–
1007	2-Chloro-2,6-diethylacetanilide	2-Chloro-2,6-d_ilide	6967-29-9	61618	Deg	–	–
1008	4-(Hydroxymethyl)pendimethalin	4-(Hydroxymeth_halin	56750-76-6	61665	Deg	–	–
1016	Terbufos-O-analogue sulfone	Terbufos-O-ana_lfone	56070-15-6	61674	Deg	–	–
1033	3,4-Dichloroaniline	3,4-Dichloroaniline	95-76-1	61625	Deg	–	–
1043	3-Phenoxybenzyl alcohol	3-Phenoxybenzy_cohol	13826-35-2	61629	Deg	–	–
1044	*c*-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	*c*-Methyl-3-(2,_ylate	[1] *c*-61898-95-1	79842	Deg	–	–
1044	*t*-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	*t*-Methyl-3-(2,_ylate	[1] *t*-61898-95-1	79843	Deg	–	–
1049	Paraoxon-ethyl	Paraoxon-ethyl	311-45-5	61663	Deg	–	–
1060	Malaoxon	Malaoxon	1634-78-2	61652	Deg	–	–
1062	2-(4-tert-butylphenoxy)-cyclohexanol	2-(4-tert-buty_xanol	1942-71-8	61637	Deg	–	–
1067	Disulfoton sulfone	Disulfoton sulfone	2497-06-5	61640	Deg	–	–
1067	Disulfoton sulfoxide	Disulfoton sulfoxide	2497-07-6	61641	Deg	–	–
1071	Endosulfan sulfate	Endosulfan sulfate	[2] 1031-07-8	61590	Deg	–	–
1076	Tefluthrin metabolite [R 152912]	Tefluthrin met_2912]	--	61672	Deg	–	–
1093	3,5-Dichloroaniline	3,5-Dichloroaniline	626-43-7	61627	Deg	–	–
1099	2,5-Dichloroaniline	2,5-Dichloroaniline	95-82-9	61614	Deg	–	–
1124	O-Ethyl-O-methyl-S-propylphosphorothioate	O-Ethyl-O-meth_ioate	76960-87-7	61660	Deg	–	–

Table 2. Pesticides and degradates included in new method—Continued

Rank	Name	Short name	CASRN	P-Code	Use	Class	Remark code
1126	Fenamiphos sulfone	Fenamiphos sulfone	31972-44-8	61645	Deg	–	–
1231	Tebupirimphos oxygen analogue	Tebupirimphos,_logue	--	61669	Deg	–	–
1002	2-Ethyl-6-methylaniline	2-Ethyl-6-meth_iline	24549-06-2	61620	Deg	–	E
1012	Chlorpyrifos oxygen analog	Chlorpyrifos,_nalog	5598-15-2	61636	Deg	–	E
1013	2-Amino-N-isopropylbenzamide	2-Amino-N-isop_amide	30391-89-0	61617	Deg	–	E
1014	Paraoxon-methyl	Paraoxon-methyl	950-35-6	61664	Deg	–	E
1015	4-Chloro-2-methylphenol	4-Chloro-2-met_henol	1570-64-5	61633	Deg	–	E
1024	3-Trifluoromethylaniline	3-Trifluoromet_iline	98-16-8	61630	Deg	–	E
1032	1-Naphthol	1-Naphthol	90-15-3	49295	Deg	–	E
1032	1,4-Naphthaquinone	1,4-Naphthaquinone	130-15-4	61611	Deg	–	E
1034	Phorate oxon	Phorate oxon	2600-69-3	61666	Deg	–	E
1053	Azinphos-methyl-oxon	Azinphos-methyl-oxon	961-22-8	61635	Deg	–	E
1054	Fonofos oxygen analog	Fonofos, oxyge_nalog	944-21-8	61649	Deg	–	E
1071	Endosulfan ether	Endosulfan ether	3369-52-6	61642	Deg	–	E
1076	Tefluthrin metabolite [R 119364]	Tefluthrin met_9364]	--	61671	Deg	–	E
1101	4,4'-Dichlorobenzophenone	4,4'-Dichlorob_enone	90-98-2	61631	Deg	–	E
1105	4-Chlorobenzylmethyl sulfone	4-Chlorobenzyl_lfone	98-57-7	61634	Deg	–	E
1125	Phosmet oxon	Phosmet oxon	3735-33-9	61668	Deg	–	E
1126	Fenamiphos sulfoxide	Fenamiphos sulfoxide	31972-43-7	61646	Deg	–	E
1134	Ethion monoxon	Ethion monoxon	17356-42-2	61644	Deg	–	E
1153	Dichlorvos	Dichlorvos	62-73-7	38775	Fum	Organophosphate	E
1227	Fenthion sulfoxide	Fenthion sulfoxide	3761-41-9	61647	Deg	–	E
	Internal standards						–
	Acenaphthene-d_{10}	Acenaphthene-d_{10}	15067-26-2	–	IS	–	–
	Chrysene-d_{12}	Chrysene-d_{12}	1719-03-5	–	IS	–	–
	Phenanthrene-d_{10}	Phenanthrene-d_{10}	1517-22-2	–	IS	–	–
	Surrogates						–
	alpha-HCH-d_6, surrogate	*alpha*-HCH-d_6,_ogate	319-84-6-d_6	99224	SUR	–	–
	Diazinon-d_{10}, surrogate	Diazinon-d_{10},_ogate	100155-47-3	99223	SUR	–	–

[1]Letter prefix added to CASRN because CASRN not available for *cis*-, *trans*- or E-, Z-isomers.
[2]CASRN number for endosulfan sulfate was changed from "1031-07-7" to "1031-07-8" in the electronic (pdf) file, February 4, 2002 (mws).

Table 3. Relation of pesticide degradates included in new method to parent pesticides in U.S. Geological Survey methods 2001, 2050, and 2002

[Table sorted by increasing order of degradate-use rank, then parent pesticide-use rank. Some degradates have more than one possible parent pesticide, but use lowest rank. Degradate rank, national-use rank of degradate used in table 1; P-Code, National Water Information System parameter code; CASRN, Chemical Abstracts Service Registry Number; Degradate short name and corresponding long name given in table 1; --, no CASRN available; –, no Parent method]

Degradate rank	P-Code	CASRN	Degradate short name	Parent CASRN	Parent name	Parent method
1002	61620	24549-06-2	2-Ethyl-6-meth_iline	51218-45-2	Metolachlor	2001
1002	61615	61520-53-4	2-[2-Ethyl-6-m_panol	51218-45-2	Metolachlor	2001
1007	61618	6967-29-9	2-Chloro-2,6-d_ilide	15972-60-8	Alachlor	2001
1008	61665	56750-76-6	4-(Hydroxymeth_halin	40487-42-1	Pendimethalin	2001
1012	61636	5598-15-2	Chlorpyrifos, _nalog	2921-88-2	Chlorpyrifos	2001
1013	61617	30391-89-0	2-Amino-N-isop_amide	25057-89-0	Bentazon	2050
1014	61664	950-35-6	Paraoxon-methyl	298-00-0	Methyl parathion	2001
1015	61633	1570-64-5	4-Chloro-2-met_henol[1]	94-74-6	MCPA (and salts and esters)	2050
1015	61633	1570-64-5	4-Chloro-2-met_henol[1]	94-81-5	MCPB (and salts and esters)	2050
1016	61674	56070-15-6	Terbufos-O-ana_lfone	13071-79-9	Terbufos	2001
1024	61630	98-16-8	3-Trifluoromet_iline[1]	2164-17-2	Fluometuron	2050
1032	61611	130-15-4	1,4-Naphthaquinone[1]	63-25-2	Carbaryl	2001
1032	49295	90-15-3	1-Naphthol[1]	63-25-2	Carbaryl	2001
1032	61611	130-15-4	1,4-Naphthaquinone[1]	15299-99-7	Napropamide	2001
1032	49295	90-15-3	1-Naphthol[1]	15299-99-7	Napropamide	2001
1033	61625	95-76-1	3,4-Dichloroaniline[1]	330-54-1	Diuron	2050
1033	61625	95-76-1	3,4-Dichloroaniline[1]	709-98-8	Propanil	2001
1033	61625	95-76-1	3,4-Dichloroaniline[1]	330-55-2	Linuron	2001
1033	61625	95-76-1	3,4-Dichloroaniline[1]	555-37-3	Neburon	2050
1034	61666	2600-69-3	Phorate oxon	298-02-2	Phorate	2001
1044	61629	[3] 13826-35-2	3-Phenoxybenzy_cohol	52645-53-1	Permethrin	2001
1044	79842	[3] *c*-61898-95-1	*c*-Methyl-3-(2,_ylate	52645-53-1	Permethrin	2001
1044	79843	[3] *t*-61898-95-1	*t*-Methyl-3-(2,_ylate	52645-53-1	Permethrin	2001
1044	79842	[3] *c*-61898-95-1	*c*-Methyl-3-(2,_ylate	52315-07-8	Cypermethrin	2002
1044	79843	[3] *t*-61898-95-1	*t*-Methyl-3-(2,_ylate	52315-07-8	Cypermethrin	2002
1044	79842	[3] *c*-61898-95-1	*c*-Methyl-3-(2,_ylate	68359-37-5	Cyfluthrin	2002
1044	79843	[3] *t*-61898-95-1	*t*-Methyl-3-(2,_ylate	68359-37-5	Cyfluthrin	2002

Table 3. Relation of pesticide degradates included in new method to parent pesticides in U.S. Geological Survey methods 2001, 2050, and 2002—Continued

Degradate rank	P-Code	CASRN	Degradate short name	Parent CASRN	Parent name	Parent method
1049	61663	311-45-5	Paraoxon-ethyl	56-38-2	Parathion	2001
1053	61635	961-22-8	Azinphos-methyl-oxon	86-50-0	Azinphos-methyl	2001
1054	61649	944-21-8	Fonofos, oxyge_nalog	944-22-9	Fonofos	2001
1060	61652	1634-78-2	Malaoxon	121-75-5	Malathion	2001
1062	61637	1942-71-8	2-(4-tert-buty_xanol	2312-35-8	Propargite	2001
1067	61640	2497-06-5	Disulfoton sulfone	298-04-4	Disulfoton	2001
1067	61641	2497-07-6	Disulfoton sulfoxide	298-04-4	Disulfoton	2001
1071	61590	1031-07-7	Endosulfan sulfate	959-98-8	*alpha*-Endosulfan	2002
1071	61590	1031-07-7	Endosulfan sulfate	33213-65-9	*beta*-Endosulfan	2002
1071	61642	3369-52-6	Endosulfan ether	959-98-8	*alpha*-Endosulfan	2002
1071	61642	3369-52-6	Endosulfan ether	33213-65-9	*beta*-Endosulfan	2002
1076	61671	--	Tefluthrin met_9364]	79538-32-2	Tefluthrin	2002
1076	61672	--	Tefluthrin met_2912]	79538-32-2	Tefluthrin	2002
1093	61627	626-43-7	3,5-Dichloroaniline	36734-19-7	Iprodione	2002
1099	61614	95-82-9	2,5-Dichloroaniline	133-90-4	Chloramben	2050
1101	61631	90-98-2	4,4'-Dichlorob_enone	115-32-2	Dicofol	[4] –
1105	61634	98-57-7	4-Chlorobenzyl_lfone	28249-77-6	Thiobencarb	2001
1124	61660	76960-87-7	O-Ethyl-O-meth_ioate	13194-48-4	Ethoprop	2001
1125	61668	3735-33-9	Phosmet oxon	732-11-6	Phosmet	2002
1126	61646	31972-43-7	Fenamiphos sulfoxide	22224-92-6	Fenamiphos	2002
1126	61645	31972-44-8	Fenamiphos sulfone	22224-92-6	Fenamiphos	2002
1134	61644	17356-42-2	Ethion monoxon	563-12-2	Ethion	2002
1153	38775	62-73-7	Dichlorvos[2]	300-76-5	Naled	[4] –
1227	61647	3761-41-9	Fenthion sulfoxide	55-38-9	Fenthion	2002
1231	61669	--	Tebupirimphos,_logue	96182-53-5	Tebupirimphos	2002

[1]Degradates might also be formed from one or more of the parent pesticides as a result of thermal degradation of the parent pesticide in the injection port of the gas chromatograph during gas chromatography/mass spectrometry analysis.
[2]Dichlorvos is also applied as a parent pesticide.
[3]Letter prefix added to CASRN because CASRN not available for *cis*-, *trans*- or E-, Z-isomers.
[4]Last modifed: February 4, 2002 (mws).

Permanently E-Coded Compounds. Two classes of data are reported from the method: (1) compounds that are reported without qualification, and (2) compounds that are always reported as estimated. Compounds that are reported without qualification are reproducibly well recovered by the method, as defined by median recoveries between 60 and 120 percent and with variation (as indicated by the nonparametric statistic, relative F-pseudosigma; Hoaglin, 1983) less than 25 percent. Estimated-value compounds, which are "E-coded" in the data base, do not meet these performance criteria for unqualified quantification, but are retained in the method because the compounds are important owing to high use or potential environmental effects and because analytical performance has been consistent and reproducible. Estimated-value compounds, when reported, have been identified as present with a high degree of confidence according to method-specific criteria, but greater uncertainty exists in the quantitative determination of concentration than for compounds reported without qualification. It is important to note, however, that there is no qualitative difference between unqualified compounds and estimated-value compounds. The identification of the compounds is equally reliable, and, in reality, bias and variability for different compounds span a continuum of performance rather than corresponding to categories. For example, some unqualified compounds perform similarly to estimated-value compounds that fall just outside the unqualified category criteria. Thus, data users should consider the estimated-value designation as a categorical warning to pay extra attention to potential use and adjustment of numerical concentration results, but not as a distinct boundary between acceptable and unacceptable data, as defined at the beginning of this paragraph.

2. Summary of Method

Water samples are filtered at the collection site by using glass-fiber filters with nominal 0.7-µm pore diameter to remove particulate material (Sandstrom, 1995). About 1 L of the filtered water sample is pumped through a disposable, polypropylene SPE column that contains porous silica coated with an octadecyl (C-18) phase that is chemically bonded to the surface of the silica. The SPE columns are dried using a gentle stream of nitrogen to remove residual water. The adsorbed analytes (pesticides and degradates) then are removed from the SPE columns by elution with 2 mL of ethyl acetate. A procedural internal standard in toluene is added, and the eluant is further evaporated to a small volume (150 µL) using a gentle stream of nitrogen.

Extracts are analyzed by a capillary-column GC/MS operated in the SIM mode. The analytes are identified by comparing their retention times and selected-ion ratios to calibration standards analyzed under the same GC/MS conditions. Analytes are quantified by relating the mass spectrometer (MS) response of the quantitation ion of the analyte to the quantitation ion of an **internal standard**. Quantitation of an analyte at a concentration less than the lowest calibration standard or greater than the highest calibration standard is qualified as “estimated” (E) to signify the lower confidence in the extrapolated concentration.

The internal standard quantitation is a procedural quantitation method in which the internal standard is added to the sample extract prior to evaporation and transfer-to-vial sample-processing steps. The use of the **procedural internal standard quantitation** compensates for any bias in the extract

evaporation and transfer-to-vial sample-processing steps, but not the SPE and elution steps of the analytical method.

Surrogate analytes, which are added to each sample in known concentration, are used to monitor method performance with each sample.

A reagent-water sample fortified with 0.1 µg/L of the analytes (a **fortified reagent-water-set sample** or a set spike) and a pesticide-grade blank water sample (a laboratory reagent blank or set blank) are extracted, processed, and analyzed with each set of 10 samples.

3. Interferences

Interferences might be caused by organic compounds that have gas-chromatograph retention times and characteristic ions with a mass identical to those of the pesticides and degradates of interest. Contaminants in laboratory air, solvents, reagents (including water), glassware, sample bottles and caps, SPE columns, and sample-processing equipment can cause artifacts or false positives in the chromatograms. All of these materials must be routinely demonstrated to be free from interference [less than the MDL, or long-term method detection level (LT–MDL), once determined] under conditions of analysis by analyzing laboratory reagent blanks.

Glassware must be washed with detergent in hot water and rinsed with tap water and distilled or deionized water. Glassware then should be drained, dried, and heated in a laboratory furnace at 450°C for at least 4 hours before use. Solvent rinsing with methanol, followed by air drying, may be substituted for oven heating for other equipment, including sample collection bottles, sample splitters, and filtration devices.

Matrix interferences might be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary, depending on the nature of the sample matrix.

Residual chlorine in treated water samples might cause degradation of some analytes, especially organophosphorus compounds (Dennis and others, 1979). Suitable reagents that might be used to dechlorinate chlorinated water samples have not been tested for their effect on all analytes.

Pesticide degradates might be formed by degradation of the parent pesticide in the hot injection port of the GC. These degradates are considered artifacts of the analytical process, and are not representative of the concentration of analytes in the water samples. The extent of GC injection-port degradation depends on a number of factors, including surface activity, quantity of coextracted organic material, and extent of impurities on the injection-port liner. Degradates that are susceptible to this thermal degradation are identified in table 3. For example, 3,4-dichloroaniline can be formed from thermal degradation of diuron if it is in the water sample.

4. Apparatus and Instrumentation

4.1 Manual sample extraction

4.1.1 *Cleaning and elution module for SPE columns*—Supelco, Inc., Visiprep Solid-Phase Extraction Vacuum Manifold and Visidry Drying Attachment or equivalent.

4.1.2 *SPE pump, ceramic-piston, valveless pump*—Capable of pumping 0 to 30 mL/min, with fittings for 3.18-mm outside diameter (OD) tubing; Fluid Metering Inc., Model QSY - 2 CKC or equivalent. For on-

site SPE, an SPE pump powered by a 12-V dc motor is needed; Fluid Metering Inc., Model RHB - 0 CKC or equivalent.

4.1.3 *Teflon-perfluoralkoxy (PFA) tubing*—3.18-mm OD; Cole-Parmer Instrument Co., CL-06375-01 or equivalent.

4.1.4 *Tefzel-ethylenetetrafluoro-ethylene (Tefzel-ETFE) female Luer connector with 1/4-28 thread*—Tefzel-ETFE union with 1/4-28 thread, and Tefzel-ETFE nut with 1/4-28 thread and 3.18-mm OD tubing connector; Upchurch Scientific or equivalent.

4.1.5 *Pump control box (optional)*—For 12-V dc pumps, fitted with a 4-A fuse, toggle switch, and 10-ohm 1.58-A variable resistor.

4.1.6 *Sample-preparation workstation (optional)*—For pre-cleaning SPE column; Zymark Inc., BenchMate II Workstation or equivalent.

4.1.7 *Bottle-top solvent dispenser*—Adjustable from 2 to 10 mL; Brinkman Dispensette, Van Waters & Rogers (VWR) Scientific or equivalent, for adding solvents to SPE columns during manual cleaning and conditioning steps.

4.1.8 *Luer flow-control valves (optional) or on-off valves*—Constructed of inert materials; Burdick & Jackson (B&J) Inert PTFE flow-control valve, Baxter Diagnostics, Inc. or equivalent.

4.1.9 *Vacuum pump*—Any vacuum pump with sufficient capacity to maintain a slight vacuum of 1.5 to 3 kPa in the cleaning/elution module.

4.2 Automated sample extraction

4.2.1 *Zymark Inc. AutoTrace SPE Workstation*—Configured for 3-mL SPE columns. The setup conditions and processing steps for using the AutoTrace Workstation are listed in Supplement A at the end of this report.

In the automated method, environmental and quality-control samples are extracted in batches of six. The time required for extraction is 58 minutes. One operator typically can process 30 samples in an 8-hour day using this apparatus.

4.3 Manual and automated sample extraction

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

4.3.2 *Analytical balances*—Capable of accurately weighing 1,200 ±1 g (water samples), 10.0000 g ±0.0001 g (SPE columns), and 10.000 g ±0.001 mg (analytical standards).

4.3.3 *Automated solvent evaporator*—The sample extracts are concentrated with a Zymark TurboVap LV. The TurboVap water bath is set to 30°C, and nitrogen gas pressure is adjusted to 28 kPa.

4.4 Sample analysis

4.4.1 *GC/MS instrument*—Agilent Technologies Model 5890 Series II gas chromatograph, connected via capillary direct interface to an Agilent Technologies 5971 or 5972 mass selective detector (MSD).

4.4.2 *Fused-silica capillary column*—Provides adequate resolution, capacity, accuracy, and variability. A 30-m by 0.25-mm inside diameter (ID) fused-silica capillary column coated with a 0.10-µm bonded film of 95-percent dimethyl 5-percent diphenyl polysiloxane is used; Agilent Technologies HP-Ultra II or equivalent.

4.4.3 *Recommended GC conditions*—Oven, 85°C (hold 1.5 min), then program to 240°C at 4°C/min, then program to 340°C at 15°C/min and hold for 2 minutes; injection port, 225°C; carrier gas, helium; column flow nominal 0.65 mL/min (30 cm/sec linear velocity); injection volume, 1 µL, splitless injection; split-vent flow, 30 mL/min; septum purge, 1 mL/min. Total analysis time is 49 minutes.

4.4.4 *Mass spectrometer conditions*—Interface, 290°C; source, 180°C; analyzer, 100°C; dwell time, 20 milliseconds; mass ions monitored are listed in table 5 (see section 9, Calibration).

5. Reagents and Consumable Materials

5.1 *Helium carrier gas*, 99.999 percent purity.

5.2 *Nitrogen gas,* for SPE column drying and solvent evaporation, ultrapure.

5.3 *SPE columns,* Isolute C-18 (EC) columns, packed with 500 mg of a C-18 hydrocarbon phase chemically bonded to silica (International Sorbent Technology Ltd., Mid Glamorgan, UK). The C-18 phase is end-capped to reduce polar secondary interactions with surficial silanol groups. The columns use stainless-steel frits to keep the sorbent phase in place.

5.4 *Disposable culture tubes*, borosilicate glass, 16 by 100 mm, baked at 450°C for 2 hours; Kimax Brand, VWR or equivalent.

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

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

5.7 *Solvents*, hexane, toluene, ethyl acetate, methylene chloride, and methanol; B&J Brand ultrapure pesticide quality or equivalent.

5.8 *Pesticide-grade water*, any high-purity water such as ultrapure B&J Brand water for high-performance liquid chromatography (HPLC) or equivalent, that has been tested and demonstrated to be free from analytes and interferences in this analytical method.

5.9 *Detergent solution,* a dilute mixture (0.2 percent in tap water) of laboratory-grade phosphate-free liquid detergent; Liquinox, Alconox Inc. or equivalent.

6. Sampling Methods, Sample-Collection Equipment, and Cleaning Procedures

6.1 *Sampling methods:* Use sampling methods capable of collecting water samples that accurately represent the water-quality characteristics of the surface water or ground water at a given time or location. Detailed descriptions of sampling methods used by the USGS for obtaining depth- and width-integrated surface-water samples and of sampling methods for obtaining ground-water samples, and of sample processing (splitting, filtration, shipping) are described by Wilde and others (1999).

6.2 *Sample-collection equipment:* Use sample-collection equipment, including automatic samplers, that are free of tubing, gaskets, and other components made of nonfluorinated plastic material that might leach interferences into water samples or sorb the pesticides and degradates from the water. Material suitable for sample-collection and

processing equipment includes fluorocarbon polymers (Teflon, ETFE), metals (stainless steel, aluminum), glass, and ceramics.

6.3 *Sample filtration:* Water samples need to be filtered prior to SPE using procedures described by Sandstrom (1995). Filtration removes particulate material that might block the SPE column. Filter the water samples as soon as possible after collection, preferably at the sample-collection site, because filtration removes microorganisms that might degrade analytes.

6.4 *Cleaning procedures:* Wash all sample-collection equipment with phosphate-free detergent, rinse with tap water to remove all traces of detergent, and finally rinse with methanol (contained in a Teflon squeeze-bottle). Allow the methanol to drain and evaporate from the equipment. When dry, cover equipment orifices with aluminum foil. If it is not practical for the methanol to evaporate from the equipment, use pesticide-grade water to rinse methanol from the equipment.

NOTE: Methanol needs to be collected and disposed of in accordance with local regulations.

6.5 *Quality-control samples:* Collection of quality-control (QC) samples is a required component of sample collection for water-quality studies. QC samples are collected, usually at the field site, to identify, quantify, and document bias and variability in data resulting from the collection, processing, shipping, and handling of samples by field and laboratory personnel. The type, number, and distribution of QC samples are determined by the design and data-quality requirements of the study. Detailed discussion of the description and purpose of QC samples is presented by Wilde and others (1999).

6.5.1 *Blanks*—The primary purpose of a blank sample is to identify potential sources of sample contamination and assess the magnitude of contamination with respect to concentration of target analytes. Field blanks are collected and processed at the field site in the same manner and using the same equipment as the environmental sample(s). The field blank is comprised of an aliquot of blank water processed sequentially through each component of the sampling system. The source solution needed for blank samples must be produced and certified by a laboratory to have analyte concentrations that do not exceed a specified method detection limit. Pesticide-grade blank water (PBW) and volatile-grade blank water (VBW) are required for blanks that will be analyzed for pesticides and volatile organic compounds, respectively. VBW can also be used for pesticide blanks.

6.5.2 *Replicates*—The primary purpose of replicate samples is to identify and (or) quantify the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or higher multiples—are considered identical in composition and are analyzed for the same chemical properties.

6.5.3 *Fortified matrix samples*—Fortified (spike) samples are used to answer questions such as "What loss or gain of target analytes occurred because of water-matrix characteristics; the field processing, shipping, or handling procedures used; holding time; or laboratory analytical procedures?" A sample is fortified by adding a mixture of target compounds obtained from the laboratory to an environmental sample after the sample has been processed. An unfortified environmental sample must accompany each fortified sample. Training is required before personnel attempt to fortify samples. The fortification

kits provided to USGS personnel by the NWQL include the fortification solution, equipment, bottle labels, and detailed instructions. The numbers and types of matrix samples used depend on the objectives and data-quality requirements of individual studies, as determined by the project chiefs. Although analyses for a set of fortified samples—laboratory fortified sample, field-fortified sample, and field-fortified replicate—provide the most complete information relating to the performance of the analytical method, the data from only laboratory fortified samples, or perhaps only one field-fortified sample, could be sufficient to meet study needs.

7. Standards

7.1 *Stock standards:* The pesticides and degradates were obtained as pure materials from the USEPA National Pesticide Standard Repository (Ft. Meade, Md.) or commercial vendors (ChemService; EQ Laboratories). Deuterated PAH standards in solution were obtained from commercial vendors (ChemService). Isotopically labelled pesticide standards of diazinon-d_{10} and *alpha*-HCH-d_6 were purchased from Cambridge Isotope Laboratories (Woburn, Massachusetts).

7.1.1 *Stock internal standard (200 ng/µL)*—Prepare a 200-ng/µL concentration of PAH internal standard by accurately weighing, to the nearest 0.001 mg, 1 mg of the pure material of acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} in a 5-mL volumetric flask and dilute to volume with toluene. Alternatively, the mixed stock may be obtained from commercial vendors. Transfer the stock standards to clean vials and store in a freezer. The stock standards are stable for about 6 months.

7.1.2 *Stock surrogate (100 ng/µL)*—Prepare a 100-ng/µL concentration of surrogate by accurately weighing, to the nearest 0.001 mg, 0.5 mg of diazinon-d_{10} and *alpha*-HCH-d_6 in a 5-mL volumetric flask and dilute with toluene. Transfer the stock standard to clean vials and store in a refrigerator at 4°C ± 3°C. The stock standards are stable for about 6 months.

7.1.3 *Stock standard (10,000 ng/µL)*—Prepare standards of pesticides and degradates of about 10,000 ng/µL by accurately weighing, to the nearest 0.001 mg, 50 mg of the pure material in a 5-mL volumetric flask and dilute with ethyl acetate. Transfer the stock standards to clean vials and store in a refrigerator at 4°C ± 3°C. The stock standards for most compounds are stable for about 6 months.

7.2 *Primary combined fortification standard (100-ng/µL)*—The stock standard or standards are used to prepare two primary combined fortification standards that contain pesticides and degradates (there are too many analytes to include all parents and degradates in one solution). Alternatively, mixtures of the analytes may be obtained from commercial suppliers. Prepare a 100-ng/µL concentration primary combined fortification standard by combining appropriate volumes of the individual stock standard in a 10- or 5-mL volumetric flask. Use adjustable micropipet (0–50 or 0–100 µL) to dispense an appropriate volume into the volumetric flask and dilute with ethyl acetate. Transfer the primary combined fortification standard to a clean vial and store in a refrigerator. This standard is stable for about 6 months. Alternatively, the primary combined fortification standard can be purchased as a custom mixture from a commercial vendor.

7.3 *Primary recovery standard (1 ng/µL):* Prepare a primary recovery standard by diluting the primary combined fortification standards in 5-mL volumetric flasks with methanol. Store in a refrigerator at 4°C ± 3°C. Add a 100-µL aliquot of this primary recovery standard to a 1-L water sample to obtain a concentration of 0.1 µg/L for the method performance-evaluation studies.

7.4 *Polycyclic aromatic hydrocarbon (PAH) internal standard (1 ng/µL):* Prepare a dilute solution of the PAH internal standard stock at 1 ng/µL with toluene. Transfer the PAH internal standard to a clean vial and store in a refrigerator. This standard is stable for about 6 months when refrigerated. A 100-µL aliquot of this standard is added to every sample extract to quantify analyte concentrations.

7.5 *Surrogate standard (1 ng/µL):* Prepare a standard of diazinon-d_{10} and *alpha*-HCH-d_6 from the stock standard in methanol at a concentration of 1 ng/µL. Store in a refrigerator at 4°C ± 3°C. A 100-µL aliquot of this standard is added to every sample to monitor the extraction and sample preparation process.

7.6 *Calibration standards:* Prepare a series of working calibration standards in toluene that contain all pesticides and degradates at concentrations ranging from 0.01 to 20.0 ng/µL, as well as the surrogate and the PAH internal standard at a constant concentration of 1.0 ng/µL. Prepare these calibration standards by appropriate dilutions of the 100-ng/µL primary combined fortification, and surrogate stock standards in 5- or 10-mL volumetric flasks (refer to table 4). Alternatively, prepare serial dilutions of a 20-ng/µL calibration standard.

8. Gas Chromatograph/Mass Spectrometer Performance

8.1 Gas chromatograph performance evaluation

8.1.1 The gas chromatograph performance normally is indicated by peak shape and by the variation of the selected-compound (pesticide or degradate) response factors relative to response factors obtained by using a new capillary column and freshly prepared calibration standards. An example of the separation and peak shape of the pesticides and degradates is shown in a total ion chromatogram of a 0.625-ng/µL standard (fig. 1). If peak shape deteriorates or if response factors fail to meet the calibration criteria, either change the injection liner or maintain the capillary column to bring the gas chromatograph into compliance. Part of the inlet end of the capillary column can be removed to restore performance. Specifically, a loss or gain in response greater than 30 percent for pesticides and degradates susceptible to loss on injection indicates a need for immediate action.

8.2 Mass spectrometer performance evaluation

8.2.1 Check the mass spectrometer prior to analysis for excessive water and air that would indicate leaks in the vacuum. If detected, locate and fix leaks. Also, check the instrument at the beginning of each series of analyses to ensure mass spectrometer performance according to the perfluorotributylamine (PFTBA) tuning

Table 4. Volumes of primary combined fortification, internal, and surrogate standards needed to prepare suggested concentrations of calibration standards. For comparison, the equivalent concentration of calibration standards in water samples is shown.

[ng/µL, nanogram per microliter; µL, microliter; mL, milliliter; µg/L, microgram per liter]

	Concentration of calibration standards										
Nominal concentration, in ng/µL	0.019	0.039	0.078	0.156	0.312	0.625	1.25	2.5	5.0	10	20
Volume of primary combined fortification standard (100 ng/µL), in µL	1.95	3.9	7.8	15.6	15.6	31.2	62.5	125	250	500	1,000
Volume of stock internal standard (200 ng/µL), in µL	50	50	50	50	25	25	25	25	25	25	25
Volume of stock surrogate standard (100 ng/µL), in µL	100	100	100	100	100	100	100	100	100	100	100
Final volume of calibration standard, in mL	10	10	10	10	5	5	5	5	5	5	5
Equivalent concentration in water sample, in µg/L[1]	0.002	0.004	0.008	0.016	0.031	0.063	0.125	0.250	0.500	1.0	2.0

[1]If the extract volume is about 100 µL, the nominal "on-column" concentration of calibration standards corresponds to actual sample concentrations of 0.002 to 2.0 µg/L.

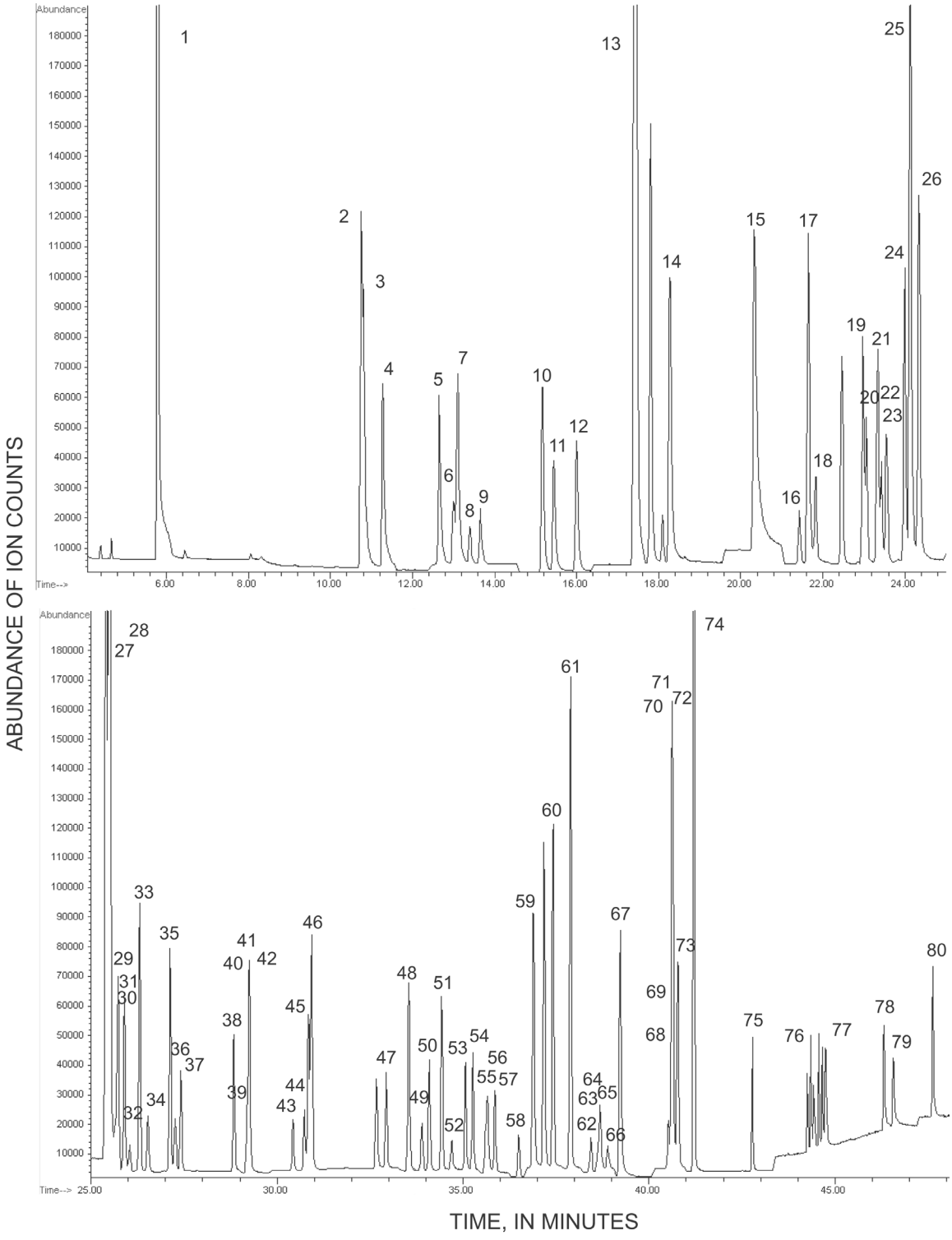

Figure 1. Selected ion chromatogram of pesticides and degradates in a 0.625-nanogram-per-microliter (ng/µL) standard. Numbers shown above each peak correspond to analytes listed in table 5.

criteria outlined in section 8.2.2. In addition, initially adjust the mass spectrometer to ensure that detection at the established reporting-level concentration for each selected compound can be achieved.

8.2.2 Verify the mass spectrometer tune prior to each analysis, and tune if necessary by using the procedure and standard software supplied by the manufacturer. Parameters in the tuning software are set to give ±0.15 atomic mass unit resolution at masses 69, 219, and 414 in the spectrum of PFTBA. Manually adjust the resolution so that the mass 69 ion has 100-percent relative abundance, mass 219 ion is 20- to 60- percent relative abundance, and mass 414 ion is 2- to 7-percent relative abundance. Check mass assignments to ensure accuracy to ±0.15 atomic mass unit and that mass peak widths measured at one-half the peak height are about 0.5±0.15 atomic mass unit. A complete quantitative recalibration with all analytes is needed if the mass spectrometer is re-tuned for mass or resolution.

8.2.3 *Mass spectrometer background interference*—Leaks of atmospheric air into the analyzer, or the presence of other compounds, might compromise instrument performance. Common air background and contaminant ions are 18, 28, 32, 40, and 44 atomic mass units. Check the air background and print the result before beginning an analytical *batch* (the group of samples whose data are evaluated by the quality-control samples associated with them).

9. Calibration

9.1 *Initial calibration:* Eight of the eleven calibration standards listed in table 4 are recommended to calibrate over the expected analytical range of about 2 ng/L to 2 µg/L. The highest level standard selected will depend on the expected upper concentration range of samples.

9.2 Inject 1 µL of each calibration standard into the GC/MS according to the GC/MS conditions described in section 4.3 and tabulate peak area response and concentration for each analyte and corresponding internal standard.

Isomers (*cis*-, *trans*-, Z/E)—Some of the compounds are resolved into two or more isomers, depending on the resolution of the chromatographic column. In the case of *c*- and *t*-methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate, E- and Z-dimethomorph, and *cis*- and *trans*-propiconazole, the peak area of each isomer is used to calibrate independently, quantitate, and report each isomer separately. We assume that the stock standards contain equal amounts of each isomer. Other methods, for example, method 2060, report propiconazole rather than the individual *cis*- and *trans*-isomers, so in situations in which results from the different methods are compared, the sum of the *cis*- and *trans*-isomers should be calculated for comparison. For the pyrethroid compounds cypermethrin and cyfluthrin, which are resolved into 4 isomers, the peak areas for each isomer are summed and used for calibration and quantitation of the compound.

9.3 The GC/MS data-processing software uses standard regression techniques (Miller and Miller, 1993) to construct calibration equations and plot calibration curves for each analyte. The internal standard calibration technique is used, where regression of the area ratios (A_c/A_i) against the concentration ratios (C_c/C_i) is determined for each analyte after analysis of a series of the calibration standards:

where A_C = area of the quantitation ion for the selected compound or surrogate compound;
A_i = area of the quantitation ion for the internal standard;
C_C = concentration of the selected compound or surrogate compound, in nanograms per microliter; and
C_i = concentration of the internal standard, in nanograms per microliter.

The slope of the calibration curve is equivalent to the average response factor (RF_C) of the analyte relative to the internal standard. Zero should be included in the calibration curve, although the curve does not need to be forced through zero.

For most analytes, linear or quadratic regression equations provide the best fit to the data. For linear regression, the equation follows:

$$\frac{A_c}{A_i} = m \times \frac{C_c}{C_i} + b \quad , \qquad (1)$$

where m = slope of the regression equation, and
b = intercept of the regression equation.

Note that the quantitation ratio in equation 1 can be written as a mass ratio:

$$\frac{A_c}{A_i} = m \times \frac{M_c}{M_i} + b \quad , \qquad (2)$$

where M_i = mass of the internal standard, in nanograms; and
M_C = mass of the selected compound or surrogate compound, in nanograms.

The quantitation ion and internal standard used in the calculation are listed in table 5.

9.4 Calculate the relative retention time (RRT_C) for each selected compound or surrogate compound in the calibration solution, as follows:

$$RRT_C = \frac{RT_C}{RT_i} \quad , \qquad (3)$$

where RT_C = uncorrected retention time of the quantitation ion of the selected compound or surrogate compound, and
RT_i = uncorrected retention time of the quantitation ion of the internal standard (acenaphthene-d_{10}, phenanthrene-d_{10}, or chrysene-d_{12}).

9.5 *Verification of initial calibration:* Analyze a solution prepared from standard materials from a source other than those used to prepare the initial calibration curve. Calculate the concentration from the calibration curve. The calculated concentration should be within 20 percent of its true value. This step verifies the validity of the calibration standard materials and the calibration curve prior to sample analysis.

10. Procedure

10.1 *Weighing SPE columns:* Weigh the SPE columns (±0.0001 g) and record the weight on the column with waterproof ink.

NOTE: Recording the weight on the SPE columns helps to determine when the columns are dry after extraction and drying steps.

Table 5. Retention time, quantitation ion, and confirmation ions for analytes, surrogates, and internal standards, and selected ion-monitoring group and internal standard for analytes and surrogates

[Analytes sorted by retention time. No., compound number shown in figure 1; Rank, national pesticide-use rank of analyte; P-Code, National Water Information System parameter code; Approx., approximate; m/z, mass per unit charge; SIM group, selected-ion monitoring group; IS, internal standard used for quantitation: 1, Acenaphthene-d_{10}; 2, Phenanthrene-d_{10}; 3, Chrysene-d_{12}; --, not applicable; –, not analyzed]

No.	Rank	P-Code	Short name	Approx. retention time (min)	Quan-titation ion (m/z)	2d monitored ion (m/z)	3rd monitored ion (m/z)	4th monitored ion (m/z)	SIM group	IS
			Internal Standards							
13	--	--	Acenaphthene-d_{10}	17.419	162	–	–	–	--	1
28	--	--	Phenanthrene-d_{10}	25.484	188	–	–	–	--	2
70	--	--	Chrysene-d_{12}	40.627	240	–	–	–	--	3
			Surrogates							
21	--	99224	*alpha*-HCH-d_6	23.341	224	222	226	–	15	2
33	--	99223	Diazinon-d_{10}, _ogate	26.305	183	153	183	–	15	2
			Analytes							
1	1024	61630	3-Trifluoromet_iline	5.784	161	114	142	160	1	1
2	1002	61620	2-Ethyl-6-meth_iline	10.750	120	121	135	136	2	1
3	1153	38775	Dichlorvos	10.805	109	185	145	187	2	1
4	1015	61633	4-Chloro-2-met_henol	11.275	142	77	107	144	2	1
5	1124	61660	O-Ethyl-O-meth_ioate	12.652	156	124	128	129	4	1
6	1067	61641	Disulfoton sulfoxide	13.014	212	97	125	153	4	1
7	1099	61614	2,5-Dichloroaniline	13.100	161	126	163	165	4	1
8	1044	79842	c-Methyl-3-(2,_ylate	13.409	187	163	165	189	5	1
9	1044	79843	t-Methyl-3-(2,_ylate	13.650	187	163	165	189	5	1
10	1093	61627	3,5-Dichloroaniline	15.162	161	126	163	165	6	1
11	1032	61611	1,4-Naphthaquinone	15.440	158	102	104	130	6	1
12	1033	61625	3,4-Dichloroaniline	15.994	161	126	163	165	6	1
14	1032	49295	1-Naphthol	18.281	144	115	116	–	8	1
15	1002	61615	2-[2-Ethyl-6-m_panol	20.332	162	133	163	193	9	1
16	1034	61666	Phorate oxon	21.435	171	143	156	170	10	2
17	1013	61617	2-Amino-N-isop_amide	21.651	120	119	178	–	10	2
18	128	04031	Cycloate	21.822	154	155	215	–	10	2

Table 5. Retention time, quantitation ion, and confirmation ions for analytes, surrogates, and internal standards, and selected ion-monitoring group and internal standard for analytes and surrogates—Continued

No.	Rank	P-Code	Short name	Approx. rentention time (min)	Quan-titation ion (m/z)	2d monitored ion (m/z)	3rd monitored ion (m/z)	4th monitored ion (m/z)	SIM group	IS
19	83	38454	Dicrotophos	22.979	127	109	193	–	11	2
20	1076	61671	Tefluthrin met_9364]	23.065	181	141	197	–	11	2
22	230	61605	Sulfotepp	23.444	322	193	202	145	11	2
23	1054	61649	Fonofos, oxyge_nalog	23.565	230	93	109	–	11	2
24	1007	61618	2-Chloro-2,6-d_ilide	24.001	176	147	177	–	12	2
25	1105	61634	4-Chlorobenzyl_lfone	24.125	89	125	127	–	12	2
26	28	82662	Dimethoate	24.341	93	87	125	229	12	2
27	1076	61672	Tefluthrin met_2912]	25.401	91	92	197	141	13	2
29	220	04022	Terbuthylazine	25.722	173	138	214	231	14	2
30	229	61604	Propetamphos	25.895	138	194	222	236	14	2
31	1043	61629	3-Phenoxybenzy_cohol	25.895	200	171	181	201	14	2
32	1231	61669	Tebupirimphos,_logue	26.050	245	190	217	260	14	2
34	1014	61664	Paraoxon-methyl	26.520	109	200	230	247	15	2
35	76	61606	Tefluthrin	27.122	177	141	178	197	15	2
36	1071	61642	Endosulfan ether	27.251	170	239	193	277	15	2
37	231	61602	Tebupirimphos	27.411	234	137	152	261	15	2
38	1060	61652	Malaoxon	28.841	127	142	173	195	16	2
39	1062	61637	2-(4-tert-buty_xanol	29.192	135	136	150	248	16	2
40	1049	61663	Paraoxon-ethyl	29.240	109	139	220	275	16	2
41	63	04036	Prometryn	29.256	241	184	226	199	16	2
42	75	61596	Metalaxyl	29.256	206	220	146	160	16	2
43	1016	61674	Terbufos-O-ana_lfone	30.440	183	109	139	184	17	2
44	1012	61636	Chlorpyrifos, _nalog	30.733	197	109	169	199	17	2
45	227	38801	Fenthion	30.854	278	109	125	169	17	2
46	1101	61631	4,4'-Dichlorob_enone	30.923	139	141	250	252	17	2
47	228	61594	Isofenphos	32.942	213	121	185	255	18	3
48	132	61598	Methidathion	33.543	85	93	125	145	19	3
49	71	34362	*alpha*-Endosulfan	33.896	195	159	170	197	19	3
50	1067	61640	Disulfoton sulfone	34.105	213	125	153	157	20	3

Table 5. Retention time, quantitation ion, and confirmation ions for analytes, surrogates, and internal standards, and selected ion-monitoring group and internal standard for analytes and surrogates—Continued

No.	Rank	P-Code	Short name	Approx. rentention time (min)	Quan-titation ion (m/z)	2d monitored ion (m/z)	3rd monitored ion (m/z)	4th monitored ion (m/z)	SIM group	IS
51	225	61592	Flumetralin	34.426	143	145	157	159	20	3
52	126	61591	Fenamiphos	34.687	154	153	217	303	21	3
53	69	61603	Profenofos	35.068	208	97	179	206	21	3
54	30	61610	Tribuphos	35.261	169	170	171	202	21	3
55	121	61599	Myclobutanil	35.610	179	125	181	206	22	3
56	1134	61644	Ethion monoxon	35.851	171	97	125	215	22	3
57	106	61600	Oxyfluorfen	35.867	252	195	300	361	22	3
58	71	34357	*beta*-Endosulfan	36.495	195	159	170	197	23	3
59	1227	61647	Fenthion sulfoxide	36.884	125	109	153	279	24	3
60	134	82346	Ethion	37.429	231	97	125	153	24	3
61	115	38716	Sulprofos	37.887	156	139	140	322	25	3
62	1071	61590	Endosulfan sulfate	38.440	272	229	237	274	26	3
63	108	79846	*cis*-Propiconazole	38.613	173	175	259	261	27	3
64	1125	61668	Phosmet oxon	38.681	160	161	133	268	27	3
65	1008	61665	4-(Hydroxymeth_halin	38.716	268	178	269	297	27	3
66	110	79847	*trans*-Propiconazole	38.888	173	175	259	261	27	3
67	127	04025	Hexazinone	39.226	171	83	128	172	28	3
68	1126	61646	Fenamiphos sulfoxide	40.524	304	122	303	–	29	3
69	1053	61635	Azinphos-methyl-oxon	40.524	132	77	160	–	29	3
71	93	61593	Iprodione	40.644	187	189	244	246	24	3
72	1126	61645	Fenamiphos sulfone	40.747	320	122	292	–	29	3
73	125	61601	Phosmet	40.765	93	77	160	–	29	3
74	131	61580	Bifenthrin	41.209	181	165	166	182	30	3
75	102	61595	Cyhalothrin	42.780	181	141	197	199	31	3
76	129	61585	Cyfluthrin	44.388	163	165	199	226	32	3
77	114	61586	Cypermethrin	44.709	163	165	181	–	32	3
78	211	79844	(E)-Dimethomorph	46.318	301	165	166	303	33	3
79	212	79845	(Z)-Dimethomorph	46.564	301	165	166	303	33	3
80	232	61607	Temephos	47.628	125	203	406	–	34	3

10.2 *Precleaning SPE columns:* Columns are precleaned prior to use by using a vacuum pump (manual procedure) or the Zymark BenchMate II Workstation (automated procedure).

10.2.1 Manual procedure

Preclean the SPE columns by rinsing with 3 mL of the elution solvent (ethyl acetate). Allow the solvent to drain by gravity, then completely remove all solvent from the column by either nitrogen positive pressure or vacuum. Store the cleaned columns in 40-mL glass vials or in a desiccator at room temperature.

10.2.2 Automated procedure

If using the BenchMate II Workstation, place columns on the rack with culture tube and fitting (clean in lots of 100 if possible). Program the workstation to rinse the lines with ethyl acetate, then sequentially pump 3 mL ethyl acetate through each column and dry the column with nitrogen. Store the cleaned columns at room temperature in closed 40-mL glass vials or in a desiccator to minimize sorption of contaminants from the laboratory environment.

10.3 *Precleaning extraction apparatus:* Set up the SPE pumping apparatus. Use a 50-mL glass graduated cylinder to contain the cleaning solutions and prevent contamination of the inlet tubing. Rinse the Teflon-PFA tubing and pump with about 50 mL of detergent solution, followed by about 200 mL of tap water and 50 mL of methanol. Turn on the pump and adjust the flow rate of the pump to between 20 to 25 mL/min by using a graduated cylinder to measure the volume through the SPE column. Ensure that there are no leaks in any of the fittings. Keep the clean inlet tubing of the pump in the clean glass cylinder to avoid contamination of the tubing while preparing the sample and SPE column. For longer storage, wrap the tubing in aluminum foil.

If using the automated AutoTrace procedure, rinse the Teflon-PFA tubing and pump with about 50 mL of cleaning solution of isopropanol: methylene chloride: toluene (7:2:1), followed by about 50 mL of methanol and 100 mL of distilled water.

10.4 *SPE column conditioning:* Immediately before sample extraction, add 3 mL of methanol to the SPE column and allow the methanol to drain partially through the column by gravity. An optional Luer flow-control valve attached to the male Luer fitting of the SPE column can be used to control the flow of fluids through the SPE column. Conditioning is needed to solvate the C-18 phase attached to the silica particles in the SPE column to ensure maximum interaction of the C-18 phase with the sample.

NOTE: Do not allow the columns to go dry once conditioning and equilibration have started. If the fluid level drops below the upper frit of the SPE column, air will enter the SPE column bed and might prevent exposure of the water sample to the SPE C-18 phase. Maintain levels of fluids by adding additional fluid or by closing Luer fittings or flow-control valves. If the column does go dry, repeat the conditioning process with methanol followed by water.

10.5 *SPE column equilibration:* Drain the methanol to the upper frit of the SPE column. Add 3 to 6 mL of pesticide-grade water and allow the water and residual methanol to drain by gravity through the column to the upper frit. About 5 minutes is required for each column volume of the methanol and water to drip through the column.

10.6 *Sample preparation:* Water samples must have been previously filtered (Sandstrom, 1995). Weigh the sample and bottle (W_S) and record the gross sample weight (±1 g). Add methanol to the sample equivalent to 1 percent of the sample volume (about 9 mL) as a conditioner, and record the sample weight (W_m). Add a 100-µL aliquot of the surrogate solution (1 ng/µL; section 7.5) by using a micropipet with a clean disposable glass bore for each sample. (This step should result in a concentration of 0.1 µg/L for the surrogates in a 1-L sample.) Cap and gently swirl the sample in the bottle to mix thoroughly.

NOTE: Allow surrogate and fortified standards to come to room temperature before adding to samples.

10.7 *Sample extraction:* Weigh and record the weight (W_c) of a 1,000-mL plastic beaker (or similar container) that will be used to collect the volume of sample processed through the column. Place the inlet end of the Teflon-PFA tubing into the sample container, making sure that the tubing end is positioned in the lowest spot of the bottle, and turn on the pump. After all air is displaced from the tubing, attach the SPE column to the outlet fitting of the pump tubing, and collect the sample that is pumped through the column. Ensure that there are no leaks or sources of bubbles in the system. Small bubbles might form as the sample is pumped through the tubing, but they will not cause any problems if they accumulate in the pump head. Large air bubbles are a problem because they can displace the methanol conditioner in the column or cause uneven flow.

NOTE: To avoid contaminating the sample, do not handle the outside of the clean section of tubing that is placed in the sample bottle. Wrap the clean tube in aluminum foil, or insert into 0.5-mm ID Teflon-PFA tubing when not in use. A piece of tape attached to the top of the tubing indicates which section of the tubing can be handled and which section is clean and will be in contact with the sample.

Pump the entire sample through the SPE column at a flow rate of between 20 to 25 mL/min, and turn off the pump when completed. Disconnect the column from the pump system, and remove residual interstitial water with a positive air pressure using a syringe with a Luer fitting and short length of silicone tubing to connect the Luer fitting to the open end of the SPE column. Weigh the extracted water sample, and record the final weight (W_a) of the sample processed through the column and the collection container. Discard the extracted sample according to appropriate waste-disposal practices, weigh the empty sample bottle, and record the tare weight (W_b).

10.8 *SPE pump cleaning:* Clean the pump and Teflon-PFA tubing with detergent solution, tap water, and methanol (or other solvent mixture) to prepare for the next sample.

10.9 *SPE column drying:* All SPE columns are dried in the laboratory prior to elution. Attach a universal adapter to the large, open end of the SPE column. Next attach the adapter to the male Luer fitting on the gas-pressure module of the SPE vacuum manifold, and then dry the column using a positive pressure (138 kPa for 20 minutes) of nitrogen to remove all interstitial water. Verify that all water is removed from the column by periodically weighing the column and comparing the weight to the pre-extraction weight. Store dry columns in a desiccator (no longer than 7 days) until elution.

NOTE: Do not dry the column for excessive periods. Pesticides and degradates might evaporate and be removed in the gas phase.

10.10 *Elution of compounds:* Label a 16- by 100-mm culture tube with sample identification and place in a holding rack. Add 100 µL of the PAH internal standard (1 ng/µL; section 7.4) to the culture tube using a micropipet or syringe. Place the dried SPE columns in the appropriate culture tube. The open end of the SPE column should rest on the edge of the culture tube to keep the male Luer end of the SPE column raised a few centimeters above the bottom of the culture tube. Add 2 mL of ethyl acetate to the SPE column, and allow the solvent to drain by gravity into the culture tube (about 15–20 minutes). Air pressure (with a 50-mL glass syringe) can be used to gently force interstitial solvent that remains in the column into the vial.

10.11 *Evaporation of solvent:* Preheat the TurboVap evaporator water bath to 30°C, and adjust the gas pressure to 28 kPa. Place culture tubes in the TurboVap evaporator for about 15 minutes to concentrate the eluant to about 100 µL under a gentle stream of nitrogen. Periodically check the sample volumes. At no time should the eluant be allowed to evaporate completely because this will result in loss of compounds.

10.12 *Transfer to vials:* Use a baked disposable glass Pasteur pipet to withdraw eluant, and transfer eluant to an appropriately labeled GC vial that contains a 400-µL insert for GC/MS analysis.

NOTE: A glass syringe fitted with a short length of silicone tubing to attach the glass Pasteur pipet is the preferred equipment for withdrawing eluant into the pipet. Solvent vapors in contact with rubber or latex pipet bulbs might contaminate the eluant with plasticizers.

Rinse the culture tube with about 150 to 200 µL of toluene using a syringe to dispense the solvent, and take care not to allow the tip of the syringe to contact the walls of the culture tube. If the tip does contact the culture tube, rinse with solvent. Vortex the culture tube, ensuring the solvent reaches the height of the original 2-mL solvent volume. Transfer the toluene rinse into the GC vial insert. A 200- to 300-µL volume of extract should fill about half the volume of the glass insert. Cap the GC vial, and refrigerate until GC/MS analysis is performed.

NOTE: Use of a pipet or squeeze bottle to rinse the culture tube is not good practice because this might result in excess solvent and require additional evaporation to obtain the desired final volume of about 200 to 300 µL.

10.13 *Sample analysis and data evaluation:* Ensure that GC/MS conditions for the analysis of the selected compounds in sample extracts are the same as those used in the analysis of the calibration standards. Prior to the analysis of any sample extracts, ensure that the PFTBA mass-spectral performance criteria have been met, and that the selected-compound calibration data conform to the criteria set forth above. In addition, optimize the system so that the reporting level for each selected compound can be achieved as described in section 8.2. Inject 1 µL of the sample extract, and acquire data using the GC/MS conditions described in sections 4.4 and 9.

11. Calculation of Results

11.1 Qualitative identification

11.1.1 The observed retention time of the GC peak of the quantitation ion for the selected compound of interest needs to be within ±6 seconds of the expected retention time (RT) based on the RRT_C

obtained from the internal-standard analysis (eq. 3). The expected retention time is calculated as follows:

$$RT = RRT_c \times RT_i \quad , \qquad (4)$$

where RT = expected retention time of the selected compound or surrogate compound in the sample;

RRT_c = relative retention time of the selected compound or surrogate compound from the calibration standards; and

RT_i = uncorrected retention time of the quantitation ion of the internal standard in the sample.

11.1.2 Mass-spectral ions are verified for each selected compound by comparing the relative integrated abundance values of the three or four significant ions monitored with the relative integrated abundance values obtained from calibration solutions determined by the GC/MS according to procedures previously given. The relative ratios of the three or four ions need to be within ±20 percent of the relative ratios of those obtained on injection of a 1-ng/mL calibration solution in the absence of any obvious interferences.

11.2 Quantitation

11.2.1 Calculate the weight of sample processed as follows:

$$W = (W_a - W_c) \times \frac{W_s - W_b}{W_m - W_b} \quad , \qquad (5)$$

where W = weight of sample, in grams;

W_a = weight of sample and collection container after SPE, in grams;

W_c = weight of container used to collect sample that passes through SPE column, in grams;

W_s = weight of bottle and sample, in grams;

W_b = weight of empty sample bottle, in grams; and

W_m = weight of sample, methanol, and bottle, in grams.

11.2.2 If a selected compound has passed the aforementioned qualitative identification criteria, the GC/MS data-processing software is used to calculate the total mass of the analyte from the calibration equations determined in section 9.3. For linear regression, the calibration equation is as follows:

$$M_c = \frac{M_i}{m} \times \left(\frac{A_c}{A_i} - b \right) \quad , \qquad (6)$$

where M_c = mass of the selected compound or surrogate compound in the sample, in micrograms;

M_i = mass of the internal standard added to extract, in micrograms;

m = slope of regression equation;

A_c = area of the quantitation ion for the selected compound or surrogate compound identified in the sample;

A_i = area of the quantitation ion for the internal standard in the sample; and

b = intercept of regression equation.

The mass of the internal standard added is calculated as follows:

$$M_i = C_i \times V_i \quad , \qquad (7)$$

where M_i = mass of the internal standard added to extract, in micrograms;

C_i = concentration of the internal standard added to extract, in nanograms per liter; and

V_i = volume of the internal standard (section 7.4) added to extract, in microliters.

The concentration of the analyte in the sample is calculated as follows:

$$C_c = \frac{M_c}{W} \quad , \qquad (8)$$

where C_c = concentration of compound, in micrograms per liter;

M_c = mass of the compound, in mircrograms; and

W = volume of the sample, in liters (assume 1.0 g = 1.0 mL).

11.2.3 The percent recovery of the surrogate compounds is calculated as follows:

$$R = \left[\frac{M_c}{C_S \times V_S} \right] \times 100 \quad , \qquad (9)$$

where R = recovery of the surrogate compound, in percent;

M_c = mass of the surrogate in the sample, in micrograms (from eq. 6);

C_S = concentration of the surrogate compound in the surrogate standard (section 7.5) added to the sample, in micrograms per microliter; and

V_S = volume of the surrogate standard added to the sample, in microliters.

12. Reporting of Results

This method was designed for use in studies of pesticide concentrations in water in a variety of seasons and land-use settings for which the best possible information about the presence and concentration of a pesticide in filtered water is needed. Consequently, results are not censored at a low reporting limit for detected pesticides. Results calculated to be less than the lowest calibration standard (equivalent to 0.002 µg/L in a water sample for most compounds; table 4) are qualified as “estimated” (E) to signify the lower confidence in the extrapolated concentrations.

Concentrations of pesticides are reported to the NWIS data base as follows. If the pesticide is not detected, the result is reported as less than the **laboratory reporting level** (LRL) (for example, <0.002). If the concentration is within the calibration range, the result is reported to three significant figures. If the concentration is less than the LRL or lowest calibration standard, the concentration is reported to two significant figures, and is labelled with the estimated “E” remark to signify the lower confidence in the extrapolated concentration. Similarly, if the concentration is greater than the highest concentration standard, the concentration is reported to two significant figures and the "E" code is used. Other situations in which the “E” qualifier is used

include when the **continuing calibration verification** (CCV) standard is outside of expected limits and the set is not reanalyzed, or any time the analyst feels the quantitation might not be accurate.

FINAL METHOD VALIDATION

Analytes that passed both initial GC/MS and SPE validation experiments were used in additional quantitative validation studies of bias and variability in three water types (pesticide-grade water, surface water, and ground water) at two nominal concentrations (0.10 and 1.0 µg/L), and at a low concentration (0.015 to 0.10 µg/L) to determine initial MDLs. In addition, holding-time experiments on the SPE column and in water were conducted.

A reagent-water sample, a surface-water sample collected from Boulder Creek near 75th Street, Boulder, Colo., and a ground-water sample collected from a monitor well near the wastewater-treatment plant in Denver, Colo., were used to test method performance. The reagent-water sample was split into four sets of eight subsamples each. One set of eight subsamples was fortified with 0.10 µg/L of each parent analyte, and the other set of eight subsamples was fortified with 1.0 µg/L of each parent analyte. The other two sets of eight subsamples were fortified with 0.10 and 1.0 µg/L of each degradate, respectively. Parent pesticides were analyzed separately from degradates to assess formation of degradates during sample processing and analysis.

Each of the surface- and ground-water samples was split into 17 1-L subsamples. One set of eight subsamples was fortified with 0.10 µg/L of each analyte, and the other set of eight subsamples was fortified with 1.0 µg/L of each analyte. In addition, unfortified samples of the surface water and ground water were extracted and analyzed to determine background concentrations of the pesticides. All subsamples were analyzed at the National Water Quality Laboratory using one GC/MS. Each sample set was fortified, extracted, and analyzed on different days during June–July 1999, so comparison of different matrices and concentrations includes bias from day-to-day variation. The surface- and ground-water samples did not require correction for background concentrations of analytes because no analytes were detected in either unfortified sample. Summaries of recovery and variability of the analyses are provided in tables 6 through 9.

The percent recovery of the analytes is calculated as follows:

$$R = \frac{(C_S - C_u)}{C_n} \times 100 \quad , \qquad (10)$$

where R = recovery of the pesticide or pesticide degradate, in percent;

C_S = measured concentration in the fortified sample, in micrograms per liter;

C_u = measured concentration in the unfortified sample, in micrograms per liter (use 0 for reagent-water sample); and

C_n = nominal (theoretical) concentration increase that results from fortifying the sample, in micrograms per liter.

Table 6. Bias and variability data from eight reagent-water samples fortified with parent pesticide analytes at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations

[Analytes are separated into parent pesticides and degradates and sorted by remark code and then by rank. Presence of degradate indicates breakdown of corresponding parent pesticide during sample preparation or analysis. Recovery of degradate based on expected concentration of parent pesticide. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; µg/L, microgram per liter; F-pseu, F-pseudosigma (interquartile range/1.349); Rel F-pseu, relative F-pseudosigma; –, not applicable; --, not analyzed; E, estimated remark code]

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
		Parent pesticides									
63	04036	Prometryn	0.950	0.0379	95.0	4.0	0.0838	0.0034	83.8	4.1	–
69	61603	Profenofos	0.680	0.0184	68.0	2.7	0.0671	0.0035	67.1	5.2	–
71	34362	*alpha*-Endosulfan	0.799	0.0123	79.9	1.5	0.0799	0.0026	79.9	3.2	–
75	61596	Metalaxyl	0.934	0.0426	93.4	4.6	0.0858	0.0033	85.8	3.9	–
106	61600	Oxyfluorfen	0.538	0.0485	53.8	9.0	0.0527	0.0042	52.7	7.9	–
108	79846	*cis*-Propiconazole	0.673	0.0127	67.3	1.9	0.0696	0.0020	69.6	2.8	–
110	79847	*trans*-Propiconazole	0.714	0.0085	71.4	1.2	0.0697	0.0034	69.7	4.8	–
121	61599	Myclobutanil	0.784	0.0136	78.4	1.7	0.0663	0.0033	66.3	5.0	–
126	61591	Fenamiphos	0.572	0.0192	57.2	3.4	0.0724	0.0023	72.4	3.1	–
127	04025	Hexazinone	0.578	0.0261	57.8	4.5	0.0515	0.0013	51.5	2.6	–
128	04031	Cycloate	0.829	0.0155	82.9	1.9	0.0803	0.0029	80.3	3.7	–
132	61598	Methidathion	0.795	0.0189	79.5	2.4	0.0716	0.0018	71.6	2.5	–
134	82346	Ethion	0.627	0.0344	62.7	5.5	0.0503	0.0015	50.3	3.0	–
211	79844	(E)-Dimethomorph	0.698	0.0119	69.8	1.7	0.0811	0.0044	81.1	5.4	–
212	79845	(Z)-Dimethomorph	0.683	0.0136	68.3	2.0	0.0824	0.0032	82.4	3.8	–
220	04022	Terbuthylazine	1.052	0.0568	105.2	5.4	0.1000	0.0044	100.0	4.4	–
225	61592	Flumetralin	0.534	0.0484	53.4	9.1	0.0520	0.0036	52.0	7.0	–
227	38801	Fenthion	0.988	0.0337	98.8	3.4	0.0965	0.0051	96.5	5.3	–
228	61594	Isofenphos	0.849	0.0405	84.9	4.8	0.0759	0.0035	75.9	4.6	–
229	61604	Propetamphos	0.861	0.0524	86.1	6.1	0.0828	0.0025	82.8	3.0	–
231	61602	Tebupirimphos	0.844	0.0448	84.4	5.3	0.0741	0.0033	74.1	4.5	–
28	82662	Dimethoate	0.292	0.0416	29.2	14.3	0.0515	0.0120	51.5	23.3	E
30	61610	Tribuphos	0.400	0.0468	40.0	11.7	0.0328	0.0038	32.8	11.7	E

Table 6. Bias and variability data from eight reagent-water samples fortified with parent pesticide analytes at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
71	34357	*beta*-Endosulfan	0.815	0.0194	81.5	2.4	0.0857	0.0033	85.7	3.8	E
76	61606	Tefluthrin	0.215	0.0367	21.5	17.1	0.0167	0.0022	16.7	13.4	E
83	38454	Dicrotophos	0.135	0.0249	13.5	18.5	0.0147	0.0035	14.7	23.8	E
93	61593	Iprodione	0.608	0.0265	60.8	4.4	0.0455	0.0024	45.5	5.4	E
102	61595	Cyhalothrin	0.194	0.0304	19.4	15.7	0.0091	0.0011	9.1	12.3	E
114	61586	Cypermethrin	0.270	0.0337	27.0	12.5	0.0307	0.0066	30.7	21.6	E
115	38716	Sulprofos	0.719	0.0330	71.9	4.6	0.0596	0.0045	59.6	7.5	E
125	61601	Phosmet[1]	0.586	0.0420	58.6	7.2	--	--	--	--	E
129	61585	Cyfluthrin	0.265	0.0330	26.5	12.5	0.0310	0.0061	31.0	19.7	E
131	61580	Bifenthrin	0.262	0.0555	26.2	21.2	0.0132	0.0023	13.2	17.2	E
230	61605	Sulfotepp	0.960	0.0293	96.0	3.0	0.0851	0.0023	85.1	2.8	E
232	61607	Temephos	0.283	0.0499	28.3	17.7	0.0371	0.0040	37.1	10.7	E
		Degradates									
1002	61615	2-[2-Ethyl-6-m_panol	--	--	--	--	--	--	--	--	–
1007	61618	2-Chloro-2,6-d_ilide	--	--	--	--	--	--	--	--	–
1008	61665	4-(Hydroxymeth_halin	--	--	--	--	--	--	--	--	–
1016	61674	Terbufos-O-ana_lfone	--	--	--	--	--	--	--	--	–
1033	61625	3,4-Dichloroaniline	--	--	--	--	--	--	--	--	–
1043	61629	3-Phenoxybenzy_cohol	--	--	--	--	--	--	--	--	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.015	0.0016	1.5	10.6	0.0057	0.0009	5.7	16.3	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.010	0.0007	1.0	7.5	0.0070	0.0003	7.0	3.7	–
1049	61663	Paraoxon-ethyl	--	--	--	--	--	--	--	--	–
1060	61652	Malaoxon	--	--	--	--	--	--	--	--	–
1062	61637	2-(4-tert-buty_xanol	--	--	--	--	--	--	--	--	–
1067	61640	Disulfoton sulfone	--	--	--	--	--	--	--	--	–
1067	61641	Disulfoton sulfoxide	--	--	--	--	--	--	--	--	–
1071	61590	Endosulfan sulfate	--	--	--	--	--	--	--	--	–
1071	61642	Endosulfan ether	0.007	0.0011	0.7	15.8	0.0033	0.0007	3.3	21.1	–
1076	61672	Tefluthrin met_2912]	--	--	--	--	--	--	--	--	–

Table 6. Bias and variability data from eight reagent-water samples fortified with parent pesticide analytes at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
1093	61627	3,5-Dichloroaniline	--	--	--	--	--	--	--	--	–
1099	61614	2,5-Dichloroaniline	--	--	--	--	--	--	--	--	–
1124	61660	O-Ethyl-O-meth_ioate	--	--	--	--	0.0029	0.0003	2.9	10.0	–
1126	61645	Fenamiphos sulfone	--	--	--	--	--	--	--	--	–
1231	61669	Tebupirimphos,_logue	--	--	--	--	--	--	--	--	–
1002	61620	2-Ethyl-6-meth_iline	--	--	--	--	--	--	--	--	E
1012	61636	Chlorpyrifos, _nalog	--	--	--	--	--	--	--	--	E
1013	61617	2-Amino-N-isop_amide	--	--	--	--	--	--	--	--	E
1014	61664	Paraoxon-methyl	--	--	--	--	--	--	--	--	E
1015	61633	4-Chloro-2-met_henol	--	--	--	--	--	--	--	--	E
1024	61630	3-Trifluoromet_iline	--	--	--	--	--	--	--	--	E
1032	49295	1-Naphthol	--	--	--	--	--	--	--	--	E
1032	61611	1,4-Naphthaquinone	--	--	--	--			--	--	E
1034	61666	Phorate oxon	--	--	--	--	--	--	--	--	E
1053	61635	Azinphos-methyl-oxon	--	--	--	--	--	--	--	--	E
1054	61649	Fonofos, oxyge_nalog	--	--	--	--	--	--	--	--	E
1076	61671	Tefluthrin met_9364]	--	--	--	--	--	--	--	--	E
1101	61631	4,4'-Dichlorob_enone	--	--	--	--	--	--	--	--	E
1105	61634	4-Chlorobenzyl_lfone	--	--	--	--	--	--	--	--	E
1125	61668	Phosmet oxon	--	--	--	--	--	--	--	--	E
1126	61646	Fenamiphos sulfoxide	--	--	--	--	--	--	--	--	E
1134	61644	Ethion monoxon	--	--	--	--	0.0101	0.0009	10.1	9.3	E
1153	38775	Dichlorvos	--	--	--	--	--	--	--	--	E
1227	61647	Fenthion sulfoxide	0.014	0.0009	1.4	6.2	0.0048	0.0011	4.8	22.8	E
		Surrogates	--	--	--	--	--	--	--	--	–
	99223	Diazinon-d_{10}, _ogate	0.755	0.0169	75.5	2.2	0.0996	0.0021	99.6	2.1	–
	99224	*alpha*-HCH-d_6, _ogate	0.953	0.0457	95.3	4.8	0.0859	0.0033	85.9	3.8	–

[1]Phosmet was not included in low concentration recovery experiments.

Table 7. Bias and variability data from eight reagent-water samples fortified with degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations

[Analytes are sorted by remark code and then by rank. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; Median conc., median observed concentration; µg/L, microgram per liter; F-pseu, F-pseudosigma (interquartile range/1.349); Rel F-pseu, relative F-pseudosigma; –, not applicable; E, estimated remark code]

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
		Degradates									
1002	61615	2-[2-Ethyl-6-m_panol	1.009	0.0988	100.9	9.8	0.0808	0.0053	80.8	6.6	–
1007	61618	2-Chloro-2,6-d_ilide	1.054	0.0439	105.4	4.2	0.0938	0.0018	93.8	1.9	–
1008	61665	4-(Hydroxymeth_halin	1.051	0.1364	105.1	13.0	0.0834	0.0077	83.4	9.3	–
1016	61674	Terbufos-O-ana_lfone	0.954	0.0797	95.4	8.4	0.0774	0.0071	77.4	9.1	–
1033	61625	3,4-Dichloroaniline	0.947	0.1165	94.7	12.3	0.0863	0.0084	86.3	9.7	–
1043	61629	3-Phenoxybenzy_cohol	1.132	0.0972	113.2	8.6	0.0718	0.0024	71.8	3.3	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.862	0.0574	86.2	6.7	0.0846	0.0028	84.6	3.3	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.927	0.0512	92.7	5.5	0.0891	0.0040	89.1	4.5	–
1049	61663	Paraoxon-ethyl [1]	1.198	0.3089	119.8	25.8	0.0872	0.0028	87.2	3.3	–
1060	61652	Malaoxon	1.009	0.0727	100.9	7.2	0.0919	0.0052	91.9	5.7	–
1062	61637	2-(4-tert-buty_xanol	1.060	0.0547	106.0	5.2	0.0800	0.0057	80.0	7.1	–
1067	61640	Disulfoton sulfone	0.923	0.0734	92.3	8.0	0.0783	0.0033	78.3	4.2	–
1071	61590	Endosulfan sulfate [1]	0.865	0.0209	86.5	2.4	0.0919	0.0032	91.9	3.5	–
1071	61642	Endosulfan ether	1.088	0.0430	108.8	4.0	0.1018	0.0027	101.8	2.6	–
1076	61672	Tefluthrin met_2912]	0.653	0.0898	65.3	13.7	0.0601	0.0024	60.1	4.0	–
1093	61627	3,5-Dichloroaniline	1.081	0.1030	108.1	9.5	0.0965	0.0064	96.5	6.6	–
1099	61614	2,5-Dichloroaniline	0.986	0.1050	98.6	10.7	0.0856	0.0050	85.6	5.9	–
1124	61660	O-Ethyl-O-meth_ioate	0.954	0.0856	95.4	9.0	0.0852	0.0047	85.2	5.6	–
1126	61645	Fenamiphos sulfone	0.861	0.1068	86.1	12.4	0.0637	0.0053	63.7	8.3	–
1231	61669	Tebupirimphos,_logue	0.900	0.0719	90.0	8.0	0.0722	0.0025	72.2	3.5	–
1002	61620	2-Ethyl-6-meth_iline	1.090	0.0788	109.0	7.2	0.1014	0.0019	101.4	1.9	E
1012	61636	Chlorpyrifos, _nalog	0.282	0.0466	28.2	16.5	0.0176	0.0051	17.6	28.7	E
1013	61617	2-Amino-N-isop_amide	0.675	0.0681	67.5	10.1	0.0589	0.0088	58.9	15.0	E
1014	61664	Paraoxon-methyl	0.852	0.0909	85.2	10.7	0.0695	0.0022	69.5	3.2	E

Table 7. Bias and variability data from eight reagent-water samples fortified with degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
1015	61633	4-Chloro-2-met_henol	0.817	0.1319	81.7	16.1	0.0721	0.0098	72.1	13.7	E
1024	61630	3-Trifluoromet_iline	0.451	0.1181	45.1	26.2	0.0407	0.0030	40.7	7.5	E
1032	49295	1-Naphthol	0.136	0.0542	13.6	39.9	0.0255	0.0103	25.5	40.4	E
1032	61611	1,4-Naphthaquinone	0.211	0.1189	21.1	56.2	0.0335	0.0104	33.5	31.0	E
1034	61666	Phorate oxon	0.879	0.1341	87.9	15.2	0.0727	0.0059	72.7	8.1	E
1053	61635	Azinphos-methyl-oxon	0.919	0.0993	91.9	10.8	0.0575	0.0115	57.5	19.9	E
1054	61649	Fonofos, oxyge_nalog	0.839	0.0861	83.9	10.3	0.0709	0.0019	70.9	2.7	E
1067	61641	Disulfoton sulfoxide	1.417	0.0640	141.7	4.5	0.1318	0.0070	131.8	5.3	E
1076	61671	Tefluthrin met_9364]	0.491	0.0892	49.1	18.2	0.0451	0.0034	45.1	7.6	E
1101	61631	4,4'-Dichlorob_enone	0.900	0.0763	90.0	8.5	0.0697	0.0026	69.7	3.8	E
1105	61634	4-Chlorobenzyl_lfone	0.681	0.0671	68.1	9.8	0.0654	0.0073	65.4	11.2	E
1125	61668	Phosmet oxon	0.771	0.0593	77.1	7.7	0.0294	0.0102	29.4	34.8	E
1126	61646	Fenamiphos sulfoxide	0.197	0.0277	19.7	14.0	0.0251	0.0029	25.1	11.4	E
1134	61644	Ethion monoxon	0.645	0.0837	64.5	13.0	0.0452	0.0022	45.2	4.8	E
1153	38775	Dichlorvos[1]	0.673	0.0752	67.3	11.2	0.0803	0.0041	80.3	5.1	E
1227	61647	Fenthion sulfoxide	0.823	0.1058	82.3	12.9	0.0785	0.0035	78.5	4.5	E
		Surrogates									
	99223	Diazinon-d_{10}, _ogate	1.472	0.0466	147.2	3.2	0.1083	0.0051	108.3	4.7	–
	99224	*alpha*-HCH-d_6, _ogate	0.613	0.0487	61.3	7.9	0.0596	0.0028	59.6	4.7	–

[1]Analyte was determined in parent fortification mixture.

Table 8. Bias and variability data from eight surface-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations

[Analytes are separated into parent pesticides and degradate pesticides and sorted by remark code and then by rank. Surface water collected from Boulder Creek at 75th Street on June 3, 1999. Analysis of unfortified sample indicated no analytes greater than reporting levels. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; F-pseu, F-pseudosigma (interquartile range/1.349); Rel F-pseu, relative F-pseudosigma; µg/L, microgram per liter; –, not applicable; --, not analyzed; E, estimated remark code]

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
		Parent pesticides									
63	04036	Prometryn	0.410	0.3697	41.0	90.2	0.0786	0.0040	78.6	4.0	–
69	61603	Profenofos	0.768	0.0358	76.8	4.7	0.1041	0.0063	104.1	6.3	–
71	34362	*alpha*-Endosulfan	0.796	0.0199	79.6	2.5	0.0962	0.0117	96.2	11.7	–
75	61596	Metalaxyl	0.952	0.0414	95.2	4.3	0.0910	0.0040	91.0	4.0	–
106	61600	Oxyfluorfen	0.675	0.0839	67.5	12.4	0.0927	0.0086	92.7	8.6	–
108	79846	*cis*-Propiconazole	0.239	0.2567	23.9	107.4	0.1063	0.0068	106.3	6.8	–
110	79847	*trans*-Propiconazole	0.470	0.2901	47.0	61.7	0.1089	0.0047	108.9	4.7	–
121	61599	Myclobutanil	0.798	0.0358	79.8	4.5	0.1034	0.0031	103.4	3.1	–
126	61591	Fenamiphos	0.796	0.0404	79.6	5.1	0.1024	0.0051	102.4	5.1	–
127	04025	Hexazinone	0.615	0.0818	61.5	13.3	0.0981	0.0030	98.1	3.0	–
128	04031	Cycloate	0.844	0.0598	84.4	7.1	0.1045	0.0069	104.5	6.9	–
132	61598	Methidathion	0.849	0.0496	84.9	5.8	0.1102	0.0038	110.2	3.8	–
134	82346	Ethion	0.496	0.0193	49.6	3.9	0.0800	0.0045	80.0	4.5	–
211	79844	(E)-Dimethomorph	0.846	0.0412	84.6	4.9	0.1026	0.0043	102.6	4.3	–
212	79845	(Z)-Dimethomorph	0.838	0.0248	83.8	3.0	0.1091	0.0060	109.1	6.0	–
220	04022	Terbuthylazine[1]	--	--	--	--	--	--	--	--	–
225	61592	Flumetralin	0.499	0.0939	49.9	18.8	0.0918	0.0056	91.8	5.6	–
227	38801	Fenthion	0.934	0.0501	93.4	5.4	0.0697	0.0042	69.7	4.2	–
228	61594	Isofenphos	0.883	0.0426	88.3	4.8	0.0921	0.0043	92.1	4.3	–
229	61604	Propetamphos	0.863	0.0396	86.3	4.6	0.0966	0.0072	96.6	7.2	–
231	61602	Tebupirimphos	0.767	0.0219	76.7	2.9	0.0802	0.0049	80.2	4.9	–
28	82662	Dimethoate	0.450	0.0715	45.0	15.9	0.0413	0.0011	41.3	1.1	E
30	61610	Tribuphos	0.451	0.0265	45.1	5.9	0.0825	0.0041	82.5	4.1	E
71	34357	*beta*-Endosulfan	0.703	0.0362	70.3	5.1	0.1047	0.0071	104.7	7.1	E
76	61606	Tefluthrin	0.173	0.0135	17.3	7.8	0.0414	0.0038	41.4	3.8	E

Table 8. Bias and variability data from eight surface-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
83	38454	Dicrotophos	0.164	0.0548	16.4	33.5	0.0338	0.0026	33.8	2.6	E
93	61593	Iprodione	0.690	0.0239	69.0	3.5	0.1116	0.0117	111.6	11.7	E
102	61595	Cyhalothrin	0.160	0.0170	16.0	10.6	0.0454	0.0037	45.4	3.7	E
114	61586	Cypermethrin	0.223	0.0195	22.3	8.7	0.0787	0.0093	78.7	9.3	E
115	38716	Sulprofos	0.476	0.0343	47.6	7.2	0.0792	0.0046	79.2	4.6	E
125	61601	Phosmet	0.622	0.0490	62.2	7.9	0.1058	0.0035	105.8	3.5	E
129	61585	Cyfluthrin	0.214	0.0092	21.4	4.3	0.0773	0.0026	77.3	2.6	E
131	61580	Bifenthrin	0.144	0.0108	14.4	7.5	0.0506	0.0041	50.6	4.1	E
230	61605	Sulfotepp	0.734	0.0380	73.4	5.2	0.0651	0.0053	65.1	5.3	E
232	61607	Temephos	0.217	0.0146	21.7	6.7	0.1425	0.0097	142.5	9.7	E
		Degradates									
1002	61615	2-[2-Ethyl-6-m_panol	0.871	0.0335	87.1	3.8	0.1055	0.0087	105.5	8.7	–
1007	61618	2-Chloro-2,6-d_ilide	0.903	0.0638	90.3	7.1	0.0980	0.0052	98.0	5.2	–
1008	61665	4-(Hydroxymeth_halin	0.993	0.0161	99.3	1.6	0.1329	0.0097	132.9	9.7	–
1016	61674	Terbufos-O-ana_lfone	0.861	0.0410	86.1	4.8	0.0923	0.0053	92.3	5.3	–
1033	61625	3,4-Dichloroaniline	0.926	0.0359	92.6	3.9	0.0765	0.0023	76.5	2.3	–
1043	61629	3-Phenoxybenzy_cohol	0.827	0.0430	82.7	5.2	0.0896	0.0073	89.6	7.3	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.788	0.0185	78.8	2.4	0.0955	0.0054	95.5	5.4	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.805	0.0239	80.5	3.0	0.0905	0.0074	90.5	7.4	–
1049	61663	Paraoxon-ethyl	0.922	0.0337	92.2	3.7	0.1012	0.0074	101.2	7.4	–
1060	61652	Malaoxon	0.873	0.0345	87.3	3.9	0.1064	0.0071	106.4	7.1	–
1062	61637	2-(4-tert-buty_xanol	0.864	0.0433	86.4	5.0	0.1042	0.0087	104.2	8.7	–
1067	61640	Disulfoton sulfone	0.869	0.0416	86.9	4.8	0.1045	0.0035	104.5	3.5	–
1071	61590	Endosulfan sulfate	0.761	0.0237	76.1	3.1	0.0915	0.0079	91.5	7.9	–
1071	61642	Endosulfan ether	0.826	0.0264	82.6	3.2	0.0805	0.0052	80.5	5.2	–
1076	61672	Tefluthrin met_2912]	0.327	0.0363	32.7	11.1	0.0675	0.0068	67.5	6.8	–
1093	61627	3,5-Dichloroaniline	0.923	0.0276	92.3	3.0	0.0913	0.0051	91.3	5.1	–
1099	61614	2,5-Dichloroaniline	0.841	0.0154	84.1	1.8	0.0819	0.0043	81.9	4.3	–
1124	61660	O-Ethyl-O-meth_ioate	0.856	0.0298	85.6	3.5	0.0978	0.0058	97.8	5.8	–
1126	61645	Fenamiphos sulfone	0.788	0.0353	78.8	4.5	0.0955	0.0047	95.5	4.7	–

Table 8. Bias and variability data from eight surface-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
1231	61669	Tebupirimphos,_logue	0.832	0.0376	83.2	4.5	0.0766	0.0051	76.6	5.1	–
1002	61620	2-Ethyl-6-meth_iline	0.786	0.0422	78.6	5.4	0.1170	0.0049	117.0	4.9	E
1012	61636	Chlorpyrifos, _nalog	0.780	0.0296	78.0	3.8	0.0496	0.0032	49.6	3.2	E
1013	61617	2-Amino-N-isop_amide	0.689	0.0878	68.9	12.8	0.0476	0.0019	47.6	1.9	E
1014	61664	Paraoxon-methyl	0.884	0.0501	88.4	5.7	0.1047	0.0032	104.7	3.2	E
1015	61633	4-Chloro-2-met_henol	0.814	0.0515	81.4	6.3	0.0693	0.0034	69.3	3.4	E
1024	61630	3-Trifluoromet_iline	0.733	0.0928	73.3	12.7	0.0432	0.0011	43.2	1.1	E
1032	49295	1-Naphthol[1]	--	--	--	--	--	--	--	--	E
1032	61611	1,4-Naphthaquinone[1]	--	--	--	--	0.0733	0.0042	73.3	4.2	E
1034	61666	Phorate oxon	0.862	0.0463	86.2	5.4	0.0848	0.0049	84.8	4.9	E
1053	61635	Azinphos-methyl-oxon	0.875	0.0470	87.5	5.4	0.1316	0.0004	131.6	0.4	E
1054	61649	Fonofos, oxyge_nalog	0.774	0.0463	77.4	6.0	0.0922	0.0065	92.2	6.5	E
1067	61641	Disulfoton sulfoxide	0.966	0.0507	96.6	5.3	0.1051	0.0069	105.1	6.9	E
1076	61671	Tefluthrin met_9364]	0.217	0.0143	21.7	6.6	0.0404	0.0052	40.4	5.2	E
1101	61631	4,4'-Dichlorob_enone	0.858	0.0305	85.8	3.6	0.1035	0.0079	103.5	7.9	E
1105	61634	4-Chlorobenzyl_lfone	0.684	0.0919	68.4	13.4	0.0538	0.0040	53.8	4.0	E
1125	61668	Phosmet oxon	0.601	0.0504	60.1	8.4	0.1188	0.0021	118.8	2.1	E
1126	61646	Fenamiphos sulfoxide[1]	--	--	--	--	0.0552	0.0120	55.2	12.0	E
1134	61644	Ethion monoxon	0.771	0.0296	77.1	3.8	0.1007	0.0045	100.7	4.5	E
1153	38775	Dichlorvos	0.638	0.0349	63.8	5.5	0.0444	0.0023	44.4	2.3	E
1227	61647	Fenthion sulfoxide	0.775	0.0336	77.5	4.3	0.0965	0.0038	96.5	3.8	E
		Surrogates									
	99223	Diazinon-d_{10}, _ogate	1.209	0.0290	120.9	2.4	0.0781	0.0023	78.1	2.3	–
	99224	*alpha*-HCH-d_6, _ogate	0.865	0.1916	86.5	22.1	0.0980	0.0047	98.0	4.7	–

[1]Terbuthylazine, 1-naphthol, 1,4-naphthaquinone, and fenamiphos sulfoxide not included in fortification mixture.

Table 9. Bias and variability data from eight ground-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations

[Analytes are separated into parent pesticides and degradate pesticides and sorted by remark code and then by rank. Ground water collected in northeast Denver on June 3, 1999. Analysis of unfortified sample indicated no analytes greater than reporting limits. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; µg/L, microgram per liter; F-pseu, F-pseudosigma (interquartile range/1.349); Rel F-pseu, relative F-pseudosigma; –, not applicable; --, not analyzed; E, estimated remark code]

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
		Parent pesticides									
63	04036	Prometryn	1.010	0.031	101.0	3.1	0.0821	0.0057	82.1	6.9	–
69	61603	Profenofos	0.782	0.037	78.2	4.8	0.0926	0.0086	92.6	9.3	–
71	34362	*alpha*-Endosulfan	0.818	0.034	81.8	4.2	0.0951	0.0056	95.1	5.9	–
75	61596	Metalaxyl	0.952	0.027	95.2	2.9	0.0910	0.0047	91.0	5.2	–
106	61600	Oxyfluorfen	0.849	0.038	84.9	4.5	0.0917	0.0051	91.7	5.6	–
108	79846	*cis*-Propiconazole	0.604	0.016	60.4	2.6	0.1144	0.0076	114.4	6.7	–
110	79847	*trans*-Propiconazole	0.877	0.034	87.7	3.8	0.1102	0.0109	110.2	9.9	–
121	61599	Myclobutanil	0.881	0.029	88.1	3.3	0.1069	0.0040	106.9	3.7	–
126	61591	Fenamiphos	0.771	0.024	77.1	3.2	0.1048	0.0098	104.8	9.4	–
127	04025	Hexazinone	0.645	0.026	64.5	4.1	0.0902	0.0103	90.2	11.4	–
128	04031	Cycloate	0.942	0.070	94.2	7.4	0.0950	0.0056	95.0	5.9	–
132	61598	Methidathion	0.848	0.012	84.8	1.5	0.1033	0.0055	103.3	5.3	–
134	82346	Ethion	0.637	0.047	63.7	7.3	0.0850	0.0042	85.0	4.9	–
211	79844	(E)-Dimethomorph	0.851	0.031	85.1	3.6	0.0958	0.0042	95.8	4.3	–
212	79845	(Z)-Dimethomorph	0.844	0.032	84.4	3.8	0.1006	0.0041	100.6	4.1	–
220	04022	Terbuthylazine[1]	--	--	--	--	--	--	--	--	–
225	61592	Flumetralin	0.973	0.092	97.3	9.5	0.0949	0.0062	94.9	6.6	–
227	38801	Fenthion	0.993	0.022	99.3	2.2	0.0789	0.0050	78.9	6.3	–
228	61594	Isofenphos	0.948	0.033	94.8	3.4	0.0918	0.0043	91.8	4.7	–
229	61604	Propetamphos	0.876	0.032	87.6	3.7	0.0908	0.0040	90.8	4.4	–
231	61602	Tebupirimphos	0.841	0.025	84.1	3.0	0.0787	0.0050	78.7	6.3	–
28	82662	Dimethoate	0.328	0.007	32.8	2.1	0.0447	0.0033	44.7	7.4	E
30	61610	Tribuphos	0.541	0.057	54.1	10.5	0.0842	0.0089	84.2	10.6	E
71	34357	*beta*-Endosulfan	0.775	0.043	77.5	5.5	0.0982	0.0125	98.2	12.7	E
76	61606	Tefluthrin	0.339	0.041	33.9	12.2	0.0461	0.0051	46.1	11.1	E

Table 9. Bias and variability data from eight ground-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
83	38454	Dicrotophos	0.147	0.011	14.7	7.4	0.0186	0.0052	18.6	28.3	E
93	61593	Iprodione	0.708	0.049	70.8	6.9	0.1051	0.0128	105.1	12.2	E
102	61595	Cyhalothrin	0.361	0.034	36.1	9.4	0.0479	0.0050	47.9	10.5	E
114	61586	Cypermethrin	0.435	0.033	43.5	7.6	0.0767	0.0067	76.7	8.8	E
115	38716	Sulprofos	0.622	0.047	62.2	7.5	0.1014	0.0079	101.4	7.8	E
125	61601	Phosmet	0.771	0.035	77.1	4.6	0.0869	0.0074	86.9	8.6	E
129	61585	Cyfluthrin	0.415	0.035	41.5	8.5	0.0749	0.0032	74.9	4.3	E
131	61580	Bifenthrin	0.373	0.041	37.3	11.0	0.0575	0.0055	57.5	9.6	E
230	61605	Sulfotepp	0.844	0.019	84.4	2.3	0.0783	0.0067	78.3	8.5	E
232	61607	Temephos	0.471	0.026	47.1	5.5	0.1296	0.0101	129.6	7.8	E
		Degradates									
1002	61615	2-[2-Ethyl-6-m_panol	0.838	0.016	83.8	2.0	0.1030	0.0049	103.0	4.8	–
1007	61618	2-Chloro-2,6-d_ilide	0.837	0.072	83.7	8.6	0.0934	0.0067	93.4	7.1	–
1008	61665	4-(Hydroxymeth_halin	0.993	0.010	99.3	1.0	0.1159	0.0055	115.9	4.8	–
1016	61674	Terbufos-O-ana_lfone	0.820	0.016	82.0	1.9	0.0879	0.0108	87.9	12.3	–
1033	61625	3,4-Dichloroaniline	0.836	0.020	83.6	2.4	0.0853	0.0046	85.3	5.4	–
1043	61629	3-Phenoxybenzy_cohol	0.804	0.019	80.4	2.3	0.0848	0.0059	84.8	6.9	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.834	0.017	83.4	2.0	0.0893	0.0063	89.3	7.1	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.832	0.018	83.2	2.2	0.0891	0.0078	89.1	8.7	–
1049	61663	Paraoxon-ethyl	0.908	0.033	90.8	3.7	0.0894	0.0114	89.4	12.8	–
1060	61652	Malaoxon	0.809	0.023	80.9	2.9	0.0933	0.0089	93.3	9.5	–
1062	61637	2-(4-tert-buty_xanol	0.875	0.027	87.5	3.1	0.0915	0.0081	91.5	8.9	–
1067	61640	Disulfoton sulfone	0.850	0.024	85.0	2.8	0.1059	0.0062	105.9	5.8	–
1071	61590	Endosulfan sulfate	0.809	0.036	80.9	4.4	0.0892	0.0045	89.2	5.1	–
1071	61642	Endosulfan ether	0.846	0.023	84.6	2.7	0.0794	0.0055	79.4	6.9	–
1076	61672	Tefluthrin met_2912]	0.500	0.028	50.0	5.5	0.0641	0.0048	64.1	7.5	–
1093	61627	3,5-Dichloroaniline	0.881	0.030	88.1	3.4	0.0919	0.0067	91.9	7.3	–
1099	61614	2,5-Dichloroaniline	0.725	0.031	72.5	4.3	0.0810	0.0060	81.0	7.4	–
1124	61660	O-Ethyl-O-meth_ioate	0.807	0.024	80.7	2.9	0.0889	0.0065	88.9	7.3	–
1126	61645	Fenamiphos sulfone	0.813	0.008	81.3	1.0	0.0886	0.0048	88.6	5.4	–

Table 9. Bias and variability data from eight ground-water samples fortified with parent pesticides and degradates at high (1.0 microgram per liter) and low (0.1 microgram per liter) concentrations—Continued

Rank	P-Code	Short name	High				Low				Remark code
			Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	
1231	61669	Tebupirimphos,_logue	0.840	0.018	84.0	2.1	0.0739	0.0061	73.9	8.2	–
1002	61620	2-Ethyl-6-meth_iline	0.772	0.008	77.2	1.0	0.1034	0.0082	103.4	8.0	E
1012	61636	Chlorpyrifos, _nalog	0.662	0.072	66.2	10.9	0.0440	0.0088	44.0	19.9	E
1013	61617	2-Amino-N-isop_amide	0.548	0.010	54.8	1.8	0.0588	0.0031	58.8	5.2	E
1014	61664	Paraoxon-methyl	0.817	0.058	81.7	7.1	0.0844	0.0086	84.4	10.2	E
1015	61633	4-Chloro-2-met_henol	0.619	0.017	61.9	2.7	0.0681	0.0049	68.1	7.3	E
1024	61630	3-Trifluoromet_iline	0.466	0.023	46.6	4.9	0.0518	0.0033	51.8	6.3	E
1032	49295	1-Naphthol	0.341	0.083	34.1	24.4	0.0063	0.0018	6.3	28.9	E
1032	61611	1,4-Naphthaquinone[1]	--	--	--	--	0.0781	0.0065	78.1	8.3	E
1034	61666	Phorate oxon	0.842	0.016	84.2	1.9	0.0802	0.0079	80.2	9.8	E
1053	61635	Azinphos-methyl-oxon	0.810	0.039	81.0	4.8	0.1258	0.0058	125.8	4.6	E
1054	61649	Fonofos, oxyge_nalog	0.694	0.038	69.4	5.5	0.0776	0.0067	77.6	8.6	E
1067	61641	Disulfoton sulfoxide	0.960	0.029	96.0	3.0	0.0996	0.0056	99.6	5.6	E
1076	61671	Tefluthrin met_9364]	0.394	0.044	39.4	11.2	0.0432	0.0046	43.2	10.7	E
1101	61631	4,4'-Dichlorob_enone	0.844	0.038	84.4	4.5	0.0928	0.0073	92.8	7.9	E
1105	61634	4-Chlorobenzyl_lfone	0.506	0.006	50.6	1.1	0.0552	0.0023	55.2	4.2	E
1125	61668	Phosmet oxon	0.735	0.034	73.5	4.7	0.0999	0.0083	99.9	8.3	E
1126	61646	Fenamiphos sulfoxide[1]	--	--	--	--	0.0174	0.0010	17.4	5.9	E
1134	61644	Ethion monoxon	0.811	0.034	81.1	4.2	0.1002	0.0043	100.2	4.3	E
1153	38775	Dichlorvos	0.451	0.040	45.1	8.8	0.0312	0.0083	31.2	26.5	E
1227	61647	Fenthion sulfoxide	0.750	0.022	75.0	3.0	0.0850	0.0061	85.0	7.2	E
		Surrogates									
	99223	Diazinon-d_{10}, _ogate	1.238	0.028	123.8	2.3	0.0750	0.0030	75.0	4.0	–
	99224	*alpha*-HCH-d_6, _ogate	1.036	0.280	103.6	27.0	0.0941	0.0058	94.1	6.1	–

[1]Terbuthylazine, 1,4-naphthaquinone, and fenamiphos sulfoxide not included in fortification mixture.

Method Detection Limits

Short-term method detection limits (MDLs) for pesticides and pesticide degradates were estimated by determining the analytes in eight reagent-water samples fortified at concentrations of 0.015 µg/L for most analytes. The MDLs usually are calculated as about three standard deviations of the mean concentration (U.S. Environmental Protection Agency, 1997). For this report, the F-pseudosigma rather than the standard deviation was used to calculate the MDLs.

$$MDL = F \times t_{(n-1,\,1-\alpha=0.99)} \quad , \qquad (11)$$

where F = F-pseudosigma of replicate analyses, in micrograms per liter;
n = number of replicate samples;
t = Student's t-value for a one-tailed test appropriate for the 99-percent confidence level ($1-\alpha = 0.99$) with n-1 degrees of freedom; and
α = level of significance.

For eight replicates and a 99-percent confidence level, the value of t is 2.998. The phrase, short-term MDL, is used to differentiate these one-time and one-analytical-instrument estimates from long-term MDLs (LT–MDLs) determined over a longer time and that use results from different analytical instruments (Childress and others, 1999). Exercise caution in interpreting these MDLs and the preliminary LRLs because they are based on short-term studies, and for some of the analytes, the fortification level was greater than 2 to 5 times the MDL as recommended in the procedure (U.S. Environmental Protection Agency, 1997).

Some analytes that had low recovery or instrumental response were fortified at successively higher concentrations (0.025, 0.075, and 0.1 µg/L). Samples were analyzed on one instrument. The preliminary estimated MDLs ranged from 0.001 to 0.7 µg/L, with a median MDL of 0.002 µg/L for all analytes (table 10). More than 80 percent of the analytes had MDLs less than 0.01 µg/L.

The LRLs are usually calculated as at least twice the LT–MDLs (Childress and others, 1999). Because of the limitations of the short-term MDL noted above, preliminary LRLs calculated using short-term MDLs were, in some cases, much lower than the lowest calibration standard that can be measured. Recently, the LRL calculation has been modified to include the bias introduced by low analyte recovery by calculating the LRL as twice the MDLs divided by the median recovery (expressed as a fraction) (Foreman and others, 2001). This new calculation resulted in preliminary LRLs for this method that were consistent with analysis of low calibration standards for most analytes (table 10). Eight analytes had calculated preliminary LRLs that were too low for reliable detection (greater than the maximum 1 percent false negative error rate; Childress and others, 1999). Therefore, the concentration of the lowest calibration standard that could be reliably detected was used instead as an estimate of the preliminary LRL for these analytes (shown in bold in table 10). The preliminary LRLs range from 0.003 to 0.267 µg/L for most analytes (table 10).

Data Analysis

The data summaries presented in tables 6 through 10 use nonparametric equivalents of the more commonly used summary statistics. For a description of the data, the median has been used rather than the arithmetic mean or average. Similarly, for the dispersion or spread of the data, the

Table 10. Method detection limits and preliminary laboratory reporting levels for pesticides and pesticide degradates calculated from determination of the analytes in eight reagent-water samples fortified at concentrations from 0.015 to 0.1 microgram per liter

[Analytes are separated into parent pesticides and degradates and sorted by remark code and then by rank. Analyses performed on one instrument. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; µg/L , microgram per liter; Median conc., median concentration; F-pseu, F-pseudosigma; Rel F-pseu, relative F-pseudosigma; MDL, method detection limit; LRL, laboratory reporting level; **bold** numbers are estimated LRLs based on lowest calibration standard observed; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	Fortification level (µg/L)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	MDL (µg/L)	Preliminary LRL (µg/L)	Remark code
		Parent pesticides								
63	04036	Prometryn	0.015	0.0112	0.00067	74.7	6.0	0.0020	0.0054	–
69	61603	Profenofos	0.015	0.0067	0.00044	44.7	6.6	0.0013	0.0059	–
71	34362	*alpha*-Endosulfan	0.015	0.0078	0.00041	52.3	5.2	0.0012	0.0047	–
75	61596	Metalaxyl	0.015	0.0123	0.00069	81.7	5.6	0.0021	0.0051	–
106	61600	Oxyfluorfen	0.015	0.0065	0.00053	43.6	8.2	0.0016	0.0073	–
108	79846	*cis*-Propiconazole	0.015	0.0056	0.00021	37.4	3.8	0.0006	**0.008**	–
110	79847	*trans*-Propiconazole	0.015	0.0030	0.00044	19.9	14.8	0.0013	0.0133	–
121	61599	Myclobutanil	0.015	0.0056	0.00037	37.4	6.6	0.0011	**0.008**	–
126	61591	Fenamiphos	0.1	0.1010	0.00489	101.0	4.8	0.0154	0.0290	–
127	04025	Hexazinone	0.025	0.0079	0.00068	31.6	8.6	0.0020	0.0129	–
128	04031	Cycloate	0.015	0.0133	0.00070	88.7	5.3	0.0021	0.0047	–
132	61598	Methidathion	0.015	0.0068	0.00044	45.1	6.5	0.0013	0.0058	–
134	82346	Ethion	0.015	0.0059	0.00026	39.4	4.4	0.0008	0.0040	–
211	79844	(E)-Dimethomorph	0.075	0.0126	0.00057	16.8	4.6	0.0017	0.0203	–
212	79845	(Z)-Dimethomorph	0.075	0.0104	0.00106	13.9	10.2	0.0032	0.0457	–
220	04022	Terbuthylazine	0.015	0.0132	0.00150	88.0	11.4	0.0045	0.0102	–
225	61592	Flumetralin	0.015	0.0053	0.00018	35.1	3.4	0.0005	**0.004**	–
227	38801	Fenthion	0.015	0.0064	0.00110	42.8	17.1	0.0033	0.0154	–
228	61594	Isofenphos	0.015	0.0100	0.00038	66.9	3.8	0.0011	0.0034	–
229	61604	Propetamphos	0.015	0.0101	0.00043	67.3	4.3	0.0013	0.0038	–
231	61602	Tebupirimphos	0.015	0.0110	0.00067	73.3	6.1	0.0020	0.0055	–
28	82662	Dimethoate	0.015	0.0052	0.00035	34.6	6.8	0.0011	0.0061	E
30	61610	Tribuphos	0.015	0.0054	0.00026	35.7	4.9	0.0008	0.0044	E
71	34357	*beta*-Endosulfan	0.025	0.0145	0.00137	58.0	9.5	0.0041	0.0142	E
76	61606	Tefluthrin	0.015	0.0048	0.00041	31.9	8.6	0.0012	0.0077	E
83	38454	Dicrotophos	0.1	0.0377	0.00530	37.7	14.1	0.0167	0.0843	E
93	61593	Iprodione	0.1	0.4120	0.23721	412.0	57.6	0.7456	1.4223	E
102	61595	Cyhalothrin	0.025	0.0049	0.00029	19.6	5.9	0.0009	0.0089	E
114	61586	Cypermethrin	0.025	0.0064	0.00037	25.8	5.8	0.0011	0.0086	E
115	38716	Sulprofos	0.015	0.0039	0.00067	26.0	17.3	0.0020	0.0155	E
125	61601	Phosmet	0.025	0.0055	0.00029	22.1	5.3	0.0009	0.0079	E
129	61585	Cyfluthrin	0.025	0.0104	0.00019	41.6	1.8	0.0006	**0.008**	E
131	61580	Bifenthrin	0.015	0.0038	0.00022	25.1	6.0	0.0007	0.0053	E
230	61605	Sulfotepp	0.015	0.0106	0.00030	70.7	2.8	0.0009	0.0025	E
232	61607	Temephos[1]	0.1	0.0339	0.01509	33.9	44.5	0.0361	0.2669	E

Table 10. Method detection limits and preliminary laboratory reporting levels for pesticides and pesticide degradates calculated from determination of the analytes in eight reagent-water samples fortified at concentrations from 0.015 to 0.1 microgram per liter—Continued

Rank	P-Code	Short name	Fortification level (µg/L)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	MDL (µg/L)	Preliminary LRL (µg/L)	Remark code
		Degradates								
1002	61615	2-[2-Ethyl-6-m_panol	0.1	0.087	0.01831	87.4	20.9	0.0575	0.1256	–
1007	61618	2-Chloro-2,6-d_ilide	0.015	0.013	0.00070	83.3	5.6	0.0021	0.0050	–
1008	61665	4-(Hydroxymeth_halin)[1]	0.1	0.081	0.01920	80.6	23.6	0.0455	0.1428	–
1016	61674	Terbufos-O-ana_lfone	0.075	0.039	0.00587	52.1	15.0	0.0176	0.0676	–
1033	61625	3,4-Dichloroaniline	0.015	0.010	0.00049	64.6	5.0	0.0015	0.0045	–
1043	61629	3-Phenoxybenzy_cohol	0.075	0.042	0.00436	56.1	10.3	0.0131	0.0466	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.015	0.004	0.00165	25.2	10.5	0.0049	0.0393	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.015	0.007	0.00250	44.7	19.9	0.0075	0.0335	–
1049	61663	Paraoxon-ethyl	0.025	0.016	0.00063	62.6	5.7	0.0019	**0.008**	–
1060	61652	Malaoxon	0.025	0.013	0.00042	50.4	6.6	0.0013	**0.008**	–
1062	61637	2-(4-tert-buty_xanol	0.015	0.011	0.00133	74.0	15.3	0.0040	0.0108	–
1067	61640	Disulfoton sulfone	0.015	0.006	0.00113	42.5	7.3	0.0034	0.0159	–
1071	61642	Endosulfan ether	0.015	0.015	0.00068	103.0	7.5	0.0020	0.0041	–
1071	61590	Endosulfan sulfate	0.015	0.009	0.00056	57.8	4.8	0.0017	0.0058	–
1076	61671	Tefluthrin met_9364]	0.015	0.005	0.00083	32.0	8.2	0.0025	0.0156	–
1093	61627	3,5-Dichloroaniline	0.015	0.012	0.00061	78.0	5.9	0.0018	0.0047	–
1099	61614	2,5-Dichloroaniline	0.015	0.010	0.00293	67.3	10.9	0.0088	0.0261	–
1124	61660	O-Ethyl-O-meth_ioate	0.015	0.010	0.00094	68.3	24.9	0.0028	0.0083	–
1126	61645	Fenamiphos sulfone	0.075	0.027	0.00046	35.7	6.9	0.0014	0.0077	–
1231	61669	Tebupirimphos,_logue	0.015	0.010	0.00069	65.8	7.0	0.0021	0.0063	–
1002	61620	2-Ethyl-6-meth_iline	0.015	0.011	0.00054	72.3	5.0	0.0016	0.0045	E
1012	61636	Chlorpyrifos, _nalog	0.075	0.027	0.00332	35.4	12.5	0.0099	0.0562	E
1013	61617	2-Amino-N-isop_amide	0.015	0.007	0.00038	46.3	5.4	0.0011	0.0049	E
1014	61664	Paraoxon-methyl	0.075	0.048	0.00321	64.3	6.7	0.0096	0.0299	E
1015	61633	4-Chloro-2-met_henol	0.015	0.007	0.00044	46.7	6.3	0.0013	0.0056	E
1024	61630	3-Trifluoromet_iline	0.015	0.005	0.00055	30.5	12.0	0.0016	0.0108	E
1032	49295	1-Naphthol	0.025	0.021	0.01212	82.4	58.8	0.0363	0.0882	E
1032	61611	1,4-Naphthaquinone	0.025	0.008	0.00277	32.6	23.3	0.0083	0.0509	E
1034	61666	Phorate oxon	0.075	0.012	0.00258	15.9	10.3	0.0077	0.0973	E
1053	61635	Azinphos-methyl-oxon	0.015	0.025	0.00027	33.5	3.3	0.0008	**0.016**	E
1054	61649	Fonofos, oxyge_nalog	0.015	0.008	0.00020	55.9	3.2	0.0006	0.0021	E
1067	61641	Disulfoton sulfoxide	0.075	0.081	0.00040	107.5	8.3	0.0012	0.0024	E
1076	61672	Tefluthrin met_2912]	0.015	0.009	0.00104	60.3	8.1	0.0031	0.0103	E
1101	61631	4,4'-Dichlorob_enone	0.015	0.013	0.00048	85.3	6.1	0.0014	0.0034	E
1105	61634	4-Chlorobenzyl_lfone	0.015	0.008	0.00265	52.2	8.5	0.0083	0.0304	E
1125	61668	Phosmet oxon	0.1	0.031	0.00287	31.1	8.6	0.0086	0.0553	E

Table 10. Method detection limits and preliminary laboratory reporting levels for pesticides and pesticide degradates calculated from determination of the analytes in eight reagent-water samples fortified at concentrations from 0.015 to 0.1 microgram per liter—Continued

Rank	P-Code	Short name	Fortification level (µg/L)	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	MDL (µg/L)	Preliminary LRL (µg/L)	Remark code
1126	61646	Fenamiphos sulfoxide	0.075	0.033	0.00014	44.5	2.2	0.0004	**0.031**	E
1134	61644	Ethion monoxon	0.015	0.006	0.00241	43.0	29.6	0.0072	0.0336	E
1153	38775	Dichlorvos	0.025	0.011	0.00089	45.2	7.9	0.0027	0.0118	E
1227	61647	Fenthion sulfoxide	0.015	0.008	0.00068	51.6	8.8	0.0021	0.0079	E
		Surrogates								
	99223	Diazinon-d_{10}, _ogate	0.015	0.081	0.00187	81.0	2.3	0.0056	0.0138	–
	99224	*alpha*-HCH-d_6, _ogate	0.015	0.091	0.00065	91.3	0.7	0.0019	0.0043	–

[1]MDL for temephos and 4-(hydroxymethyl)pendamethalin were estimated from reagent-water set-spike data (table 17) with $t = 2.39$.

F-pseudosigma has been used rather than the standard deviation. The F-pseudosigma is defined as the interquartile range divided by 1.349 (Hoaglin, 1983). Because the nonparametric summaries are less likely to be influenced by an outlying result, they are more robust than their parametric equivalents in the small data sets produced in the method validation experiments.

Recovery at different concentrations: The median recovery of most compounds was comparable at 1.0, 0.1, or 0.01 µg/L (tables 6 through 10), which indicated no major bias caused by the concentration of the analyte over the concentration range tested. For all sample matrices, samples were grouped by concentration and compared by using the nonparametric Mann-Whitney test to examine the null hypothesis that the median recoveries were equal to the median recovery at 0.1 µg/L in each concentration (Miller and Miller, 1993). For other compounds, the median recoveries were significantly higher ($p < 0.05$; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L set. These differences were small (4 to 15 percent) and might be the result of variation in instrument performance because each sample set (same matrix and concentration) was analyzed at different times. The CCVs for the ground-water low-concentration set were also high, perhaps explaining an instrument analytical effect rather than sample matrix or concentration effects for some of the analytes determined in this set.

Recovery in different matrices: The mean recovery of some compounds was lower in the reagent-water sample sets (tables 6 and 7) compared to samples of surface water (table 8) or ground water (table 9). Again, these differences were small (4 to 15 percent) and might be the result of variation in instrument performance because each sample set was analyzed at different times.

Recommended Holding Time

The recommended holding time of analytes in pesticide-grade water at 4ºC and after extraction on the SPE column with storage on the dry column at room temperature was estimated by modifying a standard practice (ASTM Procedure D-4841-88) for estimating holding time for constituents in water samples (American

Society for Testing and Materials, 2000). In that standard, the maximum holding time is defined as the maximum period that a sample can be stored before the analyte degrades so that the systematic error exceeds the 99-percent confidence interval (not to exceed 15 percent) of the mean concentration determined at time zero. Holding time is estimated by replicate analyses at discrete time intervals of a large volume of sample. A plot of the data then is prepared, and a line is fit to the data. The point where the line crosses the lower tolerable range of variation is the estimated holding time. An estimate of the analyte variability is needed to calculate the number of replicates required for each discrete time interval prior to determining the holding time.

It should be noted that the holding-time estimates were determined in reagent water. In environmental samples, the sample matrix might result in holding times different than those determined in a relatively clean matrix like reagent water. These holding times are recommended to provide a balance between the practical requirements of sample collection, shipping and processing, and the limited information provided by these estimated holding-time experiments. In general, the best approach is to extract samples by SPE and elute from the SPE column as quickly as possible.

The practice was modified for use in this report to better match the data produced in the validation experiments and identify analytes that have holding times shorter than those described in the complementary method 2001 (Zaugg and others, 1995). In method 2001, the recommended maximum holding times are 4 days in water prior to SPE, and 7 days on the SPE column after SPE (Zaugg and others, 1995, p. 39). The relative F-pseudosigma was used instead of the relative standard deviation to calculate the number of replicates needed at each discrete time interval. Similarly, instead of the standard deviation, the F-pseudosigma was used to calculate the tolerable range of variation. The F-pseudosigma generally is similar to the standard deviation for most compounds, and, therefore, the modification is expected to have little effect except when variability is high because of outliers. In that case, the F-pseudosigma provides a more conservative estimate than the standard deviation. A linear fit of the data rather than other graphical estimates was used to estimate maximum holding time to simplify the analysis. Visual examination of the data was used to make sure the linear fit did not underestimate the holding times for water and on the SPE column given in Zaugg and others (1995), although, in some cases, other types of graphical fit might provide better numerical estimates of holding time.

Calculation of replicates required for holding-time experiments: The relative F-pseudosigma of samples fortified in pesticide-grade water at 0.1 µg/L (tables 6 and 7) was used to estimate the number of samples needed to evaluate a significant change in concentration over time. The number of replicates required for the holding-time experiments was calculated according to the following equation:

$$n = \left(\frac{t \times Rel\ Fpseu}{D} \right)^2 \quad , \qquad (12)$$

where n = number of replicate samples;

t = Student's t-value for a two-tailed test appropriate for the 99-percent confidence level;

$Rel\ Fpseu$ = Relative F-pseudosigma, in percent (tables 6 and 7); and

D = 15 percent, maximum variation from mean to be tolerated.

The value of t is 3.499 for eight replicates and a 99-percent confidence level. For most compounds, the calculated number of replicates n was less than four (tables 11 and 12), so this value was selected as a practical number of replicates to use for the holding-time study. For some of the more variable analytes, the use of four replicates is insufficient to characterize the estimated holding time.

SPE holding-time experiment: Reagent-water samples were fortified with parent pesticides or degradates at 0.1 µg/L, extracted by SPE, and the column was dried on day zero. The SPE columns then were stored at room temperature. Four replicate samples were eluted from the SPE columns at discrete (0, 1, 3, 7, 14, and 28 days) intervals over 28 days. Parent pesticides and degradates were prepared and determined in separate experiments to avoid bias from formation of degradates during the holding-time experiment.

Pesticide-grade water holding-time experiment: Reagent-water samples were fortified with parent pesticides or degradates at 0.1 µg/L and stored at 4ºC. Four replicate samples were extracted at discrete (0, 1, 3, 7, 14, and 28 days) intervals over 28 days. Parent pesticides and degradates were prepared and determined in separate experiments to avoid bias from formation of degradates during the holding-time experiment.

Holding-time data analysis: All samples from either the SPE or water holding-time experiments were analyzed in one batch at the end of the experiment. The tolerable variation d that was calculated from the following formula is listed in tables 13 and 14:

$$d = \pm \frac{t \times Fpseu}{\sqrt{n}} \quad , \qquad (13)$$

where d = range of tolerable variation from initial recovery, in percent;

t = Student's t-value, for a two-tailed test appropriate for the 99-percent confidence level;

$Fpseu$ = F-pseudosigma (tables 6 and 7) converted to percent; and

n = 4, number of replicates.

The value of t is 3.499 for eight replicates and a 99-percent confidence level. The estimated d value, in percent recovery, then was subtracted from the day-zero value to give the lower tolerable range of variation from the day-zero recovery. Straight lines were fit to the data, and the day-zero intercept was calculated from the regression line. The equation for the regression line is

$$R = m \times t + b \quad , \qquad (14)$$

where R = recovery, in percent;

m = slope of linear regression;

t = time, in days; and

b = time zero intercept, in percent recovery.

The intercept of the linear fit of the concentration in relation to the time line with the lower tolerable range of concentration gives the estimated holding time. The slope and intercept for the linear fit of the data are provided to allow estimates of holding times by using other estimates of the tolerable range of variation.

Holding time on dry SPE column: Ten parent pesticides had holding times on the dry SPE column that were 30 days or less (table 13). Two organothiophosphate pesticides, sulfotepp and sulprofos, had holding times

Table 11. Number of replicates required to determine estimated holding time of parent pesticides in water and on solid-phase-extraction columns

[Number of replicates needed at each time step to estimate the mean concentration within 15 percent (*n*), (equation 12); P-Code, National Water Information System parameter code; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	Number of replicates (*n*)	Remark code
		Parent pesticides		
63	04036	Prometryn	1	–
69	61603	Profenofos	2	–
71	34362	*alpha*-Endosulfan	1	–
75	61596	Metalaxyl	1	–
106	61600	Oxyfluorfen	4	–
108	79846	*cis*-Propiconazole	1	–
110	79847	*trans*-Propiconazole	2	–
121	61599	Myclobutanil	2	–
126	61591	Fenamiphos	1	–
127	04025	Hexazinone	1	–
128	04031	Cycloate	1	–
132	61598	Methidathion	1	–
134	82346	Ethion	1	–
211	79844	(E)-Dimethomorph	2	–
212	79845	(Z)-Dimethomorph	1	–
220	04022	Terbuthylazine[1]	2	–
225	61592	Flumetralin	3	–
227	38801	Fenthion	2	–
228	61594	Isofenphos	2	–
229	61604	Propetamphos	1	–
231	61602	Tebupirimphos	2	–
28	82662	Dimethoate	30	E
30	61610	Tribuphos	8	E
71	34357	*beta*-Endosulfan	1	E
76	61606	Tefluthrin	10	E
83	38454	Dicrotophos	31	E
93	61593	Iprodione	2	E
102	61595	Cyhalothrin	9	E
114	61586	Cypermethrin	26	E
115	38716	Sulprofos	4	E
125	61601	Phosmet	3	E
129	61585	Cyfluthrin	22	E
131	61580	Bifenthrin	17	E
230	61605	Sulfotepp	1	E
232	61607	Temephos[1]	7	E
		Surrogates		
	99223	Diazinon-d_{10}, _ogate	1	–
	99224	*alpha*-HCH-d_6, _ogate	1	–

[1]Terbuthylazine and temephos are not included in holding-time experiments.

Table 12. Number of replicates required to determine estimated holding time of degradates in water and on solid-phase-extraction columns

[Number of replicates needed at each time step to estimate the mean concentration within 15 percent (*n*), (equation 12); P-Code, National Water Information System parameter code; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	Number of replicates (*n*)	Remark code
		Degradates		
1002	61615	2-[2-Ethyl-6-m_panol	3	–
1007	61618	2-Chloro-2,6-d_ilide	1	–
1008	61665	4-(Hydroxymeth_halin	5	–
1014	61664	Paraoxon-methyl	1	–
1033	61625	3,4-Dichloroaniline	6	–
1043	61629	3-Phenoxybenzy_cohol	1	–
1044	79842	*c*-Methyl-3-(2,_ylate	1	–
1044	79843	*t*-Methyl-3-(2,_ylate	2	–
1049	61663	Paraoxon-ethyl[1]	1	–
1060	61652	Malaoxon	2	–
1062	61637	2-(4-tert-buty_xanol	3	–
1067	61640	Disulfoton sulfone	1	–
1071	61642	Endosulfan ether	1	–
1071	61590	Endosulfan sulfate[1]	1	–
1076	61672	Tefluthrin met_2912]	1	–
1076	61671	Tefluthrin met_9364]	4	–
1093	61627	3,5-Dichloroaniline	3	–
1099	61614	2,5-Dichloroaniline	2	–
1124	61660	O-Ethyl-O-meth_ioate	2	–
1126	61645	Fenamiphos sulfone	4	–
1231	61669	Tebupirimphos,_logue	1	–
1002	61620	2-Ethyl-6-meth_iline	1	E
1012	61636	Chlorpyrifos, _nalog	45	E
1013	61617	2-Amino-N-isop_amide	13	E
1015	61633	4-Chloro-2-met_henol	11	E
1016	61674	Terbufos-O-ana_lfone	5	E
1024	61630	3-Trifluoromet_iline	4	E
1032	49295	1-Naphthol	89	E
1032	61611	1,4-Naphthaquinone	53	E
1034	61666	Phorate oxon	4	E
1053	61635	Azinphos-methyl-oxon	22	E
1054	61649	Fonofos, oxyge_nalog	1	E
1067	61641	Disulfoton sulfoxide	2	E
1101	61631	4,4'-Dichlorob_enone	1	E
1105	61634	4-Chlorobenzyl_lfone	7	E
1125	61668	Phosmet oxon	66	E
1126	61646	Fenamiphos sulfoxide	8	E
1134	61644	Ethion monoxon	2	E
1153	38775	Dichlorvos[1]	2	E
1227	61647	Fenthion sulfoxide	2	E
		Surrogates		
	99223	Diazinon-d_{10}, _ogate	2	–
	99224	*alpha*-HCH-d_6, _ogate	2	–

[1]Dichlorvos, endosulfan sulfate, and paraoxon-ethyl were analyzed in parent fortification mixture.

Table 13. Statistical data used to determine estimated holding time of parent pesticides on dry solid-phase-extraction columns maintained at 25 degrees Celsius

[Holding times less than 7 days shown in boldface. Reagent-water samples were fortified at 0.1 microgram per liter, isolated on the SPE column on day 0, and four replicate samples were eluted from the SPE column on days 0, 1, 3, 7, 14, and 28. P-Code, National Water Information System parameter code; *d*, tolerable range of variation in initial concentration (in percent recovery); Mean–*d*, mean recovery on day 0 minus *d*; Intercept, intercept of linear fit to holding-time results; Slope, slope of linear fit to holding-time results; Holding time, estimated holding time (days) from least-squares regression (using a straight-line model); --, estimated holding time greater than 28 days because compound did not decrease in concentration over 28-day test period; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
		Parent pesticides							
63	04036	Prometryn	6.0	84.8	78.7	83.3	0.014	--	–
69	61603	Profenofos	6.1	70.9	64.8	69.7	-0.955	7	–
71	34362	*alpha*-Endosulfan	4.5	97.8	93.3	102.0	0.026	--	–
75	61596	Metalaxyl	5.8	88.3	82.5	88.5	-0.043	--	–
106	61600	Oxyfluorfen	7.3	63.9	56.5	63.5	-0.170	--	–
108	79846	*cis*-Propiconazole	3.4	70.0	66.6	70.9	0.025	--	–
110	79847	*trans*-Propiconazole	5.9	82.5	76.6	82.8	0.007	--	–
121	61599	Myclobutanil	5.8	78.5	72.6	79.5	-0.001	--	–
126	61591	Fenamiphos	4.0	54.6	50.6	66.5	-0.085	--	–
127	04025	Hexazinone	2.4	56.5	54.1	60.8	-0.086	28	–
128	04031	Cycloate	5.1	77.8	72.6	76.2	0.114	--	–
132	61598	Methidathion	3.1	75.9	72.7	76.5	0.021	--	–
134	82346	Ethion	2.7	66.6	64.0	65.8	-0.048	--	–
211	79844	(E)-Dimethomorph	7.7	68.5	60.9	68.9	-0.038	--	–
212	79845	(Z)-Dimethomorph	5.5	63.9	58.4	65.2	-0.075	--	–
220	04022	Terbuthylazine[1]	7.7	–	–	–	–	–	–
225	61592	Flumetralin	6.3	68.6	62.3	69.9	-0.254	25	–
227	38801	Fenthion	6.2	85.5	78.8	82.3	-1.363	[2] 7	–
228	61594	Isofenphos	4.3	85.0	78.3	82.1	-0.038	--	–
229	61604	Propetamphos	5.8	82.6	83.8	81.6	-0.022	--	–
231	61602	Tebupirimphos	21.0	89.6	0.0	87.1	-0.019	--	–
28	82662	Dimethoate	6.7	16.7	46.4	16.7	-0.004	[2] --	E
30	61610	Tribuphos	3.9	53.1	38.4	50.8	-0.287	[2] 24	E
71	34357	*beta*-Endosulfan	5.7	107.2	101.4	109.8	-0.193	30	E
76	61606	Tefluthrin	6.1	42.3	4.5	40.3	-0.018	--	E
83	38454	Dicrotophos	4.3	10.6	87.2	14.9	0.086	--	E
93	61593	Iprodione	2.0	91.4	29.2	88.2	0.072	[2] --	E
102	61595	Cyhalothrin	11.6	31.2	36.4	30.2	-0.090	[2] 22	E
114	61586	Cypermethrin	7.4	48.0	31.9	49.9	-0.075	[2] --	E
115	38716	Sulprofos	7.8	71.6	63.8	68.8	-1.415	**6**	E
125	61601	Phosmet	10.7	39.3	36.5	37.3	-0.281	[2] 27	E
129	61585	Cyfluthrin	4.0	47.1	29.0	50.9	-0.029	--	E

Table 13. Statistical data used to determine estimated holding time of parent pesticides on dry solid-phase-extraction columns maintained at 25 degrees Celsius—Continued

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
131	61580	Bifenthrin	9.0	32.9	76.5	32.2	0.053	[2] --	E
230	61605	Sulfotepp	4.1	83.2	79.1	80.2	-1.218	**4**	E
232	61607	Temephos[1]	7.0	–	–	–	–	–	E
		Surrogates							
	99223	Diazinon-d_{10}, _ogate	3.7	97.9	94.2	94.6	-0.316	12	–
	99224	*alpha*-HCH-d_6, _ogate	5.7	91.0	85.3	88.9	-0.126	--	–

[1]Terbuthylazine and temephos were not included in holding-time experiments.
[2]Holding times (days) were corrected in pdf version of the report, February 4, 2002 (mws).

Table 14. Statistical data used to determine estimated holding time of degradates on solid-phase-extraction columns maintained at 25 degrees Celsius

[Holding times less than 7 days shown in boldface. Reagent-water samples were fortified at 0.1 microgram per liter, isolated on the SPE column on day 0, and four replicate samples were eluted from the SPE column on days 0, 1, 3, 7, 14, and 28. P-Code, National Water Information System parameter code; *d*, tolerable range of variation in initial concentration (in percent recovery); Mean–*d*, mean recovery on day 0 minus *d*; Intercept, intercept of linear fit to holding-time results; Slope, slope of linear fit to holding-time results; Holding time, estimated holding time (days) from least-squares regression (using a straight-line model); –, not applicable; --, estimated holding time greater than 28 days because compound did not decrease in concentration over 28-day test period; E, estimated qualifier remark]

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
		Degradates							
1002	61615	2-[2-Ethyl-6-m_panol	9.3	91.8	82.5	90.1	-0.836	12	–
1007	61618	2-Chloro-2,6-d_ilide	3.2	92.9	89.8	94.6	-0.153	21	–
1008	61665	4-(Hydroxymeth_halin	13.5	91.0	77.5	92.1	0.105	--	–
1016	61674	Terbufos-O-ana_lfone	14.7	93.9	91.2	87.4	-1.060	12	–
1043	61629	3-Phenoxybenzy_cohol	4.2	70.0	65.8	74.7	-0.334	13	–
1044	79842	*c*-Methyl-3-(2,_ylate	4.9	95.4	90.5	93.2	-0.101	--	–
1044	79843	*t*-Methyl-3-(2,_ylate	7.0	94.4	87.4	94.6	-0.109	--	–
1049	61663	Paraoxon-ethyl[1]	5.0	70.5	65.5	67.8	-0.596	9	–
1060	61652	Malaoxon	9.1	92.6	83.5	88.5	-0.855	11	–
1062	61637	2-(4-tert-buty_xanol	9.9	83.6	73.7	88.0	-0.157	--	–
1067	61640	Disulfoton sulfone	5.8	86.0	80.2	86.3	-0.049	--	–
1071	61642	Endosulfan ether	4.7	105.8	101.1	108.9	-0.233	21	–
1071	61590	Endosulfan sulfate[1]	5.7	102.5	96.8	103.4	-0.032	–	–
1076	61672	Tefluthrin met_2912]	4.2	69.0	64.8	69.2	-0.291	15	–
1093	61627	3,5-Dichloroaniline	11.2	107.5	96.3	109.6	-0.794	15	–
1099	61614	2,5-Dichloroaniline	8.8	89.5	80.7	92.4	-0.268	--	–
1124	61660	O-Ethyl-O-meth_ioate	8.3	87.8	79.5	89.3	-0.042	--	–

Table 14. Statistical data used to determine estimated holding time of degradates on solid-phase-extraction columns maintained at 25 degrees Celsius—Continued

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
1126	61645	Fenamiphos sulfone	9.3	65.2	55.9	67.3	-0.152	--	–
1231	61669	Tebupirimphos,_logue	4.4	78.7	74.3	80.5	-0.375	12	–
1002	61620	2-Ethyl-6-meth_iline	3.4	87.0	83.6	95.5	-0.783	**5**	E
1012	61636	Chlorpyrifos, _nalog	8.8	71.0	62.2	60.7	-17.963	**1**	E
1013	61617	2-Amino-N-isop_amide	15.4	93.4	78.0	95.2	-0.159	--	E
1014	61664	Paraoxon-methyl	12.4	57.4	81.6	52.4	-0.879	12	E
1015	61633	4-Chloro-2-met_henol	3.9	78.0	53.6	79.9	0.048	**5**	E
1024	61630	3-Trifluoromet_iline	17.2	56.5	60.8	61.4	-0.852	--	E
1032	49295	1-Naphthol	5.3	229.3	51.2	145.7	-5.886	7	E
1032	61611	1,4-Naphthaquinone	18.2	40.4	22.2	20.1	-1.186	16	E
1033	61625	3,4-Dichloroaniline	10.3	105.9	76.7	108.3	-1.321	**5**	E
1034	61666	Phorate oxon	18.0	86.9	211.3	77.2	-2.107	**4**	E
1053	61635	Azinphos-methyl-oxon	20.0	53.5	33.5	48.8	-0.479	--	E
1054	61649	Fonofos, oxyge_nalog	3.4	82.7	79.3	77.8	-1.412	**3**	E
1067	61641	Disulfoton sulfoxide	12.2	153.5	141.3	172.4	0.343	--	E
1076	61671	Tefluthrin met_9364]	6.0	69.8	63.8	69.2	-0.583	11	E
1101	61631	4,4'-Dichlorob_enone	4.6	80.1	75.5	81.0	-0.957	**5**	E
1105	61634	4-Chlorobenzyl_lfone	12.8	58.2	45.4	62.9	-0.055	--	E
1125	61668	Phosmet oxon	17.9	31.0	13.1	19.9	-0.194	--	E
1126	61646	Fenamiphos sulfoxide	5.0	15.3	10.3	19.6	-0.008	--	E
1134	61644	Ethion monoxon	3.8	67.7	63.9	66.9	-0.198	20	E
1153	38775	Dichlorvos[1]	7.1	59.8	52.6	38.9	-1.672	**5**	E
1227	61647	Fenthion sulfoxide	6.2	69.6	63.4	70.5	-0.057	--	E
		Surrogates							
	99223	Diazinon-d_{10}, _ogate	9.0	101.3	92.3	102.9	-0.321	28	–
	99224	*alpha*-HCH-d_6, _ogate	5.0	100.9	96.0	100.1	0.002	--	–

[1]Dichlorvos, endosulfan sulfate, and paraoxon-ethyl were analyzed in parent fortification mixture.

less than 7 days. Because this is shorter than the holding time recommended in method 2001 (Zaugg and others, 1995), these compounds are reported with an estimated remark qualifier. Another organothio-phosphate pesticide, profenofos, had a slightly longer holding time of 7 days.

More pesticide degradates (table 14) had holding times less than 30 days when compared to the parent pesticides (table 13). Eight degradates had estimated holding times less than 7 days. This is shorter than the holding time recommended in method 2001 (Zaugg and others, 1995), so these compounds are reported with an estimated remark qualifier. Two organophosphate degradates, chlorpyrifos oxygen analog and fonophos oxygen analog, appeared to be unstable with holding times of 3 days or less. This might eliminate any advantages to on-site SPE for these compounds.

Holding time in pesticide-grade water: Twelve parent pesticides had calculated

holding times in pesticide-grade water of less than 30 days (table 15). An organothiophosphate pesticide (phosmet), an isomer of an organochlorine pesticide (*beta*-endosulfan), and a pyrethroid pesticide (cyhalothrin) had holding times of 4 days or less, which is the recommended holding time in water for method 2001. As a result, these analytes are reported with an estimated remark qualifier.

In addition to cyhalothrin, other pyrethroid pesticides, cyfluthrin, cypermethrin, and tefluthrin had calculated holding times of less than 30 days. This might be caused by sorption to the walls of the glass sample bottles over the duration of the experiments because these compounds have high octanol-water partition coefficients (log K_{ow}) compared to the other analytes (Mackay and others, 1997). None of the degradates had holding times in water less than 4 days (table 16).

Fortified Reagent-Water-Set Samples

Environmental water samples collected by some NAWQA projects were analyzed in 1999 as part of a pilot test during implementation of the new method. Reagent-water samples were fortified with the analytes at 0.1 µg/L and analyzed with each set of 10 samples. The median recovery and variability of 74 of these fortified reagent-water-set samples prepared during March–December, 1999, are listed in table 17. Degradates were included in all 74 samples, while parent pesticides were included only in the last 49 samples. These fortified reagent-water-set samples are comparable to the low-concentration, reagent-water samples analyzed during method validation (tables 6 and 7). They probably better represent the performance of the analytes in pesticide-grade water because they were analyzed in many different sets and over a longer period compared to the reagent-water data listed in tables 6 and 7. For most analytes, median recovery in the fortified reagent-water-set samples was comparable to that in the reagent-water method validation data listed in tables 6 and 7, although the variability is somewhat larger.

NOTE: During the pilot test of the method, environmental samples were extracted by SPE, generally within 4 days of collection, processed, and the extracts stored in a freezer until GC/MS analysis. Repeated GC/MS analysis of a CCV standard stored for a 20-week period indicated no significant loss of any analytes.

The average median recovery for the fortified reagent-water-set samples for all compounds was 68 percent, with an average F-pseudosigma of 12 percent.

Some analytes, however, exhibited significantly larger variability in the fortified reagent-water-set samples, perhaps indicating analytes that are more susceptible to procedural error than others. A plot of the median concentration and F-pseudosigma for all analytes is shown in figure 2. A line of relative F-pseudosigma equal to 25 percent is plotted to indicate analytes that have high F-pseudosigma compared to other analytes. Compounds that had an F-pseudosigma greater than 25 percent include the following: 1,4-naphthaquinone; 1-naphthol, 3-trifluoromethylaniline; 4-chloro-2-methylphenol; azinphos-methyl-oxon; chlorpyrifos oxygen analog, cyhalothrin; cypermethrin; dichlorvos; ethion monoxon; fenamiphos sulfoxide; fenthion sulfoxide; iprodione; phosmet; phosmet oxon; and temephos.

Qualification of Some Compounds

During quantitative method validation, some compounds exhibited performance

Table 15. Statistical data used to determine estimated holding time of parent pesticides in pesticide-grade water maintained at 4 degrees Celsius

[Analytes with holding times less than 4 days shown in bold. Reagent-water samples were fortified at 0.1 microgram per liter, and four replicate samples were extracted and prepared for analysis on days 0, 1, 3, 7, 14, and 28. P-Code, National Water Information System parameter code; *d*, tolerable range of variation from mean recovery, in percent; Mean –d, mean recovery on day 0 minus d; Intercept, intercept of linear fit to holding-time results; Slope, slope of linear fit to holding-time results; --, estimated holding time greater than 28 days because compound did not decrease in concentration over 28-day test period; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
		Parent pesticides							
63	04036	Prometryn	6.0	84.7	78.7	84.9	0.142	--	–
69	61603	Profenofos	6.1	72.2	66.0	66.8	-0.832	8	–
71	34362	*alpha*-Endosulfan	4.5	92.2	87.7	80.7	-0.851	6	–
75	61596	Metalaxyl	5.8	87.9	82.1	90.5	0.204	--	–
106	61600	Oxyfluorfen	7.3	61.8	54.5	58.6	-0.124	--	–
108	79846	*cis*-Propiconazole	3.4	69.7	66.2	68.0	-0.017	--	–
110	79847	*trans*-Propiconazole	5.9	79.7	73.8	77.2	0.023	--	–
121	61599	Myclobutanil	5.8	76.4	70.6	76.2	0.086	--	–
126	61591	Fenamiphos	4.0	70.9	66.9	70.2	0.141	--	–
127	04025	Hexazinone	2.4	62.4	60.0	60.7	-0.272	9	–
128	04031	Cycloate	5.1	81.0	75.8	84.4	-0.224	24	–
132	61598	Methidathion	3.1	71.1	68.0	69.3	-0.045	--	–
134	82346	Ethion	2.7	64.6	61.9	62.4	-0.042	--	–
211	79844	(E)-Dimethomorph	7.7	71.4	63.8	73.9	0.008	--	–
212	79845	(Z)-Dimethomorph	5.5	69.0	63.5	68.5	0.040	--	–
220	04022	Terbuthylazine[1]	7.7	–	–	–	–	–	–
225	61592	Flumetralin	6.3	66.2	59.9	64.7	-0.042	--	–
227	38801	Fenthion	9.0	77.9	68.9	79.9	0.080	--	–
228	61594	Isofenphos	6.2	85.3	79.1	83.7	0.035	--	–
229	61604	Propetamphos	4.3	81.8	77.5	81.4	0.089	--	–
231	61602	Tebupirimphos	5.8	84.3	78.5	86.4	0.090	--	–
28	82662	Dimethoate	21.0	17.6	0.0	27.1	0.570	--	E
30	61610	Tribuphos	6.7	53.9	47.2	50.1	-0.070	--	E
71	34357	*beta*-Endosulfan	5.7	98.5	92.7	78.8	-1.714	**4**	E
76	61606	Tefluthrin	3.9	43.4	39.5	47.4	-0.148	27	E
83	38454	Dicrotophos	6.1	18.2	12.1	22.2	-0.142	--	E
93	61593	Iprodione	4.3	80.0	75.7	74.6	-0.661	7	E
102	61595	Cyhalothrin	2.0	29.8	27.8	23.5	-0.700	**3**	E
114	61586	Cypermethrin	11.6	52.6	41.0	53.0	-0.784	15	E
115	38716	Sulprofos	7.8	61.3	53.5	62.3	-0.061	--	E
125	61601	Phosmet	7.4	27.0	19.6	27.0	-4.525	**2**	E
129	61585	Cyfluthrin	10.7	51.6	40.9	52.2	-0.750	15	E
131	61580	Bifenthrin	4.0	37.2	33.3	37.8	-0.084	--	E
230	61605	Sulfotepp	4.1	79.2	75.1	79.8	-0.496	9	E
232	61607	Temephos[1]	7.0	–	–	–	–	–	E
		Surrogates							
	99223	Diazinon-d_{10}, _ogate	3.7	89.8	86.2	93.1	-0.036	--	–
	99224	*alpha*-HCH-d_6, _ogate	5.7	88.8	83.1	94.5	0.002	--	–

[1]Terbuthylazine and temephos were not included in holding-time experiments.

Table 16. Statistical data used to determine estimated holding time of degradates in pesticide-grade water maintained at 4 degrees Celsius

[Analytes with holding times less than 4 days shown in bold. Reagent-water samples were fortified at 0.1 microgram per liter, and four replicate samples were extracted and prepared for analysis on days 0, 1, 3, 7, 14, and 28. P-Code, National Water Information System parameter code; *d*, tolerable range of variation from mean recovery, in percent; Mean –d, mean recovery on day 0 minus d; Intercept, intercept of linear fit to holding-time results; Slope, slope of linear fit to holding-time results; --, estimated holding time greater than 28 days because compound did not decrease in concentration over 28-day test period; –, not applicable; E, estimated qualifier remark]

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
		Degradates							
1002	61615	2-[2-Ethyl-6-m_panol	9.3	72.3	63.0	73.3	0.104	--	–
1007	61618	2-Chloro-2,6-d_ilide	3.2	86.1	82.9	86.3	0.042	--	–
1008	61665	4-(Hydroxymeth_halin	13.5	106.5	92.9	105.1	0.018	--	–
1016	61674	Terbufos-O-ana_lfone	12.4	59.6	47.2	52.4	-0.332	--	–
1033	61625	3,4-Dichloroaniline	14.7	85.3	70.7	89.9	0.258	--	–
1043	61629	3-Phenoxybenzy_cohol	4.2	74.0	69.8	76.2	-0.022	--	–
1044	79842	*c*-Methyl-3-(2,_ylate	4.9	90.2	85.3	89.5	-0.083	--	–
1044	79843	*t*-Methyl-3-(2,_ylate	7.0	90.8	83.7	90.0	-0.030	--	–
1049	61663	Paraoxon-ethyl[1]	5.0	65.9	61.0	66.4	0.085	--	–
1060	61652	Malaoxon	9.1	67.4	58.3	54.0	-0.409	23	–
1062	61637	2-(4-tert-buty_xanol	9.9	80.7	70.9	81.2	-0.002	--	–
1067	61640	Disulfoton sulfone	5.8	53.5	47.7	50.9	-0.194	30	–
1071	61642	Endosulfan ether	4.7	103.9	99.2	100.6	0.016	--	–
1071	61590	Endosulfan sulfate[1]	5.7	93.2	87.5	92.3	0.034	--	–
1076	61672	Tefluthrin met_2912]	4.2	70.1	65.9	70.3	-0.074	--	–
1093	61627	3,5-Dichloroaniline	11.2	88.7	77.5	92.1	0.230	--	–
1099	61614	2,5-Dichloroaniline	8.8	81.2	72.4	83.1	0.120	--	–
1124	61660	O-Ethyl-O-meth_ioate	8.3	80.9	72.6	82.0	0.156	--	–
1126	61645	Fenamiphos sulfone	9.3	72.0	62.7	68.2	-0.140	--	–
1231	61669	Tebupirimphos,_logue	4.4	75.9	71.5	76.1	-0.058	--	–
1002	61620	2-Ethyl-6-meth_iline	3.4	89.7	86.3	93.0	0.166	--	E
1012	61636	Chlorpyrifos, _nalog	8.8	56.7	47.8	55.6	0.266	--	E
1013	61617	2-Amino-N-isop_amide	15.4	50.8	35.3	54.6	0.289	--	E
1014	61664	Paraoxon-methyl	3.9	79.7	75.8	76.0	0.359	--	E
1015	61633	4-Chloro-2-met_henol	17.2	58.0	40.8	65.3	0.393	--	E
1024	61630	3-Trifluoromet_iline	5.3	52.0	46.7	53.4	0.108	--	E
1032	49295	1-Naphthol	18.0	97.8	79.8	113.5	0.706	--	E
1032	61611	1,4-Naphthaquinone	18.2	42.2	24.1	39.4	0.002	--	E
1034	61666	Phorate oxon	10.3	72.2	62.0	70.8	-1.371	8	E
1053	61635	Azinphos-methyl-oxon	20.0	35.1	15.0	37.2	0.389	--	E
1054	61649	Fonofos, oxyge_nalog	3.4	65.0	61.7	66.8	0.181	--	E
1067	61641	Disulfoton sulfoxide	12.2	121.4	109.3	122.7	0.409	--	E
1076	61671	Tefluthrin met_9364]	6.0	55.3	49.3	54.8	-0.250	24	E
1101	61631	4,4'-Dichlorob_enone	4.6	69.0	64.4	71.8	0.104	--	E

Table 16. Statistical data used to determine estimated holding time of degradates in pesticide-grade water maintained at 4 degrees Celsius—Continued

Rank	P-Code	Short name	*d* (percent)	Mean recovery day 0 (percent)	Mean–*d* (percent)	Intercept (percent)	Slope	Holding time (days)	Remark code
1105	61634	4-Chlorobenzyl_lfone	12.8	61.7	48.9	62.3	0.064	--	E
1125	61668	Phosmet oxon	17.9	7.4	0.0	9.7	0.003	--	E
1126	61646	Fenamiphos sulfoxide	5.0	9.9	4.9	11.2	-0.034	--	E
1134	61644	Ethion monoxon	3.8	55.0	51.2	54.4	0.021	--	E
1153	38775	Dichlorvos[1]	7.1	35.3	28.2	33.1	0.055	--	E
1227	61647	Fenthion sulfoxide	6.2	63.8	57.7	64.7	0.057	--	E
		Surrogates							
	99223	Diazinon-d_{10}, _ogate	9.0	100.8	91.8	98.4	-0.068	--	–
	99224	*alpha*-HCH-d_6, _ogate	5.0	85.9	80.9	86.5	-0.104	--	–

[1]Dichlorvos, endosulfan sulfate, and paraoxon-ethyl were analyzed in parent fortification mixture.

Table 17. Bias and variability data from reagent-water-set samples fortified with analytes at low (0.1 microgram per liter) concentrations and analyzed during March through December, 1999

[Analytes with median recoveries less than 60 percent or greater than 120 percent, or having a relative F-pseudosigma greater than 25 percent are reported with an estimated (E) remark code. Additional analytes with short holding times are also reported with an estimated remark code. Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; conc., concentration; µg/L, microgram per liter; F-pseu, F-pseudosigma (interquartile range/1.349); Rel F-pseu, relative F-pseudosigma; –, not applicable; E, estimated remark code]

Rank	P-Code	Short name	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Count	Remark code
		Parent pesticides						
63	04036	Prometryn	0.089	0.009	89.3	10.5	49	–
69	61603	Profenofos	0.073	0.011	72.9	14.9	49	–
71	34362	*alpha*-Endosulfan	0.081	0.008	81.3	9.8	49	–
75	61596	Metalaxyl	0.095	0.010	95.1	10.7	49	–
106	61600	Oxyfluorfen	0.061	0.007	61.4	11.0	49	–
108	79846	*cis*-Propiconazole	0.083	0.010	82.6	12.1	49	–
110	79847	*trans*-Propiconazole	0.081	0.009	81.4	11.6	49	–
121	61599	Myclobutanil	0.080	0.007	80.3	9.2	49	–
126	61591	Fenamiphos	0.070	0.006	70.5	9.2	49	–
127	04025	Hexazinone	0.060	0.007	60.3	12.0	49	–
128	04031	Cycloate	0.089	0.006	89.3	6.3	49	–
132	61598	Methidathion	0.077	0.010	76.9	13.1	49	–
134	82346	Ethion	0.064	0.011	64.2	16.5	49	–
211	79844	(E)-Dimethomorph	0.076	0.011	75.8	15.0	49	–
212	79845	(Z)-Dimethomorph	0.073	0.010	72.8	14.0	49	–
220	04022	Terbuthylazine	0.097	0.008	96.7	8.0	18	–
225	61592	Flumetralin	0.066	0.010	66.4	15.7	49	–
227	38801	Fenthion	0.087	0.011	86.8	12.4	49	–

Table 17. Bias and variability data from reagent-water-set samples fortified with analytes at low (0.1 microgram per liter) concentrations and analyzed during March through December, 1999—Continued

Rank	P-Code	Short name	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Count	Remark code
228	61594	Isofenphos	0.086	0.008	85.6	9.7	49	–
229	61604	Propetamphos	0.087	0.010	86.7	11.5	49	–
231	61602	Tebupirimphos	0.086	0.008	86.4	8.7	49	–
28	82662	Dimethoate	0.035	0.007	35.3	21.2	49	E
30	61610	Tribuphos	0.044	0.008	43.7	17.4	49	E
71	34357	*beta*-Endosulfan	0.091	0.009	91.0	9.5	49	E
76	61606	Tefluthrin	0.032	0.006	32.4	17.7	49	E
83	38454	Dicrotophos	0.028	0.006	28.1	22.0	49	E
93	61593	Iprodione	0.074	0.034	74.3	46.1	49	E
102	61595	Cyhalothrin	0.021	0.006	20.9	30.0	49	E
114	61586	Cypermethrin	0.047	0.014	46.6	30.9	49	E
115	38716	Sulprofos	0.066	0.013	66.3	19.9	49	E
125	61601	Phosmet	0.020	0.021	20.1	104.1	49	E
129	61585	Cyfluthrin	0.044	0.010	44.3	23.3	49	E
131	61580	Bifenthrin	0.027	0.005	27.3	19.5	49	E
230	61605	Sulfotepp	0.086	0.007	86.1	8.0	49	E
232	61607	Temephos	0.034	0.015	33.9	44.5	49	E
		Degradates						
1002	61615	2-[2-Ethyl-6-m_panol	0.084	0.009	84.3	10.7	74	–
1007	61618	2-Chloro-2,6-d_ilide	0.087	0.011	86.6	12.1	74	–
1008	61665	4-(Hydroxymeth_halin	0.081	0.019	80.6	23.6	74	–
1016	61674	Terbufos-O-ana_lfone	0.073	0.012	72.6	16.8	49	–
1033	61625	3,4-Dichloroaniline	0.081	0.014	80.6	17.6	74	–
1043	61629	3-Phenoxybenzy_cohol	0.074	0.010	74.3	13.6	74	–
1044	79842	*c*-Methyl-3-(2,_ylate	0.085	0.007	85.0	8.8	74	–
1044	79843	*t*-Methyl-3-(2,_ylate	0.090	0.007	90.4	7.6	74	–
1049	61663	Paraoxon-ethyl	0.085	0.011	84.9	13.4	49	–
1060	61652	Malaoxon	0.076	0.015	76.4	20.0	74	–
1062	61637	2-(4-tert-buty_xanol	0.086	0.010	86.1	11.3	74	–
1067	61640	Disulfoton sulfone	0.073	0.010	72.7	13.4	74	–
1071	61642	Endosulfan ether	0.102	0.011	101.6	11.1	74	–
1071	61590	Endosulfan sulfate	0.091	0.007	91.3	7.4	49	–
1076	61672	Tefluthrin met_2912]	0.060	0.010	60.1	16.8	74	–
1093	61627	3,5-Dichloroaniline	0.091	0.011	91.2	12.6	74	–
1099	61614	2,5-Dichloroaniline	0.078	0.014	77.8	17.5	74	–
1124	61660	O-Ethyl-O-meth_ioate	0.085	0.009	85.3	10.1	74	–
1231	61669	Tebupirimphos,_logue	0.076	0.012	76.4	15.4	74	–
1002	61620	2-Ethyl-6-meth_iline	0.096	0.011	96.1	11.1	74	E
1012	61636	Chlorpyrifos, _nalog	0.039	0.023	38.8	59.5	74	E
1013	61617	2-Amino-N-isop_amide	0.055	0.012	54.7	21.9	74	E
1014	61664	Paraoxon-methyl	0.072	0.014	72.4	19.9	74	E
1015	61633	4-Chloro-2-met_henol	0.060	0.021	60.4	34.1	74	E

Table 17. Bias and variability data from reagent-water-set samples fortified with analytes at low (0.1 microgram per liter) concentrations and analyzed during March through December, 1999—Continued

Rank	P-Code	Short name	Median conc. (µg/L)	F-pseu (µg/L)	Median recovery (percent)	Rel F-pseu (percent)	Count	Remark code
1024	61630	3-Trifluoromet_iline	0.041	0.015	41.1	35.9	74	E
1032	49295	1-Naphthol	0.061	0.055	60.7	90.9	73	E
1032	61611	1,4-Naphthaquinone	0.034	0.015	34.2	44.3	74	E
1034	61666	Phorate oxon	0.078	0.012	77.5	15.3	74	E
1053	61635	Azinphos-methyl-oxon	0.044	0.020	44.5	45.6	72	E
1054	61649	Fonofos, oxyge_nalog	0.077	0.007	77.0	8.6	49	E
1067	61641	Disulfoton sulfoxide	0.125	0.021	125.0	16.8	49	E
1076	61671	Tefluthrin met_9364]	0.034	0.008	33.7	24.2	74	E
1101	61631	4,4'-Dichlorob_enone	0.076	0.010	76.5	12.7	74	E
1105	61634	4-Chlorobenzyl_lfone	0.059	0.011	59.2	17.8	49	E
1125	61668	Phosmet oxon	0.016	0.013	15.6	86.3	49	E
1126	61646	Fenamiphos sulfoxide	0.022	0.010	21.9	46.5	48	E
1134	61644	Ethion monoxon	0.059	0.015	58.7	26.3	74	E
1153	38775	Dichlorvos	0.050	0.016	49.8	31.4	49	E
1227	61647	Fenthion sulfoxide	0.064	0.026	63.9	41.0	74	E
		Surrogates						
	99223	Diazinon-d_{10}, _ogate	0.094	0.010	94.4	10.7	74	–
	99224	*alpha*-HCH-d_6, _ogate	0.092	0.013	91.9	14.5	74	–

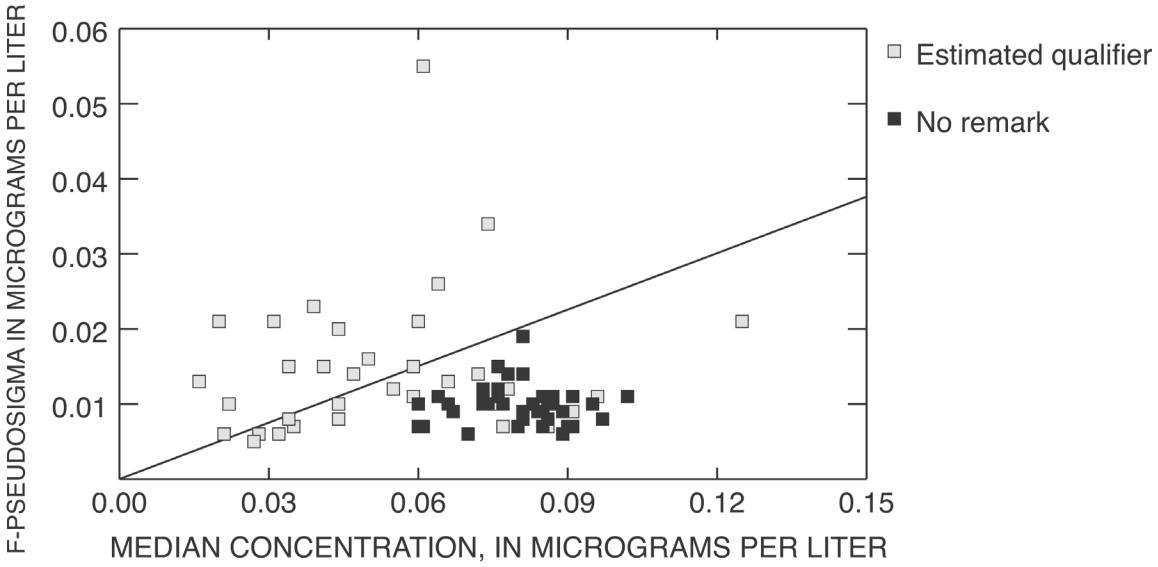

Figure 2. Bias and variability data from reagent-water-set samples fortified with analytes at low (0.1 microgram per liter) concentrations and prepared during March through December, 1999. Line shows ratio of F-pseudosigma to median of 0.25, comparable to an F-pseudosigma of 25 percent (data from table 17).

problems in all matrices and all concentrations or had short holding times. These analytes arereported with an estimated remark code to alert the data user to the greater uncertainty associated with the quantitative results. The fortified reagent-water-set sample results were used to characterize long-term bias and variability problems (table 17). Criteria for qualification as estimated were median recovery less than 60 percent or greater than 120 percent, or relative F-pseudosigma greater than 25 percent. In addition, the holding-time results were used to qualify analytes with short holding times. Criteria used were holding times in water less than 4 days or holding times on the dry SPE column less than 7 days.

The analytes qualified with "estimated" are listed in table 18. Parent pesticides qualified with estimated remark codes because of median recovery less than 60 percent were dimethoate, tribuphos, tefluthrin, dichrotophos, cyfluthrin, and bifenthrin. Degradates qualified with estimated remark codes because of low median recovery were 2-amino-N-isop_amide, 4-chlorobenzyl_lfone and tefluthrin met_9364, but disulfoton sulfoxide was qualified because of high recovery. Iprodione was qualified with estimated remark code because of relative F-pseudosigma greater than 25 percent. Cyhalothrin, cypermethrin, phosmet, and temephos were characterized by low recovery and high variability. Degradate analytes with relative F-pseudosigma greater than 25 percent included 4-chloro-2-met_henol; 1-naphthol and fenthion sulfoxide. Degradates characterized by low recovery and high variability included 1,4-naphthaquinone; chlorpyrifos, _nalog; 3-trifluoromet_iline; azinphos-methyl-oxon; phosmet oxon; fenamiphos sulfoxide; ethion monoxon; and dichlorvos.

Analytes with holding times in water less than or equal to 4 days included *beta*-endosulfan, cyhalothrin, and phosmet. None of the degradate compounds had estimated holding times less than or equal to 4 days. Sulprofos and sulfotepp are organothio-phosphate pesticides that have short holding times on the dry SPE column, even though they are apparently stable for a longer time in water. Oxidative degradation can cause loss of organothiophosphate pesticides, and it would be useful to analyze oxidative degradates of these two pesticides in the samples to determine if these pesticides were lost during storage on the SPE column. Similarly, a number of degradates appear to have short holding times on the dry SPE column, including 2-ethyl-6-meth_iline; paraoxon-methyl; 1-naphthol; phorate oxon; chlorpyrifos, _nalog; and 4,4'-dichlorob_enone. Chlorpyrifos, _nalog appears to degrade quickly on the SPE column, and this might explain high variability for this degradate in the validation experiments and fortified reagent-water samples.

OTHER CONSIDERATIONS

Automation

The method is ideally suited for automation by using laboratory systems to prepare samples. The method, with minor modifications, has been successfully used with an AutoTrace SPE Workstation. An example of the procedure and parameter setup used with the AutoTrace SPE Workstation is shown in Supplement A.

On-Site Extraction

The method also can be used with an optional on-site extraction procedure, which allows samples to be collected and processed at remote locations. This procedure reduces potential problems for some analytes that exceed the estimated pre-extraction holding-time limit in water of 4 days and avoids complications and

Table 18. Analytes qualified as estimated concentration because of large bias and variability results of fortified reagent-water-set samples (table 17) or short holding-time results (tables 13–16). Criteria for estimation were median recovery less than 60 percent, or greater than 120 percent, relative F-pseudosigma more than 25 percent, holding time in water less than 4 days, or holding time on solid-phase-extraction column less than 7 days.

[Rank, national application and use rank of pesticide; P-Code, National Water Information System parameter code; Rel F-pseu, Relative F-pseudosigma; *d*, day; SPE, solid-phase extraction; --, not within criteria; E, estimated remark code]

Rank	P–Code	Short name	Median recovery (percent)	Rel F-pseu (percent)	Water hold time (*d*)	SPE hold time (*d*)	Remark code
		Parent pesticides					
28	82662	Dimethoate	35.3	--	--	--	E
30	61610	Tribuphos	43.7	--	--	--	E
71	34357	*beta*-Endosulfan	--	--	4	--	E
76	61606	Tefluthrin	32.4	--	--	--	E
83	38454	Dicrotophos	28.1	--	--	--	E
93	61593	Iprodione	--	46.1	--	--	E
102	61595	Cyhalothrin	20.9	30.0	3	--	E
114	61586	Cypermethrin	46.6	30.9	--	--	E
115	38716	Sulprofos	--	--	--	6	E
125	61601	Phosmet	20.1	104.1	2	--	E
129	61585	Cyfluthrin	44.3	--	--	--	E
131	61580	Bifenthrin	27.3	--	--	--	E
230	61605	Sulfotepp	--	--	--	4	E
232	61607	Temephos	33.9	44.5	--	--	E
		Degradates					
1002	61620	2-Ethyl-6-meth_iline	--	--	--	5	E
1012	61636	Chlorpyrifos, _nalog	38.8	59.5	--	1	E
1013	61617	2-Amino-N-isop_amide	54.7	--	--	--	E
1014	61664	Paraoxon-methyl	--	--	--	5	E
1015	61633	4-Chloro-2-met_henol	--	34.1	--	--	E
1024	61630	3-Trifluoromet_iline	41.1	35.9	--	--	E
1032	49295	1-Naphthol	--	90.9	--	4	E
1034	61666	Phorate oxon	--	--	--	5	E
1053	61635	Azinphos-methyl-oxon	44.5	45.6	--	--	E
1054	61649	Fonofos, oxyge_nalog	--	--	--	3	E
1067	61641	Disulfoton sulfoxide	125.0	16.8	--	--	E
1076	61671	Tefluthrin met_9364]	33.7	--	--	--	E
1101	61631	4,4'-Dichlorob_enone	--	--	--	5	E
1105	61634	4-Chlorobenzyl_lfone	59.2	--	--	--	E
1125	61668	Phosmet oxon	15.6	86.3	--	--	E
1126	61646	Fenamiphos sulfoxide	21.9	46.5	--	--	E
1134	61644	Ethion monoxon	58.7	26.3	--	--	E
1032	61611	1,4-Naphthaquinone	34.2	44.3	--	--	E
1153	38775	Dichlorvos	49.8	31.4	--	--	E
1227	61647	Fenthion sulfoxide	--	41.0	--	--	E

expense of overnight shipping of samples to the laboratory. A holding-time study on damp SPE columns applicable to on-site extraction has not been conducted. Instructions for on-site processing are listed in Supplement B.

CONCLUSIONS

Solid-phase extraction with determination by gas chromatography/mass spectrometry is shown to be a sensitive and reliable method for the determination of low concentrations of a broad range of pesticides and degradates in water samples. This report presents a new method for routine analysis of 21 parent pesticides and 20 pesticide degradates in filtered natural-water samples. Estimated method detection limits range from 0.001 to 0.057 µg/L. Another 14 parent pesticides and 20 pesticide degradates demonstrated median recoveries less than 60 percent or greater than 120 percent, or had relative F-pseudosigma more than 25 percent, or holding times less than 4 days in water or 7 days on the dry solid-phase-extraction column, and, therefore, are reported in the method with an estimated remark code. This new method complements method 2001 by using the same sample preparation and analytical steps but adds 41 new analytes.

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Supplement A—Automated Solid-Phase Extraction Procedure

Zymark AutoTrace Extraction Workstation 1.20

AutoTrace Extraction Procedure: 2001 CONDITIONING/EXTRACTION 9/8/94

Estimated time for samples: 57.8 minutes
Date: 8 Sep 94

Step 1: Process 6 samples using the following procedure:
Step 2: Condition column with 3 mL of METHANOL into SOLVENT WASTE
Step 3: Condition column with 6 mL of WATER into SOLVENT WASTE
Step 4: Load 1,000 mL of sample onto column
Step 5: Dry column with gas for 4 minutes
Step 6: Pause and alert operator, resume when CONTINUE is pressed
Step 7: Clean each sample path with 50 mL cleaning solution (isopropanol: methylene chloride: toluene; 7:2:1) into SOLVENT WASTE
Step 8: Clean each sample path with 50 mL methanol into SOLVENT WASTE
Step 9: Clean each sample path with 100 mL distilled water into AQUEOUS WASTE
Step 10: Dry column with gas for 0.1 minute
Step 11: END

Setup Parameters

[mL/min, milliliters per minute; mL, milliliter]

AutoTrace Extraction Workstation

FLOW RATES (mL/min)		SOLID-PHASE EXTRACTION PARAMETERS	
Condition flow:	25	Push delay:	2 seconds
Load flow:	25	Air factor:	0.5
Rinse flow:	25	Autowash volume:	0.00 mL
Elute flow:	5		
Condition air push:	25	WORKSTATION PARAMETERS	
Rinse air push:	25	Maximum elution volume: 12.0 mL	
Elute air push:	5	Exhaust fan on:	Y Y=Yes N=No
		Beeper on:	N Y=Yes N=No

Name Solvents

Solvent 1 : Water
Solvent 2 : Methanol
Solvent 3 : Solvent 3
Solvent 4 : Solvent 4
Solvent 5 : Solvent 5

Supplement B—Instructions for On-Site Processing Using Solid-Phase Extraction (SPE)

INSTRUCTIONS FOR ON-SITE PROCESSING USING SOLID-PHASE EXTRACTION (SPE)

1. Gather the equipment and supplies needed for on-site SPE listed in table 19.

2. Record the precleaned SPE column type, lot number, and weight on the field form. Prepare the SPE column by conditioning with about 2 mL of methanol, followed by about 2 mL of water to remove excess methanol. Allow the methanol and water to flow by gravity through the column. AT NO TIME SHOULD THE COLUMN GO DRY ONCE CONDITIONING HAS STARTED (if it does, add methanol then water to recondition again). Maintain the water in the column bed by replacing the water that drains through, or by using an on-off valve to stop all water from draining out of the column.

3. Tare the weight of the amber glass 1-L sample bottle. Collect, split, and filter samples using appropriate procedures (Sandstrom, 1995). Collect about 1 L of the sample in the 1-L sample bottle (do not completely fill the bottle; leave about a 2-cm headspace to add conditioner and surrogate).

4. Weigh and record the amount of sample collected. Add about 10 mL of the methanol by using the bottle-top dispenser. Weigh and record the sample-plus-methanol weight.

5. Add the surrogate solution (1.25 ng/µL) contained in the 2-mL amber screw-cap vial (refer to Spike Kit Instruction Manual for more detailed information on use of micropipet). Use the 100-µL micropipet and a clean glass bore. Withdraw the solution into the glass bore, then put the tip into the sample bottle, below the surface of the sample (tip the bottle on the side if needed to reach below the surface with the tip of the micropipet), and press the plunger to deliver the surrogate to the sample. Withdraw the micropipet, remove and discard the glass bore, and rinse the orange-colored Teflon tip with methanol. Swirl the sample to mix. Detailed instructions on use of the micropipet are contained in the spike kit.

6. Obtain a plastic 1-L beaker for collecting the extracted water.

7. If necessary, adjust the pump flow rate to 20 to 25 mL/min by using the cleaning solutions and graduated cylinder or beaker to measure volume.

8. Insert the inlet end of the Teflon-PFA tubing from the SPE pump into the sample bottle. Turn on the pump and allow the air to be displaced from the Teflon tubing, then attach the Luer tip of the SPE column to the outlet end of the pump tubing. Invert the column to discard any conditioning water remaining in the SPE reservoir and begin collecting extracted water that passes through the column into the plastic beaker. Pump sample through the column at 20 to 25 mL/min. After sample has been pumped through column, turn off pump, disconnect SPE column, and record final weight of sample processed through the column.

9. Remove excess water from SPE column by using a syringe to blow out water. Write sample ID on side of column, and store in 40-mL glass ampule. Store columns in cool place (between 4–25°C).

CLEANING PROCEDURE

Clean all equipment after use by rinsing with a laboratory detergent (Liquinox solution, 0.2 percent), followed by rinses with about 30 mL of tap water to remove the detergent; finally, rinse with about 30 mL of methanol. Wrap all openings of cleaned material with aluminum foil.

Samples (and any materials added to samples) should contact only glass, Teflon, ceramic or stainless steel (or other metal).

QUALITY-ASSURANCE SAMPLES

Field equipment blank: Process a sample of pesticide-grade water (available from NWQL, through One Stop Shopping)[1] exactly as the samples. This includes sample bottles, compositing, splitting, and filtration equipment as well as the SPE system. Process the field-equipment blank at the start of sampling, and then after about every 10 to 15 samples. More frequent blanks are always helpful.

Field matrix spikes: Collect duplicate samples and add the 2.0-ng/µL-spike solution to one sample. Use the 100-µL micropipet to add the spike solution, which is contained in a 2-mL glass vial, after about every 20 samples. Add the surrogate to every spiked sample.

FURTHER INFORMATION

Contact Frank Wiebe (e-mail – fwwiebe@usgs.gov; 303-236-3279), or Mark Sandstrom (e-mail – sandstro@usgs.gov; 303-236-3943) for additional information.

Table 19. Equipment and supplies required for broad spectrum pesticide analysis (methods 2010 and 2011) by on-site solid-phase extraction

[mm, millimeter; in., inch; mL, milliliter; SPE, solid-phase extraction; µL, microliter; g, gram; µm, micrometer; mg, milligram; L, liter; ng/µL, nanogram per microliter]

	Number per sample
Equipment	
Filter Unit, 147-mm diameter, aluminum, and FMI Model QB-1 CKC pump and 1/4-in. diameter convoluted Teflon tubing	1
Teflon squeeze bottle, 250 mL, for methanol	1
Valveless, piston-type metering pump for SPE; FMI Model RHB 0CKC	1
Fixed volume (100-µL) micropipet	1
Portable balance (1,200.0 g)	1
Filters, 147-mm diameter, 0.7-µm pore diameter, precleaned	1–5
Bottle-top dispenser, 1–5 mL, for methanol (optional)	1
Teflon squeeze bottle, 250 mL, for pesticide-grade water	1
Supplies	
SPE columns, International Sorbent Technologies Isolute C-18, 500 mg, precleaned[1]	1
Sample bottles, 1-L, amber	1
Disposable glass bores, for 100-µL micropipet[1]	1
Surrogate mixture, 1.25 ng/µL, 2-mL vial[1]	1
Liquinox detergent, 0.2-percent solution, 200 mL	1
Pesticide-grade methanol, 200 mL	1
Pesticide-grade water, 5 mL	1
Aluminum foil, roll	1
Gloves, disposable, nonpowdered, medium	1–5
Spike kit, including Instruction Manual[1]	1
Spike mixture, 1–10 ng/µL, 2-mL vial[1]	1

[1]Supplies obtained through WRD One Stop Shopping <http://1stop.usgs.gov>.

Solid-Phase Extraction, GC/MS Analysis, Filtered Water
Methods 2010 and 2011

Station ID or Unique Number: _____ Station Name_____
Date: _____ Time _____ Collector: _____
Telephone Number of Collector: _____
Comments: _____

ON-SITE INFORMATION

☐ **Filter Sample** (0.7-µm glass fiber filter) Date filtered:_____
Prior to filtration, record bottle tare wt. _____ g

☐ **SPE Column** Brand or Type: _____
Lot #: _____
Dry Wt.: _____ g

☐ **SPE Column Conditioning:** Date of SPE procedure:_____
Methanol (2 mL): _____ mL
Pesticide-grade water (2 mL): _____ mL
(DO NOT LET COLUMN GO DRY ONCE CONDITIONING STARTED)

☐ **Sample** Sample + bottle wt.: _____ g
(-) bottle tare wt.: _____ g
= Sample wt.: _____ g
Add methanol conditioner (1% sample wt.): _____ mL
Sample + bottle + methanol: _____ g

☐ **Surrogate** Solution ID: _____
Volume added: _____ µL

☐ **QA Samples - Spike Mixture**
Solution ID: _____
Volume added (100 µL): _____ µL

☐ **Sample through column:**
Sample + plastic beaker: _____ g
plastic beaker: _____ g

☐ **Flow rate:** (=sample wt. extracted/time) _____ mL/min
Start time: _____ hr:min
Finish time: _____ hr:min

☐ Remove excess water — Write station IPD, date, time on column — Store in 40-mL vial @ 4°C

NWQL INFORMATION

Lab ID: _____ Set #: _____ Date Received_____

☐ **Dry column with N_2 or CO_2:** Date: _____
Pressure: _____ lb/in^2
Time: _____ min
Dry SPE cartridge wt.: _____ g

☐ **SPE Elution** Date: _____
Add 1.8 mL elution solvent (3:1) _____ mL

☐ **Internal Standard (PAH-d_n mixture in toluene keeper)**
Solution ID: _____
Volume added (100 µL): _____ µL

☐ **Evaporate solvent - nitrogen** Date: _____
Pressure: _____ lb/in^2
Time: _____ min

☐ **Analysis** - Instrument ID: _____ Date: _____

Comments: