METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY—DETERMINATION OF PESTICIDES IN WATER BY CARBOPAK-B SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce
kilogram/meter^2 (kg/m^2)	3.94×10^{-2}	inches of mercury
kilogram/meter^2 (kg/m^2)	1.40×10^{-3}	pounds per square inch
liter (L)	2.64×10^{-1}	gallon
meter (m)	3.28×10^{0}	foot
microliter (µL)	2.64×10^{-7}	gallon
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
nanometer (nm)	3.94×10^{-8}	inch

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

Abbreviated water-quality units used in this report are as follows:

g/L	gram per liter
kg/m^2	kilogram per square meter
µg/L	microgram per liter
µg/µL	microgram per microliter
µL/L	microliter per liter
µL/mL	microliter per milliliter
mg/L	milligram per liter
mg/mL	milligram per milliliter
mL/L	milliliter per liter
mL/min	milliliter per minute
ms	millisecond
ng/µg	nanogram per microgram
ng/L	nanogram per liter
ng/µL	nanogram per microliter
ng/mL	nanogram per milliliter

Other abbreviations also used in this report:

BDMC	4-bromo-3,5-dimethyl phenyl-n-methylcarbamate
cat. no.	catalog number
CCB	continuing calibration blank
CCV	continuing calibration verification
DAD	photodiode-array detection
DCAA	2,4-dichlorophenylacetic acid
D-R	delete code signifying sample was ruined during analysis
D-U	delete code signifying sample results were not determined because of interference
FEB	field equipment blank
FMS	field matrix spike
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
ID	identification
LCS	laboratory control spike
LRB	laboratory reagent blank
LRS	laboratory reagent spike
MDL	method detection limit
NAWQA	National Water-Quality Assessment Program
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
ODS	octadecylsilane
QA/QC	quality assurance/quality control
RF	response factor
SPE	solid-phase extraction
TFA	trifluoroacetic acid
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
v/v	volume per volume

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Abstract

In accordance with the needs of the National Water-Quality Assessment Program (NAWQA), the U.S. Geological Survey has developed and implemented a graphitized carbon-based solid-phase extraction and high-performance liquid chromatographic analytical method. The method is used to determine 41 pesticides and pesticide metabolites that are not readily amenable to gas chromatography or other high-temperature analytical techniques. Pesticides are extracted from filtered environmental water samples using a 0.5-gram graphitized carbon-based solid-phase cartridge, eluted from the cartridge into two analytical fractions, and analyzed using high-performance liquid chromatography with photodiode-array detection. The upper concentration limit is 1.6 micrograms per liter (µg/L) for most compounds. Single-operator method detection limits in organic-free water samples ranged from 0.006 to 0.032 µg/L. Recoveries in organic-free water samples ranged from 37 to 88 percent. Recoveries in ground- and surface-water samples ranged from 29 to 94 percent. 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 of 7 days.

INTRODUCTION

Some classes of pesticides that may occur in ground-water and surface-water samples are not readily amenable to analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) (Bellar and Budde, 1988; Eichelberger and others, 1988). Examples include phenyl ureas, phenoxy acids, methylcarbamates, sulfonyl ureas, and uracil-derivative pesticides. The U.S. Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) requires a broad-spectrum, sensitive analytical method for monitoring selected pesticides in these classes.

High-performance liquid chromatography (HPLC) with photodiode-array detection (DAD) and solid-phase extraction has been used for the chromatographic separation, identification, and quantification of phenyl ureas, phenoxy acids, methylcarbamates, sulfonyl ureas, and uracil-derivative pesticides isolated in natural-water samples (Di Corcia and Marchetti, 1991, 1992; Di Corcia and others, 1993). The advantages of HPLC coupled with solid-phase extraction over other methods for the determination of these pesticide classes in natural-water samples include use of less solvent, rapid extraction, field-extraction capabilities, lower solvent exposure by technicians, the ability to automate the extraction procedure and determine thermally sensitive compounds. Collectively, these advantages reduce the cost of analysis and contribute to the production of high-quality data.

Di Corcia and Marchetti (1991) demonstrated that the use of Carbopak-B graphitized-carbon as a solid-phase sorbent not only provides a broad selectivity for pesticides, but also efficiently extracts pesticides at relatively high sample-flow

rates. On the basis of these results plus the need to develop the method within a short time to meet the needs of NAWQA, the choice was made to use Carbopak-B as the solid-phase sorbent.

The pesticide compounds originally considered for detection and identification by the described method included phenyl ureas, phenoxy acids, methylcarbamates, sulfonyl ureas, and uracil-derivative pesticides. Carbopak-B was well known for its ability to retain basic and neutral species compounds, and the work by Di Corcia and Marchetti (1991) suggested that activation of the Carbopak-B with ascorbic acid would enhance the retention of acidic compounds such as the phenoxy acid herbicides. From this information, a sample-preparation technique was designed that would use the ascorbic acid activation, along with a selective differential elution (solvent mediated desorption) from the Carbopak-B, to create two extract fractions—one containing basic and neutral compounds and the other acidic compounds.

The described method was developed by the USGS for use in the USGS National Water Quality Laboratory (NWQL). The method uses graphitized carbon-based solid-phase extraction coupled with DAD-based high-performance liquid chromatography for detection. The method supplements other methods of the USGS for determination of organic substances in water that are described by Wershaw and others (1987) and by Fishman (1993).

This report provides a detailed description of all aspects of the method, including equipment, reagents, sample extraction and elution techniques, sampling protocol, tabulated quality-control data, calculations, reporting of results, and an optional on-site procedure (the latter is described in Appendix A). Accuracy and precision data and method detection limits for 41 pesticides are presented.

The scope of the report includes determination of method performance in ultrapure water samples and in two natural-water types—a ground water and a surface water from the Denver, Colorado, region. Method performance was determined at two concentrations—0.1 and 1.0 µg/L—in each water type. Method detection limits (MDL) were determined using the method outlined by the U.S. Environmental Protection Agency (1992).

This method was provisionally approved and implemented for routine sample analysis in March 1993 as laboratory analytical schedule 2050/2051. Intended primarily for the analysis of samples associated with the NAWQA program, the method has remained in use until the present (1996) with only minor modifications. The use of this analytical schedule has been expanded to include samples from non-NAWQA programs.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Pesticides, Dissolved, Carbopak-B Extraction, High-Performance Liquid Chromatography, O-1131-95 (see table 1)

1. Application

This method is suitable for the determination of pesticides and related degradation products specified in table 1 for filtered-water samples. The method is applicable for determining pesticides and pesticide metabolites that are (1) efficiently isolated from the sample matrix and absorbed onto a Carbopak-B sorbent-filled cartridge, and (2) chromatographically resolved and identified using a HPLC equipped with a DAD. The relative importance for inclusion in the list of selected compounds was primarily considered in cases where two candidate compounds were found to chromatographically interfere with one another. In such cases, the choice was made to exclude the less-used pesticide from the final list of selected compounds.

Table 1. Compound names, uses, pesticide class, codes, and Chemical Abstract Service registry numbers

[NWQL, National Water Quality Laboratory; CAS, Chemical Abstract Service. Use: F, fungicide; H, herbicide; I, insecticide; M, metabolite. Class: B, benzonitrile; C, carbamate; CP, chlorophenoxy acid; DNP, dinitrophenol; DTA, dinitroaniline; E, ether; IS, internal standard; MA, monoacid; PH, phthalimide; P, phenoxy acid; PU, phenyl urea; PY, pyridine; PYA, pyridyloxyacetic acid; PYD, pyridazinone; PYR, pyrethroid; S, surrogate; U, uracil; --, no value]

Compound	Common name	Use	Class	Parameter code	NWQL code	CAS registry number
Acifluorfen	Blazer	H	E	49315A	5410	62476-59-9
Aldicarb	Temik	I	C	49312A	5411	116-06-3
Aldicarb sulfone	Aldicarb sulfone	M	C	49313A	5413	1646-88-4
Aldicarb sulfoxide	Aldicarb sulfoxide	M	C	49314A	5412	120-62-7
Bentazon	Basagran	H	CP	38711A	5414	25057-89-0
BDMC	BDMC	--	S	99835A	5452	--
Bromacil	Bromax	H	U	04029A	5415	314-40-9
Bromoxynil	Torch	H	B	49311A	5416	1689-84-5
Carbaryl	Sevin	I	C	49310A	5417	63-25-2
Carbofuran	Carbofuran	I	C	49309A	5418	1563-66-2
3-OH-Carbofuran	3-OH-Carbofuran	M	C	49308A	5449	16655-82-6
Chloramben	Amiben, methyl	H	P	49307A	5419	1954-81-4
Chlorothalonil	Bravo	F	PH	49306A	5421	1897-45-6
Clopyralid	Stinger	H	PY	49305A	5423	1702-17-6
2,4-D	2,4-PA	H	CP	39732B	5408	1702-17-6
2,4-DB	Butyrac	H	CP	38746B	5407	94-82-6
Dacthal, MA	Dacthal, metabolite	M	CP	49304A	5447	887-54-7
DCAA	DCAA	--	IS	--	--	19719-28-9
Dicamba	Banval	H	B	38442A	5426	1918-00-9
Dichlobenil	Dichlobenil	H	B	49303A	5404	1194-65-6
Dichlorprop	2,4-DP	H	CP	49302A	5401	120-36-5
Dinoseb	DNPB	H,I	DNP	49301A	5400	88-85-7
Diuron	DCMU	H	PU	49300A	5427	330-54-1
DNOC	Sinox	H,I	DNP	49299A	5402	534-52-1
Esfenvalerate	Asana	I	PYR	49298A	5429	66230-04-4
Fenuron	Beet-Klean	H	PU	49297A	5405	101-42-8
Fluometuron	Fluometuron	H	PU	38811A	5430	2164-17-2
Linuron	Linurex	H	PU	38478A	5432	330-55-2
MCPA	Metaxon	H	CP	38482A	5433	94-74-6
MCPB	Tropotox	H	CP	38487A	5434	94-81-5
Methiocarb	Mesurol	I	C	38501A	5436	2032-65-7
Methomyl	Lannate	I	C	49296A	5437	16752-77-5
1-Naphthol	Alpha Napthol	M	C	49295A	5438	90-15-3
Neburon	Neberex	H	PU	49294A	5403	555-37-3
Norflurazon	Telok	H	PYD	49293A	5439	27314-13-2
Oryzalin	Surflan	H	DTA	49292A	5440	19044-88-3
Oxamyl	Vydate	I	C	38866A	5441	23135-22-0
Picloram	Amdon	H	PY	49291A	5442	1918-02-1
Propham	IPC	H	C	49236A	5443	122-42-9
Propoxur	Baygon	I	C	38538A	5450	114-26-1
Silvex	2,4,5-TP	H	CP	39762B	5444	93-72-1
2,4,5-T	2,4,5-T	H	CP	39742B	5409	93-767-5
Triclopyr	Crossbow	H	PYA	49235A	5446	69633-04-1

2. Summary of Method

This method is designed for the determination of 41 pesticides and pesticide metabolites (table 1) in filtered natural-water samples. The method is applicable to pesticides that are efficiently partitioned from the water onto a graphitized carbon-based solid-phase extraction (SPE) material.

Pesticides are extracted from prefiltered water samples using disposable polypropylene syringe cartridges containing 0.5 g of a graphitized carbon sorbent. One liter of prefiltered water sample is pumped through the SPE cartridge at a flow rate of 25 mL/min. After extraction, the adsorbed base and neutral compounds are eluted from the SPE cartridge using 6 mL of an 80 percent methylene chloride and 20 percent methanol mixture. The acidic compounds then are eluted into a second collection container using 8 mL of an 80 percent methylene chloride and 20 percent methanol mixture that has been acidified with trifluoroacetic acid (0.2 percent). The methylene chloride is removed from both fractions and is replaced with a water and methanol mixture to minimize interference of methylene chloride on the HPLC. The final volume for both fractions is 800 µL. Compounds are determined in each fraction by HPLC using ultraviolet spectrometry for detection, identification, and quantification.

The terms *extraction* and *elution* are used to define specific actions during sample processing. Extraction is the transfer of the selected compounds from the sample onto the SPE cartridge. Elution is the removal of the selected compounds from the SPE cartridge.

3. Interferences

Interferences may be caused by compounds recovered from a sample matrix that have similar chemical and physical properties and are not chromatographically resolved from the compounds of interest.

4. Apparatus and Instrumentation

4.1 *Liquid chromatograph*—Hewlett Packard 1090M Series II liquid chromatographic system equipped as follows: a direct-ratio (DR5) ternary-solvent delivery system, a photodiode-array ultraviolet-absorbance detector, a 250-µL automatic syringe sampler, a 100-position random-access autosampler equipped with a cooling module, a heated column oven, and a Hewlett Packard 9000 Series 300 Chemstation computerized instrument control that has a data-acquisition and reprocessing system or equivalent.

4.2 *Analytical columns*—Beckman Ultrex Ultrasphere octadecylsilane (ODS), 5 µm; 4.6-millimeter (mm) inside diameter by 25-centimeter (cm) stainless-steel column or equivalent, and guard columns, Brownlee Laboratories, cartridge holder equipped with reverse phase RP18 Newguard cartridges or equivalent.

4.3 Use the following instrument conditions:

4.3.1 Acid fraction instrument conditions

4.3.1.1 Initial instrument conditions: Autosampler, 4°C; column oven, 40°C; elution solvent composition, 78 percent HPLC water/trifluoroacetic acid (TFA, 0.25 mL/L), 16 percent methanol, 6 percent acetonitrile; flow, 0.9 mL/min.

4.3.1.2 Acid fraction gradient profile:

Time (minutes)	Water (percent)	Methanol (percent)	Acetonitril (percent)	Flow (mL/min)
1	78	16	6	0.9
53	28	57.6	14.4	.9
56	0	80	20	.9
61	0	80	20	.9
62	78	16	20	.9
68	78	16	6	.9

4.3.1.3 Ultraviolet wavelengths:

Wavelength (nm)	Bandwidth (nm)	Reference (nm)	Bandwidth (nm)
210	4	450	80
220	4	450	80
230	4	450	80
240	4	450	80
250	4	450	80

4.3.1.4 Time range: 0 to 68 minutes.

4.3.1.5 Spectral data storage parameters: sampling interval, 640 ms; spectral range, 200 to 350 nm.

4.3.2 Base-neutral fraction instrument conditions

4.3.2.1 Initial instrument conditions: Autosampler, 4°C; column oven, 40°C; elution solvent composition, 90 percent HPLC water/TFA (0.25 mL/L); 8 percent methanol, 2 percent acetonitrile; flow, 0.9 mL/min.

4.3.2.2 Base-neutral fraction gradient profile:

Time (minutes)	Water (percent)	Methanol (percent)	Acetonitril (percent)	Flow (mL/min)
1	90	8	2	0.9
40	28	51	14	.9
53	0	50	50	.9
54	0	80	20	.9
57	0	80	20	.9
59	90	8	2	.9
65	78	16	6	.9

4.3.2.3 Ultraviolet wavelengths:

Wavelength (nm)	Bandwidth (nm)	Reference (nm)	Bandwidth (nm)
210	4	450	80
220	4	450	80
230	4	450	80
240	4	450	80
250	4	450	80

4.3.2.4 Time range: 0 to 65 minutes.

4.3.2.5 Spectral data storage parameters: sampling interval, 640 ms; spectral range, 200 to 350 nm.

4.4 Sample extraction apparatus

4.4.1 Manual apparatus

4.4.1.1 *Solid-phase extraction manifold*—Supelco, Inc., Visiprep Solid-Phase Extraction Vacuum Manifold or equivalent.

4.4.1.2 *Ceramic-piston valveless sample pumps*, capable of pumping 0 to 25 mL/min, Fluid Metering Inc. Model QSY-2 CKC or equivalent.

4.4.1.3 *Sample flow path*, all Teflon-perfluoralkoxy (PFA) 1/8-inch tubing (3.18 mm) or equivalent.

4.4.1.4 *Tefzel-tetrafluoroethylene Luer connectors* or equivalent.

4.4.1.5 *Luer stopcocks*, flow control or on-off valves, Burdick & Jackson Inert PTFE flow-control valves or equivalent.

4.5 *Vacuum pump*, must be able to draw at least 30 inches (762 kg/m^2) of mercury.

4.6 *Evaporative concentrator*, temperature controlled to 30°C and nitrogen gas pressure of 15 lb/in^2 (10.547 kg/m^2), Zymark Turbo-Vap or equivalent.

4.7 Liquid-handling apparatus

4.7.1 *Syringes*—Hamilton Gastight 1750RN, 500 µL (cat. no. 81131); Gastight 1001LTN, 1,000 µL (cat. no. 81317); and Hamilton Microliter 701, 10 µL (cat. no. 80366) or equivalent.

4.7.2 *Micropipets*—Van Waters and Rogers (VWR) 10- to 100-µL variable volume digital microdispenser (cat. no. 53506201), VWR 100-µL fixed-volume microdispenser (cat. no. 53506675), and VWR 100-µL replacement tubes (cat. no. 53508499) or equivalent.

4.7.3 *Autosampler vials*—Kimble, 2-mL, amber glass for use with aluminum crimp caps, 12 x 32 mm (cat. no. 60825G or Baxter Scientific Products C48004A) or equivalent.

4.7.4 *Vial caps and septa*—Baxter Scientific Products, aluminum crimp caps that have 11-mm dual Teflon-faced silicone rubber septa (cat. no. B777021) or equivalent.

4.8 Consumables

4.8.1 *Amber glass bottles*, 1,000 mL, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps or equivalent.

4.8.2 *Solid-phase extraction cartridges*—Supelco ENVIRO-Carb Carbopak-B, graphitized nonporous carbon, 500 mg, 120/400 mesh, in 6-mL syringe barrel or equivalent.

4.8.3 *Nitrogen gas* for sample extract concentration, ultrapure.

4.8.4 *Test tubes*, borosilicate glass, 16 mm x 100 mm, baked at 450°C for 2 hours, Kimax Brand or equivalent.

5. Reagents and Solutions

All Material Safety Data Sheets need to be read prior to using any of these materials to ensure safe handling and proper disposal.

5.1 Reagents

5.1.1 *Acetonitrile*—Burdick and Jackson, ultraviolet (UV) grade or equivalent. Sparge acetonitrile with acetonitrile at least 10 minutes prior to use.

5.1.2 *Ammonium hydroxide* (NH_4OH)—28 to 30 percent, Seastar Chemicals, Inc., reagent grade or equivalent.

5.1.3 *L–(+)–Ascorbic acid*—J.T. Baker, reagent grade or equivalent.

5.1.4 *Liquinox, liquid detergent*—Alconox Inc. or equivalent.

5.1.5 *Methanol*—Burdick and Jackson, HPLC grade or equivalent. Sparge methanol with helium at least 10 minutes prior to use.

5.1.6 *Methylene chloride*—Burdick & Jackson, pesticide grade or equivalent.

5.1.7 *Sodium chloride*—EM Science, reagent grade or equivalent.

5.1.8 *Trifluoroacetic acid (TFA)*—Pierce Chemical, Inc., reagent grade or equivalent.

5.1.9 *Water, organic-free*—Deionized and distilled water that is free from interfering organic compounds and chlorine.

5.2 Solutions

5.2.1 *Acid-fraction cartridge elution solution* [80 percent methylene chloride, 20 percent methanol, and 0.2 percent TFA (v/v)]. Mix 800 mL methylene chloride (5.1.6), 200 mL methanol (5.1.5), and 2 mL TFA (5.1.8); store in calibrated adjustable dispenser.

5.2.2 *Acid-extract diluent solution.* Mix 80 mL of organic-free water (5.1.9) with 20 mL methanol (5.1.5). Add 50 µL TFA (5.1.8), cap, mix, and store.

5.2.3 *Ammonia/methanol solution.* Dissolve 10 mL ammonium hydroxide (28 to 30 percent) (5.1.2) in 90 mL of methanol (5.1.5) and mix. Cap tightly.

5.2.4 *Ascorbic-acid aqueous solution*. Dissolve 10 g ascorbic acid (5.1.3) in 1 L organic-free water (5.1.9) and store in calibrated adjustable dispenser. Replace this solution after 4 weeks.

5.2.5 *Base-neutral fraction cartridge elution solution* [80 percent methylene chloride and 20 percent methanol (v/v)]. Mix 800 mL methylene chloride (5.1.6) and 200 mL methanol (5.1.5); store in calibrated adjustable dispenser. Also use this solution to condition the Carbopak-B cartridges.

5.2.6 *Base-neutral extract diluent solution*. Mix 80 mL of organic-free water (5.1.9) with 20 mL methanol (5.1.5). Cap and store.

5.2.7 *Detergent solution*. Dilute Liquinox (5.1.4) with organic-free water (5.1.9) to a concentration of 0.2 percent.

5.3 HPLC eluent preparation

5.3.1 For the analysis of base-neutral fractions, addition of TFA to 0.017 percent normally is sufficient to achieve chromatographic separation. For this level of eluent modification, add 170 µL/L of TFA (for example, 85 µL/500 mL, 340 µL/2 L). Use class "A" volumetric flask to measure organic-free water in desired amounts (typically in either liter or one-half liter increments). Working in a fume hood, use a dedicated syringe to add TFA to the organic-free water, with tip of needle in the water as TFA is expelled. Draw up and expel at least as great a quantity of water as there was TFA added in order to rinse residual TFA from the syringe. Sparge with helium for at least 10 minutes prior to use.

5.3.2 For analysis of the acid fractions, the water eluent needs to be modified to the 0.025-percent level. In this case, add 250 µL/L of TFA to the organic-free water. Use class "A" volumetric flask to measure organic-free water in desired amounts (typically in either liter or one-half liter increments). Working in a fume hood, use a dedicated syringe to add TFA to the water, with tip of needle in the water as TFA is expelled. Draw up and expel at least as great a quantity of water as there was TFA added in order to rinse residual TFA from the syringe. Sparge with helium for at least 10 minutes prior to use.

6. Calibration and Quality-Control Standards

6.1 Quantitative compound and surrogate solutions

6.1.1 *Stock solutions*. Prepare individual stock solutions of 1 mg/mL by dissolving 25 mg of the selected pesticides in acetonitrile in a 25-mL amber-glass volumetric flask and dilute to volume, using acetonitrile. Prepare new individual stock solutions every 6 months. Prepare trichlopyr and chlorthalonil standards every 3 months because of degradation.

6.1.2 *Primary fortified standard solutions*. Prepare combined standard solutions—one for base-neutral fraction analysis and one for acid fraction analysis—by calculating the aliquot of each individual stock solution necessary to produce a final concentration of 17.5 ng/µL, calculated as follows:

$$\text{Aliquot volume (µL)} = \frac{\text{17.5 (ng/µL target concentration) X 10 mL/standard}}{\text{solution concentration (mg/mL:µg/µL)}} \quad (1)$$

Use a variable-volume microdispenser (see 4.7.2) to add the calculated aliquot of each compound to a 10-mL amber-glass volumetric flask. Dilute the combined compounds to volume using acetonitrile. Prepare a new primary fortified standard solution every 2 to 3 months.

6.1.3 *Laboratory spike solution*. Prepare a laboratory spike solution with all compounds from both the base-neutral and acid fractions, at a final concentration of 5 ng/µL each. This solution is prepared using a Class A 25-mL volumetric flask, with methanol as the dilution solvent. The aliquot of each individual compound to be used is calculated as follows:

$$\text{Aliquot volume (µL)} = \frac{\text{5 ng/µL (target concentration) X 25 mL (final volume)}}{\text{Compound standard solution concentration (mg/mL:µg/µL)}} \quad (2)$$

Use a variable-volume microdispenser (see 4.7.2) to add each compound to the volumetric flask. Bring the final solution to volume with methanol.

The addition of 100 µL of this solution to an organic-free water matrix of approxi-mately 1 L will produce a spiked sample with all compounds at an approximate concentration of 0.5 µg/L:

$$\text{Spiked compound concentration} = \frac{\text{5 ng/µL (spike concentration) X 100 µL}}{\text{Matrix volume (~1,000 mL)}} \quad (3)$$

6.1.4 *Surrogate and internal standard solutions*. Prepare method surrogate (BDMC) and internal standard (DCAA) spike solutions for both base-neutral and acid fractions, with each surrogate and internal standard solution at a final concentration of 5 ng/µL. Prepare this solution using a Class A 25-mL volumetric flask, with methanol as the dilution solvent. Calculate the volume of each individual surrogate from the stock solution concentration of that surrogate solution (see 6.1 through 6.1.2) by using equation 4:

$$\text{Aliquot volume (µL)} = \frac{\text{5 ng/µL (target concentration) X 25 mL (final volume)}}{\text{Compound standard solution concentration (mg/mL:µg/µL)}} \quad (4)$$

Use a variable-volume microdispenser (see 4.7.2) to add the individual surrogates to the volumetric flask. Bring the final solution to volume using methanol (see 5.1.5).

The addition of 100 µL of this solution to a sample, blank, or reagent-water spike matrix of approximately 1 L will produce a surrogate spike with all compounds at an approximate concentration of 0.5 µg/L:

$$\text{Spiked compound concentration} = \frac{\text{5 ng/µL (spike concentration) X 100 µL}}{\text{Matrix volume (~1,000 mL)}} \quad (5)$$

6.1.5 *Calibration solutions*. Prepare and verify calibration curves for each compound prior to sample analysis. Analyze calibration standards at four levels in addition to a system blank. Each individual concentration is made as needed by addition of a specified volume of a stock standard solution (includes compounds at 17.5 ng/µL each) to a corresponding amount of organic-free water in an autosampler vial; the total volume of the individual calibration standard in the vial is 700 µL. The preferred quantitation levels are listed in table 2. Additional levels may be used as necessary to extend the calibrated range. Acceptable calibration curves for four or more quantitation levels must have r^2 curve-fit values greater than 0.95.

6.2 Quality-control standards preparation

6.2.1 *Continuing calibration verification (CCV) standards*. Prepare a 0.5 µg/L midcalibration-level-check sample by adding an appropriate amount of the stock solution (includes compounds at 17.5 ng/µL each) for the fraction type to be analyzed into an appropriate amount of organic-free water in an autosampler vial. Close with crimp septa cap.

6.2.2 *Continuing calibration blank (CCB) standards*. Place 695 µL of organic-free water in an autosample vial. Add 5 µL of internal standard solution to the water in the vial. Close with crimp septa cap.

6.2.3 A commercially prepared "third party" spike solution containing the same selected compounds as the laboratory spike solution (6.1.3), which is prepackaged in amber-glass ampoules, is sent to customers on request for use in spiking samples on site. Store all stock and primary fortified standards and spike and surrogate solutions in a freezer at 0°C or less.

7. Safety Precautions

7.1 Use a well-vented fume hood for all steps involving organic solvents.

7.2 Wear eye protection and the appropriate type of gloves when using any reagents.

Table 2. Calibration standard levels

[HPLC, high-performance liquid chromatography; ng/µL, nanogram per microliter; STD, standard; µL, microliter; ng, nanogram; µg/L, microgram per liter]

Standard level number	Volume of HPLC water (µL)	Aliquot of 17.5 ng/µL mixed STD solution (µL)	Aliquot of internal standard solution (µL)	Amount of compound injected on column (ng)	Standard equivalency (µg/L)
1	693	2	5	12.5	0.04
2	691	4	5	25	.08
3	679	16	5	100	.32
4	663	32	5	200	.64
5	615	80	5	500	1.6

8. Procedure

8.1 Sample filtration

Filter all schedule 2050 samples at the field site because suspended sediments will clog the solid-phase extraction cartridge during extraction, preventing the flow of water through the cartridge. Refer to Sandstrom (1995) for the USGS-approved filtration method. Occasionally, samples are not filtered on site or become cloudy (particulate formation caused by chemical reactions) during transit to the laboratory. Filter these cloudy samples at the laboratory according to the procedure outlined by Sandstrom (1995) using a 14.2-cm filter holder and positive pressure pump. Use a 0.7-µm, 14.2-cm, glass-fiber filter. Flush the filtration apparatus with 100 mL of Liquinox solution, 100 mL of water, 50 mL of methanol, and 100 mL of water between samples. Dispose of methanol in a nonchlorinated waste container.

8.2 Solid-phase extraction cartridge cleaning and conditioning

8.2.1 Prepare, as needed, the 80 percent methylene chloride/20 percent methanol and 10-g/L aqueous ascorbic acid solutions for conditioning the SPE cartridges.

8.2.2 Install 6-mL Carbopack-B SPE cartridges on a vacuum extraction manifold. Use a vacuum pump to draw the conditioning solutions through the cartridge.

NOTE 1: Do not exceed 20 mm mercury vacuum pressure, or the extraction chamber might implode.

8.2.3 Pass through each cartridge two 5-mL aliquots of the 80 percent methylene chloride and 20 percent methanol solution (acid-fraction cartridge elution solution, 5.2.1).

8.2.4 Pass 5 mL of methanol through each cartridge.

8.2.5 Pass three 5-mL aliquots of aqueous ascorbic acid solution through each cartridge. Total ascorbic acid solution through each cartridge should be 15 mL.

NOTE 2: To ensure proper conditioning, keep the flow rate of ascorbic acid solution at no more than 3 mL/min.

8.2.6 Collect the conditioning solvents in the vacuum manifold; place these solvents in a chlorinated waste container for proper disposal.

8.2.7 Cover conditioned cartridges with foil and set aside until ready for use. Cartridges may be prepared up to but not

more than 8 hours in advance of extraction. **After conditioning, cartridges should never be allowed to dry.**

8.3 Solid-phase extraction

8.3.1 Prior to extraction, determine the pH of the sample using pH paper ranging from 0 to 14, and record the pH. Do not adjust the sample pH. Record the combined sample and bottle mass. Note any unusual appearance of the sample and record it. Add 100 µL of surrogate solution and 10 g of sodium chloride (NaCl) to each sample. Shake samples well to dissolve the NaCl.

8.3.2 Prepare sample set extraction blank and spike samples. Obtain two cleaned and burned 1-L amber bottles. Fill them with organic-free water and add 10 g of NaCl. Shake well to dissolve the NaCl. In preparing the spike, add 100 µL of spike solution and then record the preparation date of the spike solution. Add 100 µL of surrogate solution to each. Shake the spike and blank vigorously to mix the surrogate and NaCl in the water. This procedure is necessary for all sets including field-extracted sample sets. Samples that are to be extracted at the NWQL must be extracted within 4 working days from the time the samples are received in the laboratory.

8.3.3 Clean the SPE pumps and tubing prior to use. Flush them with sequential aliquots of 50 mL of Liquinox detergent solution, 50 mL of water, and 50 mL of methanol, using the fluid-metering pump to drive the cleansing fluids through the entire extraction apparatus. Be sure to flush air through the pump systems for 1 minute to remove any residual methanol. Dispose of methanol properly.

8.3.4 Attach the conditioned cartridges to the extraction pumps (cartridges should not be reversed because of pressure buildup).

8.3.5 Pump water samples through the conditioned cartridges using a flow rate of 25 mL/min. Approximate extraction time for 1 L of sample is 40 minutes.

8.3.6 After all of the sample constituents have been extracted onto the cartridge, remove the cartridge from the SPE apparatus and label the cartridge with the laboratory ID number. Place the cartridges onto the vacuum manifold and run the vacuum pump for 30 seconds to remove any trace of water. Wrap cartridges separately by set in aluminum foil with the set number clearly marked, and place the wrapped set of cartridges in the sample refrigerator.

NOTE 3: Spikes and blanks prepared for sets of field-extracted samples are wrapped together with the sample cartridges sent to the laboratory.

8.3.7 Weigh the empty sample bottle and record mass. If a cartridge clogs and the entire sample does not pass through it, record the combined bottle weight plus remaining sample mass.

8.4 Elution

8.4.1 Sample cartridges need to be eluted within 7 days from the extraction date or within 7 days from the date they were received by the laboratory. Samples extracted onsite should be sent to the labora-tory as soon as possible (within 2 days) for elution.

NOTE 4: The 7-day elution period is based on the extraction time required for chloro-phenoxy acids and carbamates specified by the USEPA methods 8318 and 8321.

8.4.2 Retrieve the wrapped cartridge sets from the sample refrigerator.

8.4.3 Set up the cartridge elution apparatus using a vacuum manifold with a test-tube rack in the vacuum chamber and a vacuum pump.

8.4.4 The first elution step collects the base-neutral extract fraction of the samples. Elute 1 mL of methanol through each cartridge to remove residual water. Open the vacuum manifold and dispose of the eluted liquid in each tube. Pass two 3-mL aliquots of the base-neutral fraction

cartridge elution solution through the cartridge at a rate of 3 mL/min and collect in labeled base fraction test tube.

NOTE 5: Use the vacuum pump initially to draw the elution solution into the cartridge bed, and then use the vacuum only intermittently to maintain the elution rate of 3 mL/min. After the second elution aliquot has been collected, use the vacuum pump to pass a substantial amount of air through the cartridge so that all of the base-neutral fraction can be obtained.

CAUTION: Passing the elution solvent through the sorbent bed too quickly results in incomplete removal of the pesticides, low recovery, or coelution problems.

8.4.5 Label a second set of test tubes with each sample's laboratory ID number and the letter "A" (acid). Place these test tubes in the tray inside the vacuum chamber so that they line up with their respective cartridges.

8.4.6 The second elution step collects the acid extract fraction of the samples. Elute the cartridges with two 4-mL aliquots of the acid-fraction cartridge elution solution at a rate of 3 mL/min and collect in labeled acid fraction test tube.

NOTE 6: Use the vacuum pump initially to draw the elution solution into the cartridge bed, and then use the vacuum only intermittently to maintain the 3 mL/min elution rate. Remember to pass a substantial amount of air through the cartridge so that all of the acid fraction can be obtained.

8.4.7 Prior to concentration, add 50 µL of ammonia solution (5.2.3) to the acid fractions of the samples.

8.5 Concentration

8.5.1 Place acid and base-neutral fractions of samples into the Zymark TurboVap evaporation apparatus. Using a nitrogen gas stream of 10 lb/in^2 (7,030 kg/m^2) and a bath temperature of 30°C, concentrate the samples.

8.5.2 The acid fraction normally will take 20 to 30 minutes to concentrate. Concentrate until the sample becomes a heavy syrup (about 100 µL), and then bring the volume in the test tube up to approximately 800 µL with acid-extract diluent solution. The concentrated sample is ready to be transferred to an autosampler vial.

8.5.3 The base-neutral fraction normally will take 1 hour to concentrate. Concentrate the sample to about 300 µL. Bring the sample volume up to approximately 800 µL with base-neutral extract diluent solution. The concentrated sample is ready to be transferred to an autosampler vial.

8.5.4 If the acid or base-neutral fraction contains any residual methylene chloride, this solvent must be removed. Methylene chloride interferes with HPLC chromatography. Methylene chloride is present as an immiscible pool, or as small bubbles at the bottom of the test tube, or even as a cloudy appearance in the sample. If a test tube contains methylene chloride, evaporate the volume in the test tube to approximately 300 µL. Then, add about 200 µL of the base-neutral extract diluent solution. Again evaporate the liquid in the test tube to 300 µL. Repeat this process until there is no more methylene chloride in the test tube. Vortexing the sample will help disperse the methylene chloride.

8.6 Transfer samples to autosampler vials

8.6.1 Obtain clean and burned amber autosampler vials with a preprinted label. Each sample will need two vials—one vial for the acid fraction and the other for the base-neutral fraction.

8.6.2 Label each vial with the sample's laboratory ID number and set number. Also, include on the label the letter(s) "A" if the sample is the acid fraction or "BN" if the sample is the base-neutral fraction.

8.6.3 Using clean, disposable pipets, transfer each extract to the autosampler vial from the test tube. Close the vial with a Teflon septa crimp cap. Crimp the caps tightly so they cannot be turned, but not so tight that the Teflon piece is puckered or wrinkled. A puckered or wrinkled cap can allow the sample to evaporate.

8.6.4 Place the vials in a vial tray. Keep vials of the same set on the same tray. Label the vial tray with the set number.

8.6.5 Store sample vials in the freezer or refrigerator at 4°C or less until ready for analysis.

8.7 Instrument preparation

8.7.1 Start pumps and photodiode-array detector. Allow pumps and detectors to operate for at least 10 minutes to equilibrate. Observe detector output trace and verify that a stable baseline has been achieved.

8.7.2 Check the photodiode-array detector. Initiate the DAD test program and record the lamp output in the instrument log. The test may be repeated to ensure accurate readings.

8.7.3 Verify that the current lamp output reading is not less than 30 percent of the output reading recorded when the lamp was new. When lamp output falls below 30 percent of the initial reading, replace the lamp.

8.8 Initial calibration verification

8.8.1 Prior to automatic sequential analysis, validate existing calibration curves using a continuing calibration verification (CCV) standard.

8.8.2 The calibration curves are considered acceptable as long as CCV comparisons are within 20 percent (80 to 120 percent for the example indicated above) for each compound associated with the analytical fraction being tested. In addition to the 20-percent limits for CCVs in an analytical sequence, the analyst should also note instances of consistently high or low bias for all pesticides in a CCV analysis. If the initial CCV analysis fails to meet the acceptance criteria, the analyst should prepare a second CCV analysis to check for potential problems with the first CCV standard. If the second test also fails, recalibrate the HPLC system with calibration standards.

8.9 Sample setup for analytical sequence

8.9.1 Using a 10-µL syringe, add 5 µL of internal standard solution to each sample extract, method spikes and blanks, quantitation standards, CCV standards, and system blanks. Either inject the internal standard solution through the sample vial septa (being careful not to allow the needle to contact the sample extract), or remove the vial cap and replace the cap after the internal standard solution has been added.

8.9.2 Arrange samples in autosampler trays, and set up analytical sequences as listed in table 3. Repeat this pattern of blanks, CCVs, samples, and spikes for as many iterations as desired for an analytical sequence.

Table 3. Sequence sample-run order

Vial number(s)	Vial contents
0	Continuing calibration verification (CCV)
1	Continuing calibration blank (CCB)
2-11	Ten samples of a sample set (preparation set)
12	Laboratory control spike associated with preceding sample set
13	Laboratory reagent blank associated with preceding sample set
14	Continuing calibration verification (CCV)
15	Continuing calibration blank (CCB)
16-25	Ten samples of a sample set (preparation set)
26	Laboratory reagent spike associated with preceding sample set
27	Laboratory reagent blank associated with preceding sample set
28	Continuing calibration verification (CCV)
29	Continuing calibration blank (CCB)

8.10 Sequence setup and execution

8.10.1 Load samples into the instrument's autosample unit, which is equipped with a cooling unit set at 2 to 4°C.

8.10.2 Define and populate analytical sequence tables with information about the samples to be analyzed and the instrument methods to be used. These tables are saved to the data system's hard disk for use during the analytical sequence. Initiate the analytical sequence from the data system, using the sequencing program.

8.10.3 After each set of samples is analyzed, the data system automatically invokes a data-processing program. The program examines the unprocessed chromatographic data, integrates the data, and searches for peak spectra against a library of compound reference spectra. Unprocessed chromatographic data, integrated peak data, and library search data are all stored to disk.

8.10.4 Use integrated peak data to determine the amounts of internal standards, surrogates, and method compounds contained in each sample extract by computer-aided quantitation against the calibration curves of the various compounds with volume corrections made using internal standard quantitation.

8.10.5 Pass the quantitation report data and library search data to another data-processing program, which automatically compares chromatograph retention time with spectral library match identifications. The second program computes the concentration of compounds recovered from the original water sample. Store these concentrations and use them to prepare final sample-data reports to be included in the Water Data Storage and Retrieval (WATSTORE) system, and for use in quality-control functions.

8.10.6 Remove sample extract vials from the cooled autosampler and save in a sample freezer in labeled archive boxes, allowing for sample reanalysis as necessary.

8.11 Data interpretation

8.11.1 Check all chromatograms to verify that accurate peak integrations have been achieved.

8.11.2 Produce calibration curves for each pesticide, degradation product, and surrogate, using data obtained from injections of the combined standard solution.

8.11.3 Collect and store data files on computer hard disk during the instrumental analysis of a sample extract. Collect unprocessed chromatographic data for the five specified wavelength ranges along with full UV-spectral data in those instances when a peak detection threshold is exceeded. Store full UV spectra for points at the beginning and end of the peak, as well as for the peak apex and any points of inflection along the plot of detector response data. In an ideal case, five spectra are stored for each peak.

Upon completion of the acquisition of the unprocessed chromatographic data file, start computerized data processing. The first step involves producing the five sets of two-dimensional data corresponding to each detector response at specific wavelength-range signals acquired at individual times during analysis. Add these five sets of data together (Y-data values additive) to produce a data set of combined detector responses at individual times. The data system plots these composite data, incrementally examines the data to establish general signal pattern and baseline, integrates detected peaks, and stores integrated peak data and integration events to disk files. The second step in computer automated data processing uses the integrated peak data to examine the UV-spectral data for each of the detected peaks. The program then mathematically compares the UV spectra of those peaks to previously stored library spectra for each of the selected pesticides, attempting to find a comparison with a mathematical match of 95 percent or greater. Where spectral-match factors meet or exceed the 95-percent criteria, tentative compound identifications are assumed, and the data system produces a

paper printout of the peak and its spectral-match data. The data system stores the peak spectral-match data to a disk file of spectral-match data pertinent to that sample and the extract fraction that has been instrumentally analyzed.

8.11.4 Confirmation of identified selected pesticides is archived in one or both of the following ways:

8.11.4.1 Identify a pesticide peak initially by comparing the chromatographic retention time observed for a peak in a sample chromatogram to the retention of a compound peak observed in a standard chromatogram.

8.11.4.2 Qualitative compound identification is aided by comparing UV spectra between an unknown peak and a library reference spectrum for selected pesticides or degradation products. However, this comparison may not be conclusive if the unknown compounds coelute or almost coelute with the peak in question. If comparison of the unknown peak spectrum with the library reference spectra yields dissimilar spectral curves, then the presence of the selected pesticide has not been confirmed.

8.11.5 Report selected pesticides in samples by mathematical comparison of the integrated peak area of the identified pesticide with the calibration curve produced for that selected compound. This comparison is a standard function in most computerized chromatographic data systems, and the analyst needs to be familiar with the particular calculations for the system in use. See section 9 for manual calculation procedures.

8.11.6 This interpretation process yields a list of probable compound identifications for the analyst to examine for a sample and make final determinations of confirmed compound detections. The analyst also may use the data system and the stored sample data to reintegrate peaks and perform manual library comparisons to ensure more accurate quantitations and more reliable compound confirmations.

8.11.7 *Detector sensitivity*. Although several of the pesticides and degradation products have poor UV chromaphores, a library matchable spectrum can be obtained from as little as 10 ng of any of the selected pesticides or degradation products when they are free from interferences. For those selected pesticides and degradation products that have good UV chromaphores, a matchable spectrum can be obtained from 1 ng. When the monitoring wavelengths specified for this method are used, the lowest calibration standards produce signal-to-noise ratios that are greater than 4:1 for all compounds.

8.11.8 *Detector specificity*. The photodiode-array detector senses all compounds that absorb light in the range from 200 to 350 nm (operator selected range) and stores spectral data for any compounds detected by an observed change in the amplitude of signal produced for the primary or pilot UV trace at 210 ±4 nm. The UV-chromatographic traces for this method indicate those compounds absorbing in any of the five selected UV ranges: 208 to 212 nm, 218 to 222 nm, 228 to 232 nm, 238 to 242 nm, or 248 to 252 nm. For partially resolved chromatographic peaks, the data system provides for the subtraction of spectral contributions from overlying ranges, enabling separate comparisons of the UV spectra from the individual compounds. These separate comparisons enable the identification of selected pesticides and degradation products where one or more potentially interfering compounds are not completely chromatographically resolved from the selected pesticide or degradation product.

8.12 Sample reanalyses

8.12.1 If a selected pesticide has been detected in a sample or method spike that has been analyzed in sequence between two CCVs, one of which has failed for the selected pesticide detected, reanalyze the sample in a subsequent analytical sequence.

8.12.2 Flag samples with initial selected pesticide concentrations greater than 1.6 µg/L. These samples are not

reanalyzed because this procedure was developed as a screening method and was not designed to detect and quantify pesticides at concen-trations greater than 1.6 µg/L.

9. Calculations

9.1 Calculate the response factor (RF) for each pesticide in the calibration standard by the following formula:

$$RF_c = A_c / (C_s \times V_1) \quad (6)$$

where RF_c = response factor of the schedule compound in the calibration standard, in area per nanogram;

A_c = integrated peak area of schedule compound in the calibration standard;

C_s = concentration of calibration standard, in nanograms per microliter; and

V_1 = volume of standard injected (typically 250), in microliters.

9.2 Calculate the concentration of each identified schedule compound in the original sample, using equation 7:

$$\text{Concentration, in micrograms per liter} = (A_2 \times V_2 \times I_s \times L) / (RF_c \times V_3 \times I_u \times V_4 \times M) \quad (7)$$

where A_2 = integrated peak area of identified schedule compound in sample;

V_2 = sample extract volume (assumed to be 800), in microliters;

I_s = integrated peak area of internal standard peak from calibration standard;

L = 1,000 mL/L;

RF_c = response factor of the schedule compound in the calibration standard, in area per nanogram;

V_3 = injection volume of sample extract (typically 250), in microliters;

I_u = integrated peak area of internal standard peak from sample;

V_4 = volume of whole-water sample, in milliliters; and

M = 1,000 ng/µg.

9.3 Where sample extracts have been diluted for calibration bracketing, calculate the concentration of each identified schedule compound in the original sample, using equation 8:

$$\text{Concentration, in micrograms per liter} = (A_2 \times V_2 \times V_5 \times I_S \times L) / (RF_C \times V_3 \times V_6 \times I_u \times V_4 \times M) \quad (8)$$

where A_2 = integrated peak area of identified schedule compound in sample;

V_2 = sample extract volume (assumed to be 800), in microliters;

V_5 = final dilution volume, in microliters;

I_s = integrated peak area of internal standard peak from calibration standard;

L = 1,000 mL/L;

RF_c = response factor of the schedule compound in the calibration standard, in area per nanogram;

V_3 = injection volume of sample extract (typically 250), in microliters;

V_6 = aliquot taken from sample extract for dilution, in microliters;

I_u = integrated peak area of internal standard peak from sample;

V_4 = volume of whole-water sample, in milliliters; and

M = 1,000 ng/µg.

10. Reporting of Results

Compound concentrations in environmental samples are reported in micrograms per liter (µg/L). For concentrations less than 1 µg/L, report two significant figures; for concentrations greater than 1 µg/L, report three significant figures. Surrogate data are reported in percent recovered.

11. Quality Assurance/Quality Control

Laboratory extraction samples are formed into sets of 10 environmental samples with a blank and spike for a total set number of 12. Sample cartridges extracted onsite are placed into sets of 20. A blank and spike are prepared using the laboratory extraction procedure for each set of samples extracted onsite. In addition, the following QA/QC samples are analyzed with each set of environmental samples. How often these QA/QC samples are analyzed and what they monitor also are described.

11.1 *Laboratory control spike* (LCS) (also called set spike). A 1-L organic-free water sample is spiked at 0.5 µg/L for all compounds. This sample then is included with each sample set and is carried through the entire extraction, elution, and analysis procedures. The LCS recoveries represent the best possible recoveries for a known sample matrix and are used to monitor the overall method performance, including extraction, elution, and analysis.

11.2 *Laboratory reagent blank* (LRB). A 1-L organic-free water sample is spiked with the surrogate only. This sample type then is included with each sample set and is carried through the entire extraction, elution, and analysis procedures. The LRB monitors for impurities and contamination, and, because it follows the LCS in the analysis, it monitors for carryover. Approximately 350 LRBs have been analyzed and fewer than 0.1 percent had detectable concentrations of selected compounds. The low percentage of detections indicates that false positives are rarely produced by the method.

11.3 *Continuing calibration verification* (CCV). A 0.5-µg/L calibration standard containing all of the selected compounds is inserted in an autosampler vial and placed every 10 samples throughout the analysis on the HPLC. This CCV sample is used to monitor the calibration of the HPLC for variance. Control limits for the CCV are $\pm$20 percent. If the control limits are exceeded, the environmental samples are reanalyzed. Control limits for the CCV rarely are exceeded. Changes in calibration during typical analyses are $\pm$10 percent.

11.4 *Continuing calibration blank* (CCB). Place a sample of organic-free water containing only the surrogate in an autosampler vial every 10 samples throughout the analysis on the HPLC. The CCB monitors for method contamination, and because the CCB follows the CCV, it also monitors for carryover. Approximately 350 CCBs have been analyzed, and fewer than 0.1 percent had detectable concentrations of selected compounds. The low percentage of detections indicates that false positives are rarely produced by the method.

11.5 *Surrogate*. Surrogates are organic compounds that are placed into all filtered water samples prior to extraction onto the SPE cartridge. Surrogates are expected to behave similarly to selected compounds for SPE recovery and are not expected to be present in the environment. Examination of surrogate recovery for individual samples provides insights into

method performance for that particular sample. The surrogates that have been selected for this method have not performed as expected, consequently the ability to infer performance for an individual sample has been limited.

11.6 *Field equipment blank* (FEB). A sample of organic-free water is processed exactly as environmental samples using all appropriate on-site sampling equipment and techniques. This process includes bottles, compositing, splitting, and filtering. The FEB is processed at the start of sampling and then approximately every 15 to 20 samples. The FEB monitors for contamination or carryover, or both, between environmental samples.

11.7 *Field matrix spike* (FMS). An FMS is a sample collected in triplicate with two of the triplicate samples being spiked with a known quantity of selected compounds. The unspiked triplicate is used to measure the concentration of any selected compound in the environmental sample. Any selected compound concentration measured in the unspiked sample must be subtracted from the spiked sample results to ensure recovery of accurate spike data. The FMS measures the effects of the matrix on the analysis, the possibility of compound degradation, possible degradation of selected compounds, and potential physical degradation factors (for example, hot or cold transportation conditions) that could affect data quality. Analyze this sample after every 15 to 20 environmental samples, that is, take this sample in triplicate with two of these samples being spiked. These measurements allow accuracy and precision to be calculated for the spiked environmental matrix.

12. Method Performance

12.1 Performance data

An organic-free water sample, a surface-water sample collected from the South Platte River at Englewood, Colorado, and a ground-water sample collected in Jefferson County, Colorado (Arvada Well 14) were used to test method performance. Each of the samples was split into two subsets. One set was fortified with 0.1 µg/L of each method compound, and the other set was fortified with 1.0 µg/L of each method compound. Seven 1-L aliquots of each of the six subsets were prepared and analyzed following the steps outlined in this method; they were prepared by a single technician and analyzed by a single analyst using a single HPLC instrument. Accuracy and precision data from the analyses are listed in tables 4 through 9.

A method detection limit (MDL) was calculated for each compound using the formula in equation 9:

$$MDL = S \times T_{(n-1,\ 1-alpha\ =\ 0.99)} \qquad (9)$$

where S = standard deviation of replicate analyses, in micrograms per liter;

$T_{(n-1,1-alpha\ =\ 0.99)}$ = T-value for the 99 percent confidence level with n–1 degrees of freedom (Eichelberger and others, 1988); and

n = number of replicate analyses.

NOTE 7: The MDL data provided in tables 4, 6, and 8 are single operator, single instrument based. These numbers are provided as part of the method validation. Biannual MDLs are calculated for each instrument in the Organic Chemistry Program at the NWQL. The USEPA suggests that the spike concentration be 1 to 5 times the expected MDL value. This method validation was carried out at 0.1 µg/L to provide a consistent spiking concentration that would allow MDLs to be calculated for the surface- and ground-water samples.

Table 4. Accuracy and precision data from seven determinations of the method compounds at 0.1 microgram per liter in organic-free water

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Method detection limit (µg/L)
Acifluorfen	0.056	0.003	5	56	0.008
Aldicarb	.083	.006	7	83	.016
Aldicarb sulfone	.061	.006	9	61	.016
Aldicarb sulfoxide	.061	.007	12	61	.021
Bentazon	.060	.005	8	61	.014
Bromacil	.077	.004	5	77	.011
Bromoxynil	.051	.004	8	51	.012
Carbaryl	.082	.003	3	82	.008
Carbofuran	.088	.010	11	88	.028
3-OH-Carbofuran	.068	.005	7	68	.014
Chloramben	.075	.004	5	75	.011
Chlorothalonil	.057	.002	4	57	.007
Clopyralid	.046	.006	13	46	.018
2,4-D	.050	.004	9	50	.013
2,4-DB	.058	.005	8	58	.013
Dacthal, MA	.046	.005	12	46	.017
Dicamba	.045	.004	8	45	.011
Dichlobenil	.072	.004	5	72	.012
Dichlorprop	.076	.011	15	76	.032
Dinoseb	.043	.003	8	43	.010
Diuron	.072	.004	5	72	.012
DNOC	.039	.002	5	39	.006
Esfenvalerate	.041	.007	16	41	.019
Fenuron	.080	.005	6	80	.013
Fluometuron	.050	.003	7	50	.010
Linuron	.079	.002	3	79	.006
MCPA	.049	.005	10	49	.014
MCPB	.045	.003	7	45	.010
Methiocarb	.070	.009	13	70	.026
Methomyl	.066	.006	9	66	.017
1-Naphthol	.079	.002	3	79	.007
Neburon	.076	.005	7	76	.015
Norflurazon	.073	.008	11	73	.024
Oryzalin	.052	.007	13	52	.019
Oxamyl	.046	.006	14	46	.018
Picloram	.048	.002	3	48	.004
Propham	.066	.004	6	66	.011
Propoxur	.075	.003	3	75	.008
Silvex	.050	.007	14	50	.021
2,4,5-T	.046	.004	8	46	.010
Triclopyr	.048	.003	7	48	.010

Table 5. Accuracy and precision data from seven determinations of the method compounds at 1.0 microgram per liter in organic-free water

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Acifluorfen	0.564	0.024	4	56
Aldicarb	.847	.049	6	85
Aldicarb sulfone	.463	.043	9	46
Aldicarb sulfoxide	.653	.059	9	65
Bentazon	.649	.061	9	65
Bromacil	.802	.023	3	80
Bromoxynil	.468	.051	11	47
Carbaryl	.704	.263	37	70
Carbofuran	.831	.026	3	83
3-OH-Carbofuran	.684	.024	3	68
Chloramben	.775	.045	6	77
Chlorothalonil	.554	.027	5	55
Clopyralid	.433	.037	9	43
2,4-D	.531	.031	6	53
2,4-DB	.558	.055	10	56
Dacthal, MA	.433	.039	9	43
Dicamba	.442	.048	11	44
Dichlobenil	.798	.013	2	80
Dichlorprop	.637	.029	5	64
Dinoseb	.414	.022	5	41
Diuron	.798	.013	2	80
DNOC	.443	.044	10	44
Esfenvalerate	.368	.051	14	37
Fenuron	.802	.033	4	80
Fluometuron	.383	.041	11	38
Linuron	.812	.016	2	81
MCPA	.490	.039	8	49
MCPB	.487	.033	7	49
Methiocarb	.717	.064	9	72
Methomyl	.616	.047	8	62
1-Naphthol	.808	.024	3	81
Neburon	.779	.045	6	78
Norflurazon	.721	.043	6	72
Oryzalin	.529	.032	6	53
Oxamyl	.441	.065	15	44
Picloram	.483	.018	4	48
Propham	.633	.020	3	63
Propoxur	.769	.042	5	77
Silvex	.527	.029	5	53
2,4,5-T	.468	.026	6	47
Triclopyr	.510	.022	4	51

Table 7. Accuracy and precision data from seven determinations of the method compounds at 1.0 microgram per liter in surface water

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Acifluorfen	0.726	0.098	14	73
Aldicarb	.751	.080	11	75
Aldicarb sulfone	.735	.065	8	73
Aldicarb sulfoxide	.748	.071	9	75
Bentazon	.734	.070	10	73
Bromacil	.756	.079	10	76
Bromoxynil	.452	.010	2	45
Carbaryl	.837	.066	8	84
Carbofuran	.760	.067	9	66
3-OH-Carbofuran	.695	.046	7	69
Chloramben	.739	.102	14	74
Chlorothalonil	.615	.015	3	61
Clopyralid	.715	.091	13	72
2,4-D	.712	.084	12	71
2,4-DB	.694	.120	17	69
Dacthal, MA	.714	.090	13	71
Dicamba	.676	.073	19	68
Dichlobenil	.743	.052	7	74
Dichlorprop	.633	.102	17	63
Dinoseb	.743	.094	13	74
Diuron	.848	.086	10	85
DNOC	.452	.010	2	45
Esfenvalerate	.287	.032	11	29
Fenuron	.758	.075	10	76
Fluometuron	.733	.083	11	74
Linuron	.737	.075	10	74
MCPA	.718	.062	9	72
MCPB	.705	.091	13	70
Methiocarb	.636	.073	12	64
Methomyl	.703	.056	8	70
1-Naphthol	.667	.054	8	67
Neburon	.760	.094	12	76
Norflurazon	.745	.063	8	74
Oryzalin	.756	.086	11	76
Oxamyl	.659	.067	10	66
Picloram	.755	.073	10	76
Propham	.743	.080	11	74
Propoxur	.666	.269	40	67
Silvex	.717	.089	12	72
2,4,5-T	.687	.080	12	69
Triclopyr	.614	.044	7	61

Table 8. Accuracy and precision data from seven determinations of the method compounds at 0.1 microgram per liter in ground water

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Method detection limit (µg/L)
Acifluorfen	0.091	0.007	8	91	0.021
Aldicarb	.072	.005	7	72	.014
Aldicarb sulfone	.062	.006	13	62	.019
Aldicarb sulfoxide	.065	.005	8	65	.016
Bentazon	.074	.008	10	74	.022
Bromacil	.074	.014	18	74	.040
Bromoxynil	.052	.003	7	52	.011
Carbaryl	.058	.006	10	58	.018
3-OH-Carbofuran	.054	.010	18	54	.028
Carbofuran	.061	.005	8	61	.015
Chloramben	.075	.004	5	75	.011
Chlorothalonil	.063	.004	7	63	.012
Clopyralid	.046	.002	5	46	.007
2,4-D	.070	.008	11	70	.023
2,4-DB	.078	.005	6	78	.015
Dacthal, MA	.046	.012	26	46	.035
Dicamba	.047	.009	18	47	.025
Dichlobenil	.073	.004	5	73	.012
Dichlorprop	.080	.006	8	80	.018
Dinoseb	.082	.011	13	82	.032
Diuron	.073	.004	5	73	.012
DNOC	.046	.005	11	46	.015
Esfenvalerate	.034	.011	33	34	.033
Fenuron	.055	.006	11	55	.017
Fluometuron	.058	.003	6	58	.010
Linuron	.066	.006	8	66	.016
MCPA	.061	.003	5	61	.009
MCPB	.063	.003	5	63	.009
Methiocarb	.060	.005	9	60	.015
Methomyl	.054	.003	5	54	.008
1-Naphthol	.081	.007	9	81	.023
Neburon	.052	.005	9	52	.015
Norflurazon	.065	.005	8	65	.014
Oryzalin	.057	.003	5	58	.008
Oxamyl	.056	.003	5	56	.008
Picloram	.052	.004	7	52	.011
Propham	.065	.004	6	65	.011
Propoxur	.067	.011	17	76	.033
Silvex	.094	.007	8	94	.021
2,4,5-T	.072	.013	18	72	.037
Triclopyr	.057	.002	4	57	.007

Table 9. Accuracy and precision data from seven determinations of the method compounds at 1.0 microgram per liter in ground water

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Acifluorfen	0.751	0.025	3	75
Aldicarb	.669	.076	11	67
Aldicarb sulfone	.643	.012	2	64
Aldicarb sulfoxide	.669	.018	3	67
Bentazon	.686	.085	12	69
Bromacil	.692	.032	5	69
Bromoxynil	.531	.058	2	53
Carbaryl	.642	.050	8	64
3-OH-Carbofuran	.627	.019	3	63
Carbofuran	.764	.072	9	76
Chloramben	.659	.017	3	66
Chlorothalonil	.637	.030	5	64
Clopyralid	.465	.041	9	47
2,4-D	.671	.053	8	67
2,4-DB	.712	.061	9	71
Dacthal, MA	.546	.115	21	55
Dicamba	.426	.027	6	43
Dichlobenil	.712	.031	4	71
Dichlorprop	.778	.046	6	78
Dinoseb	.722	.049	7	72
Diuron	.712	.031	4	71
DNOC	.424	.051	12	42
Esfenvalerate	.410	.097	24	41
Fenuron	.540	.039	7	54
Fluometuron	.670	.059	9	67
Linuron	.720	.066	9	72
MCPA	.636	.021	3	64
MCPB	.649	.024	4	65
Methiocarb	.629	.030	5	63
Methomyl	.576	.031	5	58
1-Naphthol	.627	.066	11	63
Neburon	.626	.046	7	63
Norflurazon	.665	.020	3	66
Oryzalin	.603	.037	6	60
Oxamyl	.569	.028	5	57
Picloram	.514	.078	15	51
Propham	.640	.020	3	64
Propoxur	.670	.086	13	67
Silvex	.774	.039	5	77
2,4,5-T	.687	.055	8	69
Triclopyr	.550	.020	4	55

12.2 Performance summary

During the course of method implementation for routine sample analysis, the procedure has not proven to be as robust as suggested by Di Corcia and Marchetti (1991), particularly those procedures related to cartridge and sample preparation. Several factors were identified as having an adverse effect on method performance. These factors include the following: (1) the adequate conditioning of the Carbopak cartridge, which requires both accurately prepared reagents and careful laboratory technique; (2) the proper storage and addition of surrogate and spiking solutions; (3) the elution of compounds from the Carbopak cartridge, which requires both accurately prepared reagents and careful laboratory technique; (4) proper sample extract reduction; and (5) additional effects caused by sample matrices.

12.2.1 Cartridge conditioning

To adequately condition each Carbopak cartridge, prepare the ascorbic acid solution at no greater than 4-week intervals because the ascorbic acid degrades during storage. It is also critical that the entire exposed surface of the Carbopak cartridge sorbent bed be fully contacted by the ascorbic acid solution for about 1 minute to allow for complete sorbent activation. Without proper sorbent activation, acidic compounds might not be retained on the cartridge.

12.2.2 Spike and surrogate care

Some surrogate and laboratory spike solution components, particularly those in the N-methylcarbamate class, are highly susceptible to thermo- and photodegradation (U.S. Environmental Protection Agency, 1986a, 1986b). As such, it is critical that the quantitative surrogate spike and laboratory spike solutions be stored cold as long as possible. It is also important that samples and field-spike samples be chilled and sent to the laboratory as soon as possible to minimize any compound degradation.

The initial development of the method contained a surrogate for each elution fraction. These surrogates were intended to mimic the selected compounds in extraction and elution behavior. The surrogates chosen did not perform as expected for a variety of reasons, including co-elution with selected compounds, natural background concentration, and poor reproducibility. Although environmental data quality still can be assessed using the laboratory control spike and the laboratory reagent blank, inferences about the recovery of selected compounds for individual samples through surrogate recovery have been obscured. This problem is currently (1996) being corrected by testing Barban, a carbamate pesticide that is no longer in use.

12.2.3 Cartridge elution technique

The compound elution procedures particularly are prone to error. During the first phase of elution, the method is designed to retain on the cartridge those compounds with acidic character while completely removing all of those compounds with basic or neutral character. The eluent solutions designed to achieve these ends must be made accurately. In addition, the entire sorbent bed must be fully contacted by the eluent solutions for about 10 minutes to completely elute compounds from the cartridge. The elution rate must be kept at 1 drop per second (approximately 3 mL/min) or the elution of compounds becomes highly variable and uncertain. In those instances when a vacuum source was used to accelerate the flow of eluent solutions through the cartridge, the data demonstrate that the complete elution of compounds becomes highly variable and uncertain.

12.2.4 Sample extract reduction

The volume reduction of the final sample extracts is another step in the sample preparation that can have adverse effects on method performance. The base-neutral extracts often have a small amount of residual water in them, which can form a layer covering the methylene chloride that

remains at the bottom of the concentration vessel as this step nears completion. Without adequate agitation, this methylene chloride "bubble" will not be evaporated from the extract; and, if not detected, it inadvertently may be transferred to the sample vial. If it remains undetected, the selected compounds will concentrate in the "bubble" at the bottom of the sample vial. Since the HPLC autosamplers draw sample extract from the bottom of the sample vials, this bubble will be injected into the instrument along with the majority of all compounds. The methylene chloride will alter the chromatographic retention and obscure the identification of compounds in the analysis. The nonhomogenous-compound distribution in the remaining sample extract will be useless for further analytical attempts, and the sample results would have to be deleted.

12.2.5 Sample matrix interference

In addition to these sample preparation problems, the sample matrix itself can adversely impact the performance of the method. Testing has shown that certain sample matrices may "bleed" the acidic compounds into the base-neutral fraction. This result may be caused by the presence of naturally occurring organic acids. These organic acids are extracted from the sample and acidify the eluent solution used to elute the base-neutral species, causing that solution also to elute a substantial part of the acidic compounds. In laboratory testing with such a matrix, it was determined that the addition of sodium hydroxide to the base-neutral eluent solution counteracted this effect, resulting in no measurable bleed.

12.2.6 Data comparison with U.S. Environmental Protection Agency

U.S Environmental Protection Agency (1986a, 1986b) methods 8318 and 8321 are used to monitor phenoxyacid herbicides and methylcarbamates using HPLC with photodiode-array detection. The NWQL recoveries and standard deviations along with USEPA single-operator results for low-level water spikes for compounds common to both methods are listed in table 10. The USEPA spiking concentrations were 600 and 10 times greater than the NWQL spiking concentrations. In addition, the NWQL data were produced using multiple operators and instruments, while the USEPA data were developed using a single operator and a single instrument. The data listed in table 10 show that the described method performs as well or better than the USEPA methods.

12.3 Method review

A joint NAWQA/NWQL Quality Assurance Committee was formed to review the method for performance, quality, and application. The review team evaluated the performance of each compound in the method. The findings and recommendations from this review are presented in Appendix B.

12.4 Method detection limit considerations

A concentration of 0.05 µg/L initially was used for the default numerical concentration to accompany all less-than concentrations in the data base for all selected pesticides. This concentration was arbitrarily chosen as the preliminary estimate of the MDL because of the time limitations associated with implementing the method. Several other method reporting limits were subsequently used for this purpose (including MDL concentrations in table 4) during the operational period, resulting in an inconsistent data base even though the actual practice of reporting detections and the basic method had not changed.

The NWQL has now implemented a single list of method reporting limits based on the data in tables 4, 6, and 8 and on additional in-house experiments. These new method reporting limits are listed in table 12 (Appendix B) and were implemented October 1, 1995.

Table 10. Summary of National Water Quality Laboratory method and U.S. Environmental Protection Agency method 8318/8321 for common compounds

[NWQL, National Water Quality Laboratory; USEPA, U.S. Environmental Protecion Agency; µg/L, microgram per liter]

Compounds	NWQL method			USEPA method 8318/8321		
	Mean percent recovery[1]	Standard deviation of percent recovery	Spiking concentration (µg/L)	Mean percent recovery[2]	Standard deviation of percent recovery	Spiking concentration (µg/L)
			Method 8318			
Aldicarb	61	31	0.5	75	14	300
Aldicarb sulfone	53	22	.5	75	7	300
Carbyryl	61	26	.5	81	9	300
Carbofuran	80	27	.5	80	9	300
3-OH-Carbofuran	64	30	.5	70	8	300
Methiocarb	59	29	.5	77	8	300
Methomyl	79	26	.5	81	8	300
			Method 8321			
2,4,5-T	77	28	.5	72	31	5
2,4-D	71	22	.5	26	13	5
2,4-DB	44	25	.5	29	24	5
Dicamba	64	23	.5	63	22	5
Dichlorprop	73	21	.5	43	18	5
Dinoseb	69	19	.5	73	11	5
MCPA	66	22	.5	60	23	5
Silvex	73	19	.5	62	14	5

[1]The NWQL results were produced using multiple operators (five) and multiple instruments (seven) over 2 years (about 350 data points).
[2]The USEPA results were produced using a single operator and a single instrument (nine data points).

CONCLUSIONS

Solid-phase extraction coupled with HPLC analysis is a viable method for measuring the concentration of polar pesticides and pesticide metabolites in surface- and ground-water samples. The single-operator average standard deviation at 0.1 µg/L in organic-free water samples is 8 percent. Recoveries in organic-free water samples ranged from 37 to 88 percent. The multiple operator (five), multiple instrument (seven) average relative standard deviation for 0.05 µg/L in organic-free water samples (for the 2-year period April 1993 to April 1995) is 25 percent. Recoveries in organic-free water samples spiked at 0.05 µg/L ranged from 22 to 100 percent.

Five compounds—chlorothalonil, dichlobenil, DNOC, esfenvalerate, and 1-naphthol—demonstrated variable SPE or HPLC performance, or both, and are reported as qualitative (estimate) only. The surrogate toluic acid was deleted because of variable SPE and HPLC performance.

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APPENDIXES

APPENDIX A: ON-SITE SOLID-PHASE EXTRACTION PROCEDURE

SOLID-PHASE EXTRACTION, HPLC ANALYSIS, FILTERED-WATER SAMPLES SCHEDULE 2051 FIELD INSTRUCTIONS

1. Verify that all components required to process samples are present in field supplies (table 11).

2. Prepare the ascorbic acid solution as needed. Place the entire contents of the vial (5 g) marked ascorbic acid (common name vitamin C) into the 500 mL of organic-free water. Use the analytical balance to weigh the 500 mL (500 g = 500 mL). The concentration should be 10 g/L of ascorbic acid. Prepare the solution in a 1-L, amber glass pesticide bottle and keep chilled (in a refrigerator) and capped at all times unless in use. Place the date and the preparer's initials on the bottle label along with a description of contents and the concentration of ascorbic acid. The shelf life of this reagent is 4 weeks. Make new solution when the shelf life is exceeded or when the supply is exhausted, or when the solution has not been capped or chilled for more than a day. Each sample requires 15 mL, so verify the volume needed for sampling before leaving for the field site.

Sample Collection and Filtration

3. Weigh the cleaned and burned glass 1-L sample bottle to the nearest 1 g using an analytical balance. Collect, split, and filter samples using appropriate procedures (Sandstrom, 1995).

4. Collect about 1 L of the filtered sample in the sample bottle. Leave approximately a 2-cm head space to allow the introduction of surrogate and spike solutions.

5. Weigh and record the weight of the sample collected. (See following field extraction checklist and reporting sheet.)

Surrogate/Spike Addition

6. Add the surrogate/spike solution contained in the 2-mL amber screw vial (refer to Spike Kit Instruction Manual for more detailed information on the use of micropipets). Use the 100-µL micropipet and a clean glass bore. Draw the surrogate and spike solutions into the glass bore, and then put the bore tip into the sample bottle below the surface of the water. Tip the bottle if needed to reach below the surface with the tip of the micropipet, and press the plunger to deliver the surrogate/spike into the sample. Withdraw the micropipet, remove and correctly dispose of the glass bore. Be careful not to redraw sample into the micropipet.

7. Rinse the orange-colored Teflon tip of the micropipet with methanol.

8. Add 10 g of salt (NaCl) to each sample. Cap the sample and swirl to mix.

NOTE 8: Approximately 2 cm of space above the liquid level in the bottle is necessary to allow for the addition of NaCl.

9. Add the surrogate to all samples, including field equipment blanks, duplicates, and field matrix spikes. Add the spike mixture only to those samples that are to be analyzed as field matrix spikes.

Cartridge Conditioning

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

11. If necessary, adjust the pump flow rate to 20 to 25 mL/min (approximately 1 drop per second) using the cleaning solutions and graduated cylinder or beaker and a stop watch. This should be done just before sample extraction.

12. Prepare the precleaned SPE cartridge by conditioning with 15 mL of ascorbic acid solution. Fill a clean graduated cylinder or beaker with 15 mL of the ascorbic acid solution.

Table 11. Equipment and supplies required for broad-spectrum pesticide analysis by on-site solid-phase extraction

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

Description	Number required
Equipment	
Filter unit, 147-mm diameter, aluminum	1
CKC pump, FMI Model QB-1[1], and 1/4-in. diameter convoluted Teflon tubing[1]	1
Teflon squeeze bottle, 250 mL, for methanol	1
Valveless, piston-type fluid metering pump, FMI Model RHB OCKC	1
Fixed volume (100-µL) micropipet	1
Portable balance (6,000.0 g)	1
Filters, 147-mm diameter, 0.7-µm pore diameter, precleaned[1]	1-5
Teflon squeeze bottle (250-mL) for pesticide-grade water	1
Graduated cylinder or beaker (50-mL)	2
Stopwatch	1
SPE cartridge adapter[2]	1
Tefzel male Luer connector, P-625[2]	1
Tefzel nut and union, P-623[2]	1
Supplies	
SPE cartridge, Carbopak-B, 500-mg, precleaned[2]	1
Sample bottles, 1-L, amber glass, precleaned	1
Disposable glass bores for 100-µL micropipet	1
Surrogate mixture[2]	1
Liquinox detergent, 0.2 percent solution, 4 L	1
Methanol, 4 L	1
Pesticide-grade water, 4 L	1
Aluminum foil	1
Disposable gloves, nonpowdered	1-5
Ascorbic acid solution[3], 10 g/L	
Reagent grade sodium chloride (salt), 10 g/sample	1

[1]Supplies available from the USGS Quality Water Service Unit in Ocala, Florida.

[2]Supplies obtained through NWQL-DENSUPPL. Contact Frank Wiebe.

[3]Number of samples to be taken dictates volume of ascorbic acid solution required.

Schedule 2051 Field Extraction Checklist and Reporting Sheet
Solid-Phase Extraction, HPLC Analysis, Filtered Water

Station ID or Unique Number: _____

Station Name: _____

Date: _____

Time: _____

Collector: _____

- **Filter Sample** 0.7 µm Glass Fiber Filter
- **SPE Cartridge Conditioning** Ascorbic Acid Solution _____mL [15 mL]
- **Sample**
  Sample + Bottle Weight _____g
  (-) Bottle Tare Weight _____g
  = Sample Weight _____g
- **Surrogate**
  Solution ID _____
  Volume Added _____µL
  - ◊ **QA Samples Spike Mixture**
    Solution ID _____
    Volume Added _____µL
- **Sample through Cartridge**
  Sample + Plastic Beaker _____g
  Plastic Beaker _____g
  Volume of Sample Extracted _____mL
- **Flow Rate**
  Start Time _____hr:min
  Stop Time _____hr:min

- **Write Site ID Number and Sampling Date on Cartridge**
- **Remove Excess Water**
- **Replace Cartridge in Shipping Container and Store @ 4°C**
- **Comments:**

13. Turn on the pump and then attach the cartridge adapter to the outlet end of the pump tubing.

14. Remove the SPE cartridge from the shipping container.

15. Attach the SPE cartridge to the adapter (the open end of the SPE cartridge should fit tightly over the adapter). Make sure the cartridge is seated completely against the lip of the adapter to create a leak-proof seal.

16. Place the inlet end of the pump tubing into the container holding the 15 mL of ascorbic acid solution. Pump the ascorbic acid solution through the cartridge at 20 to 25 mL/min.

17. After all of the ascorbic acid solution has been pumped through the cartridge, allow air to be pumped through the cartridge for 1 minute. The conditioned cartridge is now ready to be used for sample extraction. Extract the sample within 8 hours of the ascorbic acid conditioning.

Sample Extraction

18. Place the inlet end of the pump's Teflon tubing into the sample container.

19. Pump sample through the SPE cartridge at 20 to 25 mL/min.

20. After sample has been pumped through the cartridge, turn off the pump, disconnect the SPE cartridge, weigh the empty sample bottle, and record the final weight of sample processed through the cartridge [(Sample + Bottle Weight) – (Empty Weight of Bottle)].

Sample Shipment

21. Remove excess water from the SPE cartridge using a syringe to blow out the excess water (10–20 mL of air).

22. Write site ID number and sampling date on the side of the cartridge, fill out schedule 2051 Field Sheet, and place SPE cartridge in the shipping container. Wrap schedule 2051 Field Sheet around SPE shipping container.

23. Store in cool place (refrigerator). Ship at 4°C as soon as possible (within 24 hours) to NWQL for analysis.

Cleaning Procedure

24. Clean all equipment (pump and all tubing) after use by rinsing with 50 mL of laboratory detergent (Liquinox solution 0.2 percent), followed by 50 mL of tap or distilled water to remove the detergent, and finally rinse with about 50 mL methanol.

25. Wrap all openings of cleaned material with aluminum foil to prevent particulate contamination.

Quality-Assurance Samples

26. *Field equipment blank (FEB)*. A sample of organic-free water is processed (available from NWQL) exactly as environmental samples using all appropriate field-sampling equipment and techniques. This process includes bottles, compositing, splitting, and filtering. Process FEB at the start of sampling, and then approximately every 15 to 20 samples. The FEB monitors for contamination and carryover between environmental samples.

27. *Field matrix spikes (FMS)*. A sample is collected in triplicate with two of the triplicate samples being spiked with a known quantity of selected compounds. Use the unspiked triplicate to measure any selected compound concentration in the environmental sample. Any selected compound concentration measured in the unspiked sample must be subtracted from the spiked sample results to ensure accurate spike-recovery data. The FMS measures the effects of the matrix on the analysis, the possibility of compound degradation, and potential physical degradation factors (for example, hot or cold transportation conditions) that could affect data quality. Analyze this sample every 15 to 20

environmental samples, that is, process a sample in triplicate with two of these samples being spiked. These measurements allow accuracy and precision to be calculated for the spiked environmental matrix.

For additional information, contact Frank Wiebe (FWWIEBE, 303-467-8178), Mark Burkhardt (MRBURK, 303-467-8093), or Steve Werner (SLWERNER, 303-467-8000).

APPENDIX B: QUALITY ASSURANCE/QUALITY CONTROL REVIEW COMMITTEE FINDINGS AND RECOMMENDATIONS

A joint NAWQA/NWQL Quality Assurance Committee was formed to review the method for performance, quality, and application. The review team evaluated the method performance for each compound in the method. The review team relied most heavily on the results for laboratory control spikes (LCS). Field matrix spike (FMS) data also were examined, but were not relied on heavily for the following reasons:

1. There are fewer FMS analyses than LCS analyses;

2. There are questions about the integrity of the FMS spike solution for some selected compounds; and

3. Eleven of the 41 selected compounds only have LCS data available, because they were not in the FMS mixture.

Generally, the recovery and standard deviation for laboratory and field spikes are correlated, but the laboratory spikes tend to show 10 to 30 percent higher recoveries for most compounds and have lower relative standard deviations than the field spikes (table 12).

The review team divided the data record into periods corresponding to changes or apparent changes in analytical conditions that may have affected method performance. The periods were determined using several criteria, including new standards, known operational changes, observable data trends, and team discussion. The time periods and selection criteria are listed in table 13. Each compound then was evaluated for each period on the basis of recovery and precision and the known chemical and physical properties of the compound. Generally, mean recoveries less than 50 percent and coefficients of variation greater than 100 percent for a period resulted in a recommendation to delete data for the compound during that period.

The individual compounds, time periods used for data evaluation for each compound, and mean recovery and standard deviation for the period are listed in table 14. Five compounds—chlorothalonil, dichlobenil, DNOC, esfenvalerate, and 1-naphthol—demonstrated variable SPE or HPLC performance, or both, and results should be reported as qualitative (estimate) only. One surrogate, toluic acid, was deleted from the schedule because of variable SPE and HPLC performance. The creation of any given time period for a particular selected compound was influenced by the preceding or following time period.

After reviewing data, the team recommended that recovery and precision for most of the 41 compounds in the method generally are acceptable for publication and useful for many types of data analysis. However, data for some compounds during certain periods should be deleted. Many of the compounds have had varying performance characteristics over the period of record that should be accounted for in certain data-analysis applications. The lower-than-average recovery and precision of the method (and these polar compounds, in general) result in some unique data-analysis issues. Take the following steps when using method data:

1. Replace all data showing D-R (delete code signifying sample was ruined during analysis) and D-U (delete code signifying sample results were not determined because of interference) codes with missing value codes (or their equivalent) if not already in the data base. Those working with the National Water Information System (NWIS) will never see the D-code data. Use data with E (estimate) codes generally as is, but keep the E-code designation in mind if the data are erratic. The E code generally is not intended to indicate erratic data according to NWQL Technical Memorandum 94-12 (J.W. Pritt, U.S. Geological Survey, written commun., 1994).[1] The compounds scheduled for deletion will be marked so that automatic deletion codes will be placed in the data base for all nondetections. Detections for these compounds should be considered qualitative only. These compounds will not be removed from the schedule at this time (1996).

2. Entries that are remark-coded with <0.05 µg/L will have to be treated differently depending on the application. Probably the "best estimate" of the detection limit for a particular site is the lowest concentration actually detected and reported in that matrix, if there are detections less than the MDL. Otherwise, the best estimate is the MDL listed in table 12. For some types of data analyses, set all less-than concentrations to equal the "best estimate" of the detection level; for others, set them to zero or half way (so as to plot with different symbols), or estimate the concentration using derived statistical characteristics.

3. Most of these compounds have lower recoveries than what is common for other pesticide methods. All the MDL concentrations are not corrected for lower recoveries. For an explanation of non-detections and their significance, readers are referred to tabulated recovery concentrations with the understanding that detected concentrations and detection frequencies are biased low. As mentioned earlier in this report, data users can expect a higher rate of false negatives from this method.

Generally, do not adjust numbers on the basis of reported recovery to get a better estimate of the truth for presenting basic data. However, there are a few applications where this approach may be used, as for example, when data are compared to another study that has different recoveries.

4. When reporting data in either data reports or interpretive reports, always provide basic performance data. The basic characteristics to report for each compound are the MDL and recovery and precision for the specific time period of interest. Aggregated, multiple time period LCS data and results for some compounds for the FMS also may be required, depending on the situation.

5. On the basis of data review and demonstrated variable SPE or HPLC performance, or both, five compounds—chlorothalonil, dichlobenil, DNOC, esfenvalerate, and 1-naphthol—are reported as qualitative (estimate) only. An "E" data qualifier for these compounds is associated with all data reported to the users. The surrogate toluic acid was deleted from the schedule because of variable SPE and HPLC performance.

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[1]Description and guide for interpreting low-level data supplied by NWQL for schedules 2001, 2010, 2050, and 2051. Readers who need a copy of this technical memorandum are requested to contact the Chief of the NWQL, providing the memo number and subject, or browse the NWQL Home Page on the World Wide Web (http://wwwnwql.cr.usgs.gov/USGS).

Table 12. Method analyte list, laboratory control spike mean recovery and standard deviation, field matrix spike mean recovery and standard deviation, and method detection limits

[LCS, laboratory control spike (LCS spiked at 0.5 µg/L); std. dev., standard deviation; n, number of determinations; FMS, field matrix spike (FMS spiked at 1.0 µg/L); µg/L, microgram per liter; N, compounds not in the field matrix spike mixture; MA, monoacid]

Compound	LCS mean recovery ±std. dev. (n=350)[1] (percent)	FMS mean recovery ±std. dev. (n=81)[1] (percent)	Method detection limits[2] (µg/L)
Aciflurofen	83 ± 24	N	0.035
Aldicarb	61 ± 31	35 ± 22	.016
Aldicarb sulfone	53 ± 22	20 ± 14	.016
Aldicarb sulfoxide	100 ± 35	72 ± 32	.021
Bentazon	75 ± 24	60 ± 23	.014
Bromacil	82 ± 23	61 ± 25	.035
Bromoxynil	74 ± 22	62 ± 22	.035
Carbaryl	61 ± 26	27 ± 18	.008
Carbofuran	80 ± 27	62 ± 32	.028
3-OH-Carbofuran	64 ± 30	N	.014
Chloramben	60 ± 21	N	.011
Chlorothalonil	11 ± 22	9 ± 14	.035
Clopyralid	60 ± 29	N	.050
2,4-D	71 ± 22	62 ± 24	.035
2,4-DB	44 ± 25	37 ± 14	.035
Dacthal, MA	74 ± 20	N	.017
Dicamba	64 ± 23	52 ± 28	.035
Dichlobenil	34 ± 29	N	.020
Dichlorprop	73 ± 21	68 ± 20	.032
Dinoseb	69 ± 19	65 ± 22	.035
Diuron	61 ± 23	43 ± 18	.020
DNOC	35 ± 25	52 ± 19	.035
Esfenvalerate	17 ± 21	N	.019
Fenuron	66 ± 29	79 ± 38	.013
Fluometuron	78 ± 23	61 ± 23	.035
Linuron	74 ± 24	58 ± 22	.018
MCPA	66 ± 22	59 ± 19	.050
MCPB	39 ± 26	N	.035
Methiocarb	59 ± 29	29 ± 19	.026
Methomyl	79 ± 26	57 ± 21	.017
1-Naphthol	22 ± 26	11 ± 8	.007
Neburon	69 ± 21	51 ± 20	.015
Norflurazon	78 ± 22	N	.024
Oryzalin	68 ± 22	N	.019
Oxamyl	56 ± 28	18 ± 17	.018
Picloram	55 ± 23	47 ± 24	.050
Propham	64 ± 28	101 ± 42	.035
Propoxur	76 ± 26	55 ± 34	.035
Silvex	73 ± 19	65 ± 21	.021
2,4,5-T	77 ± 28	79 ± 33	.035
Triclopyr	63 ± 24	N	.050

[1]Mean recovery and standard deviation of compound for entire time period, in percent. **NOTE:** Performance statistics for the entire period of record may not be the most appropriate for characterizing performance for some periods.

[2]Method detection limits calculated by using U.S. Environmental Protection Agency (1992) method and NWQL in-house experiments.

Table 13. Method data-evaluation and time-period criteria

[MRDP, Methods Research and Development Program]

Time period	Time-period criteria
4/9/93 – 2/7/94	Good recovery for time period.
4/9/93 – 5/3/94	Good recovery for time period.
4/9/93 – 7/16/93	MRDP performing all sample analyses.
4/9/93 – 7/30/94	Time period following was generated using a new standard.
4/9/93 – 9/7/94	Time period following had elution control valves used for sample preparation.
5/4/93 – 7/20/94	Improper standard used.
7/21/93 – 2/7/94	Visual inspection of control charts suggested data grouping.
7/21/93 – 4/1/95	Compounds that are marked for deletion showed greater recovery for all but the 4/9/93 – 7/16/93 time period.
7/21/93 – 4/18/94	Visual inspection of control charts suggested data grouping.
7/21/93 – 5/31/94	Visual inspection of control charts suggested data grouping.
2/8/94 – 5/3/94	Visual inspection of control charts suggested data grouping.
2/8/94 – 5/31/94	Following time periods used new elution control valves and a new standard.
2/8/94 – 7/30/94	Following time periods used new elution control valves and a new standard.
2/8/94 – 9/7/94	Following time period used new elution control valves and a new standard.
4/19/94 – 4/1/95	Good recovery for time period determined by visual inspection of control charts.
5/4/94 – 9/7/94	Following time period used new elution control valves and a new standard.
6/1/94 – 4/1/95	Good recovery for time period determined by visual inspection of control charts.
7/21/94 – 9/7/94	Following time period used new elution control valves and a new standard.
8/1/94 – 4/1/95	Good recovery for time period determined by visual inspection of control charts.
8/1/94 – 9/7/94	Following time period used new elution control valves and a new standard.
9/8/94 – 4/1/95	Elution control valves used for sample preparation.

Table 14. Compound, data evaluation time periods, mean recoveries, and standard deviations from April 1993 to April 1995

[MA, monoacid]

Compound	Time period (month/day/year)	Mean recovery (percent)	Standard deviation (percent)
Aciflurofen	4/93 – 4/95	83	24
	4/9/93 – 7/16/93	83	24
	7/21/93 – 4/18/94	72	20
	4/19/94 – 4/1/95	90	24
Aldicarb	4/93 – 4/95	61	31
	4/9/93 – 7/16/93	88	23
	7/21/93 – 2/7/94	71	42
	2/8/94 – 9/7/94	50	24
	9/8/94 – 4/1/95	80	25
Aldicarb sulfone	4/93 – 4/95	53	22
	4/9/93 – 7/30/94	52	23
	8/1/94 – 4/1/95	57	21
Aldicarb sulfoxide	4/93 – 4/95	100	35
	4/9/93 – 7/16/93	77	27
	7/21/93 – 5/31/94	107	41
	6/1/94 – 4/1/95	96	27
Bentazon	4/93 – 4/95	75	24
	4/9/93 – 7/16/93	76	17
	7/21/93 – 9/7/94	71	24
	9/8/94 – 4/1/95	88	20
Bromacil	4/93 – 4/95	82	23
	4/9/93 – 7/16/93	94	10
	7/21/93 – 2/7/94	94	33
	2/8/94 – 5/31/94	74	24
	6/1/94 – 4/1/95	80	17
Bromoxynil	4/93 – 4/95	74	22
	4/9/93 – 7/16/93	69	20
	7/21/93 – 9/7/94	72	23
	9/8/94 – 4/1/95	84	14
Carbaryl	4/93 – 4/95	61	26
	4/9/93 – 7/16/93	69	29
	7/21/93 – 9/7/94	58	26
	9/8/94 – 4/1/95	70	26

Table 14. Compound, data evaluation time periods, mean recoveries, and standard deviations from April 1993 to April 1995–Continued

Compound	Time period (month/day/year)	Mean recovery (percent)	Standard deviation (percent)
Carbofuran	4/93 – 4/95	80	27
	4/9/93 – 7/16/93	103	21
	7/21/93 – 5/31/94	82	31
	6/1/94 – 4/1/95	74	22
3-OH-Carbofuran	4/93 – 4/95	64	30
	4/9/93 – 7/16/93	83	21
	7/21/93 – 4/18/94	69	33
	4/19/94 – 4/1/95	59	28
Chloramben	4/93 – 4/95	60	21
	4/9/93 – 7/16/93	77	16
	7/21/93 – 2/7/94	62	27
	2/8/94 – 5/31/94	52	15
	6/1/94 – 4/1/95	62	19
Chlorothalonil	4/93 – 4/95	11	22
	4/9/93 – 7/16/93	93	2
	7/21/93 – 4/1/95	10	21
Clopyralid	4/93 – 4/95	60	29
	4/9/93 – 7/16/93	52	19
	7/21/93 – 4/18/94	51	30
	4/19/94 – 4/1/95	65	29
2,4-D	4/93 – 4/95	71	22
	4/9/93 – 7/16/93	77	32
	7/21/93 – 9/7/94	68	21
	9/8/94 – 4/1/95	82	13
2,4-DB	4/93 – 4/95	44	25
	4/9/93 – 7/16/93	65	17
	7/21/93 – 9/7/94	40	24
	9/8/94 – 4/1/95	54	24
Dacthal, MA	4/93 – 4/95	74	20
	4/9/93 – 7/30/94	71	22
	8/1/94 – 4/1/95	79	14
Dicamba	4/93 – 4/95	64	23
	4/9/93 – 7/16/93	57	28
	7/21/93 – 9/7/94	62	23
	9/8/94 – 4/1/95	78	17

Table 14. Compound, data evaluation time periods, mean recoveries, and standard deviations from April 1993 to April 1995–Continued

Compound	Time period (month/day/year)	Mean recovery (percent)	Standard deviation (percent)
Dichlobenil	4/93 – 4/95	34	29
	4/9/93 – 7/16/93	57	31
	7/21/93 – 2/7/94	47	31
	2/8/94 – 5/31/94	26	19
	6/1/94 – 4/1/95	29	29
Dichlorprop	4/93 – 4/95	73	21
	4/9/93 – 7/16/93	78	19
	7/21/93 – 4/1/95	72	21
Dinoseb	4/93 – 4/95	69	19
	4/9/93 – 7/16/93	75	15
	7/21/93 – 9/7/94	67	20
	9/8/94 – 4/1/95	75	17
Diuron	4/93 – 4/95	61	23
	4/9/93 – 7/16/93	75	26
	7/21/93 – 2/7/94	64	31
	2/8/94 – 6/31/94	51	18
	6/1/94 – 4/1/95	63	18
DNOC	4/93 – 4/95	35	25
	4/9/93 – 7/16/93	70	25
	7/21/93 – 9/7/94	29	21
	9/8/94 – 4/1/95	44	22
Esfenvalerate	4/93 – 4/95	17	21
	4/9/93 – 7/16/ 93	38	27
	7/21/93 – 4/1/95	15	19
Fenuron	4/93 – 4/95	66	29
	4/9/93 – 2/7/94	82	27
	2/8/94 – 7/30/94	67	29
	8/1/94 – 9/7/94	37	12
	9/8/94 – 4/1/95	73	26
Fluometuron	4/93 – 4/95	78	23
	4/9/93 – 7/16/93	90	12
	7/21/93 – 2/7/94	86	28
	2/8/94 – 5/31/94	65	31
	6/1/94 – 4/1/95	77	16

Table 14. Compound, data evaluation time periods, mean recoveries, and standard deviations from April 1993 to April 1995–Continued

Compound	Time period (month/day/year)	Mean recovery (percent)	Standard deviation (percent)
Linuron	4/93 – 4/95	74	24
	4/9/93 – 7/16/93	90	19
	7/21/93 – 2/7/94	76	34
	2/8/94 – 5/31/94	64	27
	6/1/94 – 4/1/95	74	18
MCPA	4/93 – 4/95	66	22
	4/9/93 – 9/7/94	63	22
	9/8/94 – 4/1/95	80	16
MCPB	4/93 – 4/95	39	26
	4/9/93 – 7/16/93	64	16
	7/21/93 – 9/7/94	35	25
	9/8/94 – 4/1/95	49	26
Methiocarb	4/93 – 4/95	59	29
	4/9/93 – 9/7/94	57	29
	9/8/94 – 4/1/95	69	26
Methomyl	4/93 – 4/95	79	26
	4/9/93 – 7/16/ 93	91	16
	7/21/93 – 2/7/94	88	31
	2/8/94 – 5/31/94	67	24
	6/1/94 – 4/1/95	83	23
1-Naphthol	4/93 – 4/95	22	26
	4/9/93 – 7/16/93	60	21
	7/21/93 – 4/1/95	19	23
Neburon	4/93 – 4/95	69	21
	4/9/93 – 7/16/93	83	12
	7/21/93 – 5/31/94	66	24
	6/1/94 – 4/1/95	69	18
Norflurazon	4/93 – 4/95	78	22
	4/9/93 – 7/16/93	88	18
	7/21/93 – 2/7/94	84	31
	2/8/94 – 5/3/94	69	17
	5/4/94 – 9/7/94	76	20
	9/8/94 – 4/1/95	85	16
Oryzalin	4/93 – 4/95	68	22
	4/9/93 – 7/16/93	82	13
	7/21/93 – 9/7/94	64	23
	9/8/94 – 4/1/95	77	17

Table 14. Compound, data evaluation time periods, mean recoveries, and standard deviations from April 1993 to April 1995–Continued

Compound	Time period (month/day/year)	Mean recovery (percent)	Standard deviation (percent)
Oxamyl	4/93 – 4/95	56	28
	4/9/93 – 7/16/93	67	31
	7/21/93 – 9/7/94	53	27
	9/8/94 – 4/1/95	65	28
Picloram	4/93 – 4/95	55	23
	4/9/93 – 7/16/93	63	22
	7/21/93 – 9/7/94	52	24
	9/8/94 – 4/1/95	67	13
Propham	4/93 – 4/95	64	28
	4/49/93 – 7/16/93	91	19
	7/21/93 – 2/7/94	79	30
	2/8/94 – 9/7/94	51	20
	9/8/94 – 4/1/95	74	25
Propoxur	4/93 – 4/95	78	26
	4/9/93 – 7/16/93	92	12
	7/21/93 – 2/7/94	100	37
	2/8/94 – 9/7/94	68	20
	9/8/94 – 4/1/95	80	20
Silvex	4/93 – 4/95	73	19
	4/9/93 – 7/16/93	77	21
	7/21/93 – 9/7/94	70	18
	9/8/94 – 4/1/95	83	18
2,4,5-T	4/93 – 4/95	77	28
	4/9/93 – 7/16/93	68	19
	7/21/93 – 2/7/94	63	25
	2/8/94 – 9/7/94	84	28
	9/8/94 – 4/1/95	76	27
Triclopyr	4/93 – 4/95	63	24
	4/9/93 – 5/3/94	69	19
	5/4/94 – 7/19/94	37	20
	7/20/94 – 9/7/94	62	24
	9/8/94 – 4/1/95	73	22