Method of Analysis and Quality-Assurance Practices for Determination of Pesticides in Water by Solid-Phase Extraction and Capillary-Column Gas Chromatography/ Mass Spectrometry at the U.S. Geological Survey California District Organic Chemistry Laboratory, 1996–99

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CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
millimeter (mm)	.03937	inch
liter (L)	.2642	gallon
liter per minute (L/min)	15.85	gallon per minute

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

$$°F = (1.8 \times °C) + 32$$

ABBREVIATIONS

µg/mL, microgram per milliliter
µL, microliter
µm, micrometer
µS/cm, microsiemen per centimeter
mg, milligram
mg/mL, milligram per milliliter
mL, milliliter
mL/min, milliliter per minute
ng/µL, nanogram per microliter
psi, pounds per square inch

ACRONYMS

GC/MS, gas chromatography/mass spectrometry
MDL, method detection limit
NWQL, National Water-Quality Laboratory
SPE, solid-phase extraction
TIC, total ion count
USGS, U.S. Geological Survey

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ABSTRACT

A method of analysis and quality-assurance practices were developed to study the fate and transport of pesticides in the San Francisco Bay-Estuary by the U.S. Geological Survey. Water samples were filtered to remove suspended-particulate matter and pumped through C-8 solid-phase extraction cartridges to extract the pesticides. The cartridges were dried with carbon dioxide and the pesticides were eluted with three cartridge volumes of hexane:diethyl ether (1:1) solution. The eluants were analyzed using capillary-column gas chromatography/ mass spectrometry in full-scan mode. Method detection limits for pesticides ranged from 0.002 to 0.025 microgram per liter for 1-liter samples. Recoveries ranged from 44 to 140 percent for 25 pesticides in samples of organic-free reagent water and Sacramento-San Joaquin Delta and Suisun Bay water fortified at 0.05 and 0.50 microgram per liter. The estimated holding time for pesticides after extraction on C-8 solid-phase extraction cartridges ranged from 10 to 257 days.

INTRODUCTION

Pesticides are applied to a great variety of crops in the Central Valley of California and their residues can enter the hydrologic system through agricultural drains and surface runoff (Larson and others, 1997). The U.S. Geological Survey (USGS), as part of the Toxic Substances Hydrology Program, has been studying the fate, transport, and biological effects of pesticides in the San Francisco Bay-Estuary, which includes the Sacramento-San Joaquin Delta and Suisun Bay, California (fig. 1). Water samples were collected from Middle River at Bacon Island in the Sacramento-San Joaquin Delta (Sacramento-San Joaquin Delta) and Suisun Bay at the Reserve Fleet (Suisun Bay).

An analytical method and quality-assurance practices were developed to determine 26 pesticides at nanogram-per-liter levels in surface-water samples. This report describes the analytical method and quality-assurance practices of the organic-chemistry laboratory at the California District Office of the USGS during 1996-99. The method involved using solid-phase extraction (SPE) cartridges to isolate pesticides from water samples and gas chromatography/mass spectrometry (GC/MS) to identify and quantify these pesticides. Quality-control practices included evaluation of method blanks and spikes, instrument performance,

and corrective actions. Method detection levels (MDLs) were calculated based on procedures by the U.S. Environmental Protection Agency (1992). The analytical method and quality-assurance practices are similar to the method detailed in Crepeau and others (1994) with the addition of four new compounds and the use of a different GC/MS (Varian Saturn 2000).

The authors express their appreciation to Holly Day Barnett, California State University, Sacramento, Foundation, for her assistance in the field sampling; to Rene Hamlin, USGS, for her assistance in the laboratory analyses; and to Rick Iwatsubo, Peter Rogerson, and Michael Schroeder, USGS, for their technical review of the manuscript.

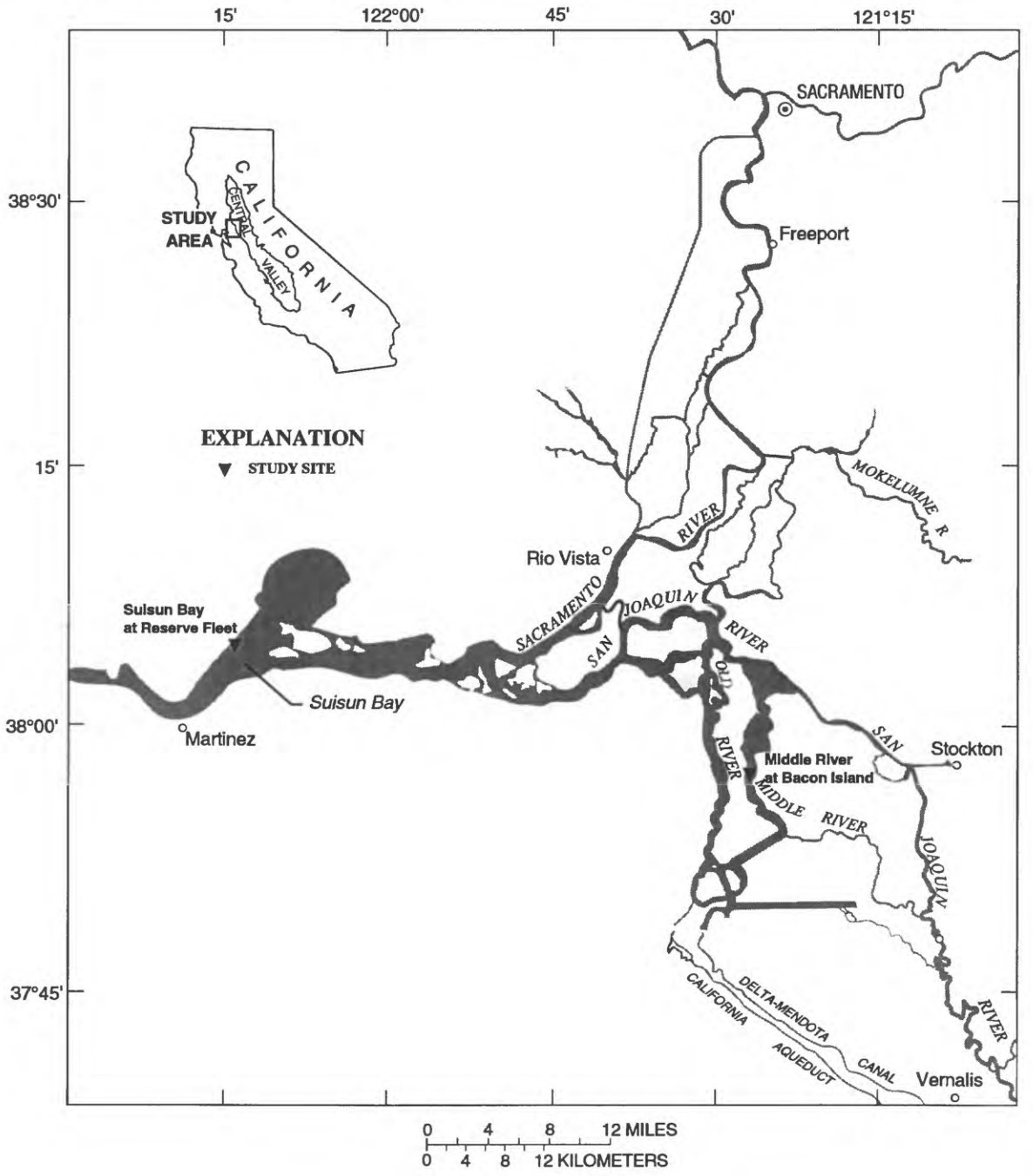

Figure 1. Study area, San Francisco Bay-Estuary, California.

ANALYTICAL METHOD

The analytical method used by the USGS California District organic-chemistry laboratory is suitable for determining nanogram-per-liter concentrations of a variety of pesticides including triazine, thiocarbamate, dinitroanaline, chloroacetamide, organophosphate, and carbamate pesticides in natural water samples. The method was developed to determine the concentration of 26 pesticides in filtered natural water (table 1). The equipment and materials required for this analysis are listed in table 2. The specific sources and models used for this

Table 1. Compound name, use, pesticide class, molecular weight, water solubility, vapor pressure, and Chemical Abstract Service registry numbers

[Data referenced from Tomlin, 1997, except where noted; g, grams; mg/L, milligram per liter; °C, degrees Celsius; mPa, millipascal; H, herbicide; TCB, thiocarbamate; DNA, dinitroaniline; I, insecticide; OP, organophosphate; TRI, triazine; CB, carbamate; AMID, Cl-acetamide; OC, organochlorine; EE, ethyl ester; DPE, diphenyl ether]

Compound (common chemical name)	Compound use	Pesticide class	Molecular weight (g)	Water solubility [mg/L (°C)]	Vapor pressure [mPa (°C)]	Chemical Abstract Service registry number
EPTC (Eptam)	H	TCB	189.3	375 (24)	[1]4500 (25)	759-94-4
Butylate (Sutan Plus)	H	TCB	217.4	36 (20)	1730 (25)	2008-41-5
Pebulate (Tillam)	H	TCB	203.3	60 (20)	4700 (25)	1114-71-2
Molinate (Ordram)	H	TCB	187.3	[1]800 (20)	746 (25)	2212-67-1
Ethalfluralin (Sonalan)	H	DNA	333.3	.3 (25)	11.7 (25)	55283-68-6
Trifluralin (Treflan)	H	DNA	335.5	.221 (25)	6.1 (25)	1582-09-8
Sulfotep	I	OP	322.3	10 (20)	14 (20)	3689-24-5
Simazine (Princep)	H	TRI	201.7	6.2 (20)	.00294 (20)	122-34-9
Carbofuran (Furandan)	I	CB	236.3	320 (20)	.072 (25)	1563-66-2
Atrazine	H	TRI	215.7	33 (20)	.039 (25)	1912-24-9
Terbuthylazine	H	TRI	229.7	8.5 (20)	.15 (25)	5915-41-3
Fonofos (Dyfonate)	I	OP	246.3	13 (22)	28 (25)	944-22-9
Diazinon	I	OP	304.3	60 (20)	12 (25)	333-41-5
Carbaryl (Sevin)	I	CB	201.2	120 (20)	.041 (23.5)	63-25-2
Alachlor (Lasso)	H	AMID	269.8	242 (25)	2.1 (25)	15972-60-8
Thiobencarb (Bolero)	H	TCB	257.8	30 (20)	2.93 (23)	28249-77-6
Malathion	I	OP	330.3	145 (25)	5.3 (30)	121-75-5
Metolachlor (Dual)	H	AMID	283.8	488 (25)	4.2 (25)	51218-45-2
Chlorpyrifos	I	OP	350.6	1.4 (25)	2.7 (25)	2921-88-2
Cyanazine	H	TRI	240.7	171 (25)	.00020 (20)	21725-46-2
Dacthal (DCPA, chlorthal-dimethyl)	H	OC	332.0	.5 (25)	.21 (25)	1861-32-1
Pendimethalin (Prowl)	H	DNA	281.3	.3 (20)	4.0 (25)	40487-42-1
Methidathion	I	OP	302.3	200 (25)	.25 (20)	950-37-8
Napropamide (Devrinol)	H	AMID	271.4	73 (20)	.53 (25)	41643-35-0
Diethatyl-ethyl	H	EE	311.8	105 (25)	.427 (30)	38727-55-8
Oxyfluorfen	H	DPE	361.7	.116 (25)	.0267 (25)	42874-03-3

[1]Weed Science Society of America, 1983.

method are included where applicable. Water samples are filtered to remove suspended-particulate matter; therefore, this method only can detect dissolved-phase pesticides or pesticides on particulate matter that can pass through the 0.7-micometer (μm) filter. The incorporation of organic-free reagent water (pesticide free) as a reference sample matrix provides a comparison for method development. The recovery of pesticides from water samples improves as the compounds partition more efficiently from the water phase to the C-8 surface phase of the SPE cartridges, provided those same compounds will be efficiently eluted by the

Table 2. List of equipment and materials required for analysis

[Sources for some items are listed to maintain quality standards. FEP, fluorinated ethylene polypropylene; OD, outside diameter; SPE, solid-phase extraction; PFA, PerfluoroalKoxy; ID, inside diameter; L, liter; mm, millimeter; μm, micrometer; mg, milligram; V, volts; mL, milliliter; m, meter]

Sampling	1-L amber pesticide bottles
Filtering	Filtration unit: Aluminum, 142-mm diameter (Geotech Environmental Equipment, Inc.) Pump: Teflon-diaphragm pump head (Cole-Parmer Model 7090-42), Masterflex drive (Cole-Parmer Model 7520-00) Filters: GF75 borosilicate glass fiber, 142-mm diameter, 0.7-μm particle retention (Advantec MFS, Inc.) Tubing: Teflon-FEP, corrugated 1/4-inch OD (Cole-Parmer Instrument Company, L-06407-60)
Extraction	SPE C-8 500 mg cartridges with steel frits (Varian, Bond-Elut, 1212-4026) Pesticide surrogate: Terbuthylazine (Chem Service, Inc., purity 98 percent) Metering pump: 12 V, ceramic piston, valveless, 1/8-inch OD tubing (Fluid Metering Inc., Model RHB-1CKC) Tubing: Teflon-PFA, 1/8-inch OD (Cole-Parmer Instrument Company) Sample Bottles: Kimax-35 1000-mL graduated media bottles with Tefon-lined caps (Kimble Glass Co.)
Drying	Carbon-dioxide gas: Coleman Instrument grade Manifold: (Supelco)*
Elution/ Concentration	n-Hexane: (EM Science, HX0296-6) Diethyl ether: preserved (JT Baker, 9259-02) Nitrogen gas: prepurified grade Internal standards: Acenaphthene d-10, purity 99 percent; Phenanthrene d-10, purity 99 percent; and Pyrene d-10, purity 98 percent) (Cambridge Isotope Laboratories, Inc.)
Analysis	Gas chromatograph: (Varian 3400 Cx) equipped with an autosampler (Varian 8200), injection port (Varian 1078), injection port liner (Supelco splitless 2.0 mm ID deactivated) and an electronic pressure controller (Varian EPC) Column: 30 m, 0.25 mm capillary ID, 0.25-μm film thickness, 5 percent phenyl-methyl silicone (J&W Scientific DB-5) Mass spectrometer with ion trap detector (Varian Saturn 2000)
Solvents	Methanol: (Spectrum, US701) Ethyl acetate: (EM Science, EX0241-1) Organic-free water: Produced on site with a recirculating Picotech water system (Hydro Service and Supplies, Inc.)
Pesticide analytical standards from Chem Service, Inc., PolyScience and the EPA Pesticide Repository[1]	

[1]EPA Pesticide Repository has been privatized.

elution solvent. The compounds must be sufficiently volatile and thermally stable to be analyzed by gas chromatography.

The USGS National Water Quality Laboratory (NWQL) developed a similar method for determining concentrations of organonitrogen herbicides in water samples (Sandstrom and others, 1991) and pesticides in water samples (Zaugg and others, 1995; Lindley and others, 1996). NWQL uses C-18-bonded phase with ethyl acetate for elution and mass spectrometry in a selected-ion monitoring mode for confirmation and quantitation. In contrast, the California District organic-chemistry laboratory uses C-8 bonded phase with hexane:diethyl ether (1:1) for elution (Hinckley and Bidleman, 1989) and an ion-trap mass spectrometer in full-scan mode for confirmation and quantitation.

The water samples were filtered into 1-liter (L) baked sample bottles using 0.7-μm pore glass-fiber filters to remove suspended-particulate matter. The volume of the filtrate was measured to 1 L using a graduated cylinder and returned to the 1-L baked bottle. Terbuthylazine, a pesticide surrogate, was added to the filtered water sample and pumped through an SPE cartridge at about 20 milliliters per minute (mL/min). The SPE cartridge was dried with a gentle stream of carbon dioxide at about 8 pounds per square inch (psi). The pesticides were eluted from the SPE cartridge with three 2-milliliter (mL) aliquots of hexane:diethyl ether (1:1). The eluant was concentrated to approximately 500 microliters (μL) in a water bath with nitrogen at 32°C. At this point, 100 μL of 2.0-nanograms per microliter (ng/μL) internal-standards solution was added to the eluant and further concentrated with nitrogen to a final volume of about 100 μL. The eluant was transferred to an auto-sample vial for analysis on the capillary-column GC/MS in full-scan mode.

Sample Processing

Filtration

Filters and sample bottles were prebaked at 450°C for 4 hours to remove any organic contaminants. Water samples were filtered in the field or within 24 hours of their arrival at the laboratory. The raw water was pumped through Teflon tubing and an aluminum filter holder with a 0.7-μm glass-fiber filter into the sample bottle. The pump incorporated a masterflex variable-speed drive and a Teflon diaphragm head. The filtered water samples were capped immediately and stored at 4°C for a maximum of 4 days before extraction.

Extraction

Each SPE cartridge sorbent bed surface was conditioned by adding a 3-mL aliquot of methanol followed by a 3-mL aliquot of organic-free water just before cartridge use. The cartridge sorbent bed surface must not become dry after conditioning or during the extraction process. The volume of each filtered-water sample was measured and recorded. Prior to extraction, 100 μL of the pesticide surrogate standard solution of terbuthylazine [2 nanograms per microliter (ng/μL)] in ethyl acetate was added to the filtered sample. The measured recovery of the surrogate provided quantitative data on the efficiency of each extraction and the variability between extractions. The filtered and spiked samples were pumped from the

sample bottle at about 20 mL/min through the SPE cartridge. After extraction, residual water was initially removed from the cartridge by forcing two 30-mL syringe volumes of air through the cartridge. The cartridges were further dried by applying a positive pressure of carbon dioxide (approximately 8 psi) for 1 hour. The extracted and dried cartridges were stored at -20°C for a maximum of 2 weeks before elution.

Elution

The pesticides were eluted from the SPE cartridge by adding three 3-mL aliquots of hexane:diethyl ether (1:1) using a 15-centimeter (cm) pasteur pipette to the cartridge and allowing the eluant to drip by gravity into a 13 × 100-millimeter (mm) glass test tube. The eluant was concentrated to approximately 500 µL by placing the test tube into a 32°C water bath and directing a nitrogen-gas stream [0.2 liters per minute (L/min)] through a 23-cm pasteur pipette to the eluant surface. Internal standard solution (100 µL of 2.0 ng/µL) was added to the concentrated eluant. The eluant was concentrated further to about 100 µL. The concentrated eluant was transferred to the autosampler vial for GC/MS analysis.

Standards

The 1.0 milligram per milliliter (mg/mL) stock solutions of analytical standards [500 micrograms per milliliter (µg/mL) for atrazine and simazine] were prepared by weighing 2–5 milligrams (mg) of each standard and adding the appropriate volume of ethyl acetate. Primary fortification standards solutions were prepared by combining the appropriate volumes of the individual stock solutions in a 10-mL volumetric flask to give a 20 ng/µL concentration. Atrazine and simazine stock solutions require a brief (15-second) sonication for addition to the solution. The internal standard stock solutions of acenapthene $d\text{-}_{10}$, phenanthrene $d\text{-}_{10}$, and pyrene $d\text{-}_{10}$ were prepared by weighing 2–5 mg of each and adding the appropriate volume of hexane. Internal standard working solution was prepared by combining 1 mL of acenapthene $d\text{-}_{10}$, phenanthrene $d\text{-}_{10}$, and pyrene $d\text{-}_{10}$ in a 5-mL volumetric flask for a 200 ng/µL concentration. The surrogate solution was prepared by diluting the stock solution of terbuthylazine in ethyl acetate to 2 ng/µL. A series of eight calibration standard solutions were prepared from the 20 ng/µL primary fortification standard solution with concentrations ranging from 0.05 to 10.0 ng/µL and a constant concentration of 2.0 ng/µL of internal standards. Matrix spike solutions at 0.5 and 5.0 ng/µL also were prepared from the 20 ng/µL primary fortification standard solution.

Gas Chromatograph/Mass Spectrometer Calibration

Initial calibration curves were generated on the GC/MS using standard solutions containing all the target pesticides before any samples were analyzed. The calibration was checked by injecting a calibration standard solution every 8 hours during sample analysis. The computer software generates linear regression equations for pesticide response over the concentration range of the calibration curve (0.05–10.0 ng/µL). If the correlation coefficients were greater than 0.99, the calibration was accepted and the software quantified the compounds detected in the sample. The conditions used for GC/MS were as follows:

Carrier gas and flow rate: Helium, research grade, 1 milliliter per minute, Electronic Pressure Control
Injector temperature and liner: 250°C isothermal, fused silica, 2.0-mm ID liner
Injection mode and volume: Splitless, 1 µL
GC column oven temperature:
[°C, degrees Celsius; min., minute]

Starting temperature (°C)	Final temperature (°C)	Ramp rate (°C/min)	Ramp time (min)	Total time (min)
60	60	0	1	1
60	120	10	6	7
120	240	5	24	31
240	275	7	5	36
275	275	0	2	38

GC injector parameters: Relay 3 (Varian injection port model #1078) on from 0.01 to 0.70 minute, for splitless injection

GC operational parameters:
- Stabilization time: 2.0 minutes
- Auxiliary heater set point: 250°C
- Detector set point: 160°C
- Column coolant flag: No
- Injector coolant flag: No
- Maximum column temperature: 350°C
- Maximum injector temperature: 350°C
- Maximum auxiliary temperature: 350°C
- Maximum detector temperature: 350°C

EPC instrumental parameters:
[psi, pounds per square inch; cm, centimeter; sec, second; mL, milliliter; min, minute]

Starting pressure (psi)	Final pressure (psi)	Ramp rate (psi/minute)	Ramp time (min)	Total time (min)	Velocity (cm/sec)	Flow (mL/min)
7.8	7.8	0.0	1	1	37.1	1.00
7.8	11.4	.6	6	7	38.2	1.01
11.4	18.6	.3	24	31	39.9	1.03
18.6	20.1	.3	5	36	39.6	1.00
20.1	20.1	.0	2	38	39.6	1.00

Auto sampler parameters:
Auto sampler - (Solvent flush bottle A, ethyl acetate)
[µL, microliter; sec, second]

Sampling mode	User defined	Lower air gap	Yes	Injection rate	5.0 µL/sec
Sample size	1.0 µL	Solvent plug size	1.0 µL	Injection time	.1 minutes
Needle depth	80 percent	Hot needle time	.0 minutes	Upper air gap	Yes

Nitrogen gas for solvent flush is prepurified grade, 40–60 psi.
MS tune parameters:
[µA, microampere; m/z, mass charge ratio; µsec, microseconds]

Segment (Electron impact)	1	Automatic gain control	1×10^5
Emission current	15 µA	Prescan ion time	100 µsec
Background mass	45 m/z	Prescan store	35.0 m/z
Tune file	Current tune file	Target value	20,000

MS instrumental parameters:

[°C, degrees Celsius; m/z, mass charge ratio; msec, milliseconds; EI, Electron Impact]

Trap temperature	220°C	Low mass	90 m/z	High mass	380 m/z
Manifold temp	40°C	Scan rate	1,000 msec	Background mass	80 m/z
Transfer line temp	275°C	Axial modulation	2.5 Volts (read back)	Scan mode	EI

Table 3 lists the compound, retention time, quantitation ion(s) and qualification ion(s) for each of the compounds used in this method.

Table 3. Retention time, quantitation ions and qualification ions for internal standards, pesticides, and surrogate compounds under analysis

[IS, internal standard; S, surrogate; A, analyte; min:s, minutes:seconds; m/z, mass per unit charge; na, not applicable]

Compound	Type	Retention time (min:s)	Quantitation ion(s) (m/z)	First qualification ion (m/z)	Second qualification ion (m/z)
Acenaphthene d-10	IS	13:32	162+164	160	134
Phenanthrene d-10	IS	19:38	188	160	94
Pyrene d-10	IS	25:58	212	106	208
Eptam	A	11:02	128+132	160	190
Butylate	A	12:29	146+156	174	218
Pebulate	A	13:08	128	160	204
Molinate	A	14:38	126	98	188
Ethalfluralin	A	17:27	276+316	292	264
Trifluralin	A	17:50	264+306	290	248
Sulfotep	A	17:54	322	294	238
Simazine	A	18:55	173+186+201	138	158
Carbofuran	A	19:01	164	131	121
Atrazine	A	19:10	200+215	202	173
Terbuthylazine	S	19:44	214	173	229
Fonofos	A	19:47	137+246	109	174
Diazinon	A	20:17	179+199+304	276	137
Carbaryl	A	22:07	115+144	116	na
Alachlor	A	22:19	160+188	146	237
Thiobencarb	A	23:26	100+125+257	132	224
Malathion	A	23:32	127	158	173
Metolachlor	A	23:41	162+238	146	211
Chlorpyrifos	A	23:53	258+314+316	286	197
Cyanazine	A	23:53	225	212	214
Dacthal	A	24:04	301+302+303	223	332
Pendimethalin	A	25:06	252	162	191
Methidathion	A	25:59	145	125	93
Napropamide	A	26:52	115+128+271	100	171
Diethatyl-ethyl	A	26:56	160+188+262	216	238
Oxyfluorfen	A	27:50	252+300	280	361

Calculation and Reporting of Results

The samples were analyzed on the GC/MS immediately after the calibration standards were analyzed. Data validation consisted of evaluating the regression lines of standard curves, evaluating the recovery of the surrogate compound, and verifying the presence or absence of targeted compounds in field samples. The blanks, matrix spike samples, and replicates were evaluated as part of the data validation. Blanks were checked to verify that no equipment or laboratory contamination had occurred during sampling and processing. The recovery of the pesticides was verified using replicate seven matrix spike samples.

The compounds must be detected throughout the range of concentrations that compose the standard curve, from 0.1 to 10 ng/μL. The MDL varies with individual compounds, according to their affinity for the cartridge sorbent bed surface, vapor pressure, thermal decomposition, chromatographic properties, and decomposition pathways during ionization. The surrogate compound, terbuthylazine, was added to assess recovery during the cartridge extraction, cartridge elution, and concentration of the samples. Samples were reanalyzed if the percent recovery of the terbuthylazine was less than or greater than the statistical control limits of ±2 standard deviations from the mean. Sample data were eliminated from the data set if poor performance of the surrogate was reproduced upon reinjection of the sample extract.

Each chromatogram was examined to verify the presence or absence of pesticides. The compounds were first qualitatively identified then quantified. The pesticide spectrum was compared with the individual compound library spectrum to verify the presence and relative abundances of significant ions. If the ion fragments were not consistent with the library spectrum, the data for that pesticide were rejected as false positives. Initial quantitation of detected pesticides was determined by manual integration of the internal standards' and detected pesticides' peak areas. The Saturn 2000 software used linear regression of response versus concentration for calibration standards to quantify the results for field samples.

Data were stored in a Lotus 1-2-3 spreadsheet format and reported electronically and by paper copy. The data included sample-site identification, date, nanograms per liter calculated by the quantitation routine for sample compounds and percent recovery of the quality-control surrogate. The concentration of each pesticide detected was reported to three significant figures. Values below the MDL are given in parentheses and nondetects are stated as such.

QUALITY-ASSURANCE PRACTICES

Method Validation

The analytical method was validated by using three water matrices: organic-free reagent water, Sacramento-San Joaquin Delta water, and Suisun Bay water. The specific conductivity and the pH of the water sample from the Sacramento-San Joaquin Delta was measured as 202 microsiemens per centimeter (μS/cm) and 7.3, respectively. The specific conductivity and the pH of the water sample from Suisun Bay was measured as

10,500 µS/cm and 6.8, respectively. The samples were split into subsamples for low- and high-spike concentrations and blanks of each pesticide. The low- and high-spike concentrations for the method were 0.05 µg/L and 0.50 µg/L, respectively. The blanks were used to determine the background concentration of the pesticides and these background concentrations were added to the matrix spike concentration for calculation of mean accuracy. Accuracy and precision data are presented in tables 4–6 and the MDLs are listed in table 7.

Table 4. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.50-microgram-per-liter concentrations in spiked, organic-free water

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

Compound	0.05 microgram per liter					0.50 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)
Eptam	0.038	0.050	0.0017	4	76	0.368	0.500	0.023	6	74
Butylate	.039	.050	.0019	5	77	.367	.500	.022	6	73
Pebulate	.039	.050	.0028	7	79	.374	.500	.030	8	75
Molinate	.041	.050	.0034	8	83	.371	.500	.015	4	74
Ethalfluralin	.032	.050	.0008	2	65	.254	.500	.015	6	51
Trifluralin	.029	.050	.0037	13	59	.252	.500	.027	11	50
Sulfotep	.036	.050	.0015	4	72	.339	.500	.014	4	68
Simazine	.038	.050	.0021	5	76	.348	.500	.030	8	70
Carbofuran	.032	.050	.0009	3	63	.267	.500	.020	7	53
Atrazine	.035	.050	.0023	7	69	.366	.500	.029	8	73
Terbuthylazine[1]	.141	.200	.0120	9	70	.147	.200	.014	10	74
Fonofos	.047	.050	.0027	6	94	.419	.500	.012	3	84
Diazinon	.038	.050	.0012	3	77	.360	.500	.010	3	72
Carbaryl	.037	.050	.0011	3	75	.262	.500	.027	10	52
Alachlor	.039	.050	.0018	5	78	.371	.500	.018	5	74
Thiobencarb	.036	.050	.0028	8	72	.406	.500	.015	4	81
Malathion	.038	.050	.0017	5	76	.388	.500	.033	9	78
Metolachlor	.042	.050	.0014	3	84	.381	.500	.017	4	76
Chlorpyrifos	.039	.050	.0012	3	78	.352	.500	.027	8	70
Cyanazine	.030	.050	.0023	8	59	.218	.500	.020	9	44
Dacthal	.035	.050	.0035	10	71	.376	.500	.019	5	75
Pendimethalin	.042	.050	.0006	1	84	.306	.500	.015	5	61
Methidathion	.042	.050	.0016	4	83	.370	.500	.022	6	74
Napropamide	.044	.050	.0013	3	89	.340	.500	.015	4	68
Diethatyl-ethyl	.041	.050	.0025	6	82	.328	.500	.014	4	66
Oxyfluorfen	.048	.050	.0026	5	97	.341	.500	.013	4	68

[1]Surrogate compound.

Accuracy and Precision

Accuracy was assessed by using recovery of spiked-sample data for the method validation. Mean recovery is calculated as follows:

Table 5. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.50-microgram-per-liter concentrations in spiked Sacramento-San Joaquin Delta water

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

Compound	0.05 microgram per liter					0.50 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)
Eptam	0.045	0.056	0.0020	5	80	0.361	0.506	0.008	2	71
Butylate	.041	.050	.0014	3	82	.366	.500	.014	4	73
Pebulate	.041	.050	.0019	5	82	.373	.500	.014	4	75
Molinate	.045	.050	.0017	4	90	.370	.500	.008	2	74
Ethalfluralin	.043	.050	.0013	3	85	.340	.500	.020	6	68
Trifluralin	.040	.051	.0021	5	78	.306	.501	.033	11	61
Sulfotep	.042	.050	.0022	5	84	.382	.500	.026	7	76
Simazine	.039	.050	.0033	8	78	.308	.500	.016	5	62
Carbofuran	.041	.050	.0024	6	82	.337	.500	.014	4	67
Atrazine	.035	.050	.0028	8	70	.295	.500	.014	5	59
Terbuthylazine[1]	.126	.200	.0126	10	63	.124	.200	.009	8	62
Fonofos	.046	.050	.0011	2	92	.406	.500	.011	3	81
Diazinon	.041	.052	.0019	5	79	.349	.502	.013	4	69
Carbaryl	.037	.050	.0025	7	75	.263	.500	.021	8	53
Alachlor	.038	.050	.0015	4	77	.319	.500	.009	3	64
Thiobencarb	.050	.050	.0038	8	100	.444	.500	.024	6	89
Malathion	.054	.050	.0045	8	109	.460	.500	.018	4	92
Metolachlor	.050	.058	.0012	2	87	.397	.508	.011	3	78
Chlorpyrifos	.047	.050	.0024	5	95	.401	.500	.015	4	80
Cyanazine	.031	.050	.0040	13	62	.278	.500	.023	8	56
Dacthal	.044	.051	.0025	6	88	.417	.501	.013	3	83
Pendimethalin	.052	.050	.0010	2	103	.349	.500	.014	4	70
Methidathion	.049	.050	.0022	4	98	.381	.500	.008	2	76
Napropamide	.047	.050	.0022	5	95	.267	.500	.030	11	53
Diethatyl-ethyl	.039	.050	.0016	4	79	.286	.500	.017	6	57
Oxyfluorfen	.059	.050	.0058	10	118	.370	.500	.011	3	74

[1]Surrogate compound.

$$Rec = [x/(M + B)] \times 100 \quad (1)$$

where

Rec = mean recovery (percent of true concentration),

x = amount determined in spiked sample (mean observed concentration),

M = amount of spike added (matrix spike), and

B = amount determined in sample without spike (background).

Table 6. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.50-microgram-per-liter concentrations in spiked Suisun Bay water

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

Compound	0.05 microgram per liter					0.50 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percentage of true conc.)
Eptam	0.046	0.052	0.0013	3	88	0.398	0.502	0.007	2	79
Butylate	.045	.050	.0021	5	89	.402	.500	.015	4	80
Pebulate	.043	.050	.0013	3	86	.391	.500	.011	3	78
Molinate	.046	.050	.0024	5	93	.407	.500	.013	3	81
Ethalfluralin	.047	.050	.0019	4	93	.374	.500	.014	4	75
Trifluralin	.043	.051	.0021	5	85	.338	.501	.018	5	67
Sulfotep	.043	.050	.0006	1	86	.384	.500	.013	3	77
Simazine	.042	.050	.0012	3	84	.344	.500	.017	5	69
Carbofuran	.046	.050	.0022	5	92	.394	.500	.032	8	79
Atrazine	.039	.050	.0013	3	78	.351	.500	.018	5	70
Terbuthylazine[1]	.153	.200	.0061	4	77	.150	.200	.007	5	75
Fonofos	.048	.050	.0013	3	96	.441	.500	.010	2	88
Diazinon	.047	.054	.0007	1	87	.383	.504	.011	3	76
Carbaryl	.045	.050	.0027	6	90	.346	.500	.036	10	69
Alachlor	.043	.050	.0020	5	85	.361	.500	.016	4	72
Thiobencarb	.045	.050	.0018	4	91	.459	.500	.016	3	92
Malathion	.057	.050	.0041	7	114	.462	.500	.014	3	92
Metolachlor	.049	.052	.0012	3	94	.409	.502	.008	2	81
Chlorpyrifos	.048	.050	.0022	4	96	.428	.500	.012	3	86
Cyanazine	.039	.050	.0021	5	79	.302	.500	.055	18	60
Dacthal	.043	.051	.0008	2	85	.453	.501	.017	4	90
Pendimethalin	.055	.050	.0012	2	111	.372	.500	.021	6	74
Methidathion	.050	.050	.0010	2	100	.398	.500	.009	2	80
Napropamide	.047	.050	.0014	3	94	.333	.500	.017	5	67
Diethatyl-ethyl	.043	.050	.0014	3	85	.325	.500	.008	2	65
Oxyfluorfen	.070	.050	.0067	10	140	.390	.500	.009	2	78

[1]Surrogate compound.

Table 7. Method detection limits calculated at the 0.05-microgram-per-liter concentration.

[Values in microgram per liter]

Compound	Organic-free water	Sacramento-San Joaquin Delta water	Suisun Bay water
Eptam	0.006	0.007	0.005
Butylate	.007	.005	.008
Pebulate	.011	.007	.005
Molinate	.012	.006	.009
Ethalfluralin	.003	.005	.007
Trifluralin	.014	.008	.008
Sulfotep	.006	.008	.002
Simazine	.008	.012	.005
Carbofuran	.003	.009	.008
Atrazine	.008	.011	.005
Terbuthylazine[1]	—	—	—
Fonofos	.010	.004	.005
Diazinon	.005	.007	.003
Carbaryl	.004	.009	.010
Alachlor	.007	.006	.007
Thiobencarb	.010	.014	.007
Malathion	.006	.017	.015
Metolachlor	.005	.004	.005
Chlorpyrifos	.005	.009	.008
Cyanazine	.008	.015	.008
Dacthal	.013	.009	.003
Pendimethalin	.002	.004	.004
Methidathion	.006	.008	.004
Napropamide	.005	.008	.005
Diethatyl-ethyl	.009	.006	.005
Oxyfluorfen	.010	.022	.025

[1]Surrogate compound.

Precision is expressed in terms of the relative standard deviation of the seven replicate water samples. The relative standard deviation equals the standard deviation (microgram per liter) divided by the mean observed concentration (microgram per liter) multiplied by 100.

Mean recoveries of pesticides depended on the sample matrix and the concentration. Eptam, trifluralin, diazinon, metolachlor, and dacthal were present in the Sacramento-San Joaquin Delta water. The background concentrations (table 5) were added to the matrix spike concentration to determine the mean recovery for these five compounds as described in equation 1. Mean recoveries for the method ranged from 53 to 118 percent for 25 pesticides fortified at 0.50 and 0.05 µg/L, respectively. The mean recovery for the compounds at 0.05 µg/L was generally greater than that at 0.50 µg/L (table 5).

The Suisun Bay water used for the method contained background concentrations for some of the pesticides (eptam, trifluralin, diazinon, metolachlor, and dacthal). The background concentrations are added to the matrix-spike concentration (table 6) to determine the mean recovery for these compounds (eq. 1). Mean recoveries for the method ranged from 60 to 140 percent for 25 pesticides fortified at 0.05 and 0.50 µg/L, respectively. The mean recovery for the compounds at 0.05 µg/L was generally greater than that at 0.50 µg/L (table 6).

Method Detection Limit

The MDL was calculated for each pesticide using the formula

$$MDL = S \times t(n-1, 1-\alpha = 0.99) \quad (2)$$

where

MDL = method detection limit,

S = standard deviation of replicate analyses (microgram per liter) at the lowest concentration,

n = number of replicate analyses, and

$t(n-1, 1-\alpha = 0.99)$ = the student's t value for the 99 percent confidence level with $n-1$ degrees of freedom (Eichelberger and others, 1988).

MDLs are compound, matrix, and method dependent. MDLs calculated for organic-free water ranged from 0.002 to 0.014 µg/L for the analytical method (table 7). MDLs calculated for Sacramento-San Joaquin Delta water ranged from 0.004 to 0.022 µg/L for the method. MDLs calculated for Suisun Bay water ranged from 0.002 to 0.025 µg/L for the method.

Estimated Holding Times

The estimated holding times of the samples extracted onto SPE cartridges and stored in the freezer at -20°C were determined using a mathematical procedure (ASTM Procedure D-4841-88) (American Society for Testing and Materials, 1993). The maximum holding time is defined as the period of time that degradation of the pesticide exceeds a tolerable range of variation (99 percent confidence interval) from the initial mean concentration.

The number of replicates that were required at each time interval for each target pesticide to determine the holding time was based on the relative standard deviation of Sacramento River water fortified at 0.25 ng/µL (table 8) and was calculated as follows:

Table 8. Summary of statistical data used to determine estimated holding time of compounds on solid-phase extraction columns held at -20°C

[Sacramento River water samples were fortified at 0.25 µg/L, and 10 replicate samples were analyzed on days 0, 1, 16, 30, 59, 130, 170, 238, and 360. n, number of replicates; d, determination; µg/L, micrograms per liter; conc., concentration; r^2, regression coefficient]

Compound	Relative standard deviation (percent)	Calculated holding time for replicates (n)	Tolerable variation (d) (99 percent) (µg/L)	Day zero conc. (µg/L)	Slope coefficient	Intercept (d)	Regression coefficient (r^2)	Estimated holding time (days)
Eptam	21	21	0.089	[1]0.391	-0.00122	0.396	0.912	77
Pebulate	18	16	.066	[1].179	-.000259	.178	.654	257
Molinate	8	4	.032	.341	-.000301	.285	.399	108
Trifluralin	10	5	.029	[1].253	-.00044	.256	.829	73
Simazine	7	2	.020	.274	-.000407	.248	.747	50
Carbofuran	3	1	.010	.272	-.000349	.241	.465	28
Atrazine	5	2	.017	.278	-.000271	.234	.672	62
Terbuthylazine	2	1	.007	.286	-.000162	.226	.629	41
Diazinon-oxon	5	1	.021	.206	-.000266	.194	.789	77
Diazinon	8	3	.023	[1].231	-.000624	.229	.668	34
Carbaryl	4	1	.012	.306	-.000158	.252	.034	76
Alachlor	4	1	.012	.298	-.00022	.237	.350	55
Thiobencarb	11	6	.038	.318	-.000271	.269	.587	139
Malathion	3	1	.009	.302	-.000111	.231	.076	79
Metolachlor	2	1	.008	.315	-.0002	.258	.261	42
Chlorpyrifos	8	4	.035	.370	-.00038	.250	.275	92
Cyanazine	7	2	.025	.322	-.00286	.270	.377	10
Dacthal	4	1	.012	.263	-.000145	.232	.504	82
Methidathion	4	1	.010	.261	-.000438	.218	.437	23
Napropamide	5	1	.021	.388	-.000284	.288	.278	74
Diethatyl-ethyl	2	1	.008	.313	-.000162	.263	.425	51

[1]Value used in calculation of estimated holding time.

$$n = (t(RSD)/D)^2 \quad (3)$$

where

n = number of replicates required in the holding time determination,

t = student's t value, 3.355, based on nine replicates used in table 8,

RSD = relative standard deviation, percent; and

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

For most of the compounds, n was calculated to be less than 7 (table 8); however, because the calculated values of n for eptam and pebulate were much higher, 10 was selected as the number of replicates for each time interval in determining the holding time.

Sacramento River water samples were filtered, fortified at 0.25 µg/L, extracted on day zero, and stored in the freezer at -20°C. The ten replicate samples were eluted from the SPE cartridges and analyzed on the GC/MS for each of the following time intervals: 0, 1, 16, 30, 59, 130, 170, 238, 360 days. Table 8 lists the tolerable variation d, calculated as

$$d = (ts)/n \quad (4)$$

where

d = range of tolerable variation from the initial mean concentration;

t = student's t value, 3.25, based on the ten replicates used in the precision study;

s = standard deviation (in concentration terms); and

n = 10, number of replicates.

The mean concentration found for each time interval was plotted against time and linear regression curves were generated to fit the data. The estimated d value, in micrograms per liter, was subtracted from the day-zero value or the day-zero intercept to give the lower tolerable range of variation from the day-zero concentration. The intercept of the lower tolerable range with the linear curve, with respect to the time axis, gives the estimated holding time. The holding times ranged from 10 days for cyanazine to 257 days for pebulate.

Instrument Performance Evaluation and Maintenance

Instrument performance evaluation and maintenance are part of the process to optimize the instrument performance and to ensure the quality of analysis. Corrective action to the instrument was taken, if required, after the assessment of the quality-control data was completed.

Analytical Balances

Class "S" weights were used to calibrate analytical balances monthly and prior to preparing pesticide-stock solutions. The readings were recorded in a log, along with the laboratory technician's initials, after each balance calibration. Balances were serviced professionally every 6 months.

Gas Chromatograph

The performance of the gas chromatograph was indicated by the peak shape and by changes in the peak areas compared with those obtained with a new capillary column and new standards. The glass injection-port liners were changed after analyzing every sample set. If the peak shape or peak area appeared to have deteriorated for certain compounds, such as for carbaryl and(or) carbofuran, the capillary column was cut on the injection-port side and the performance was rechecked. The column was replaced if the chromatographic performance had not improved.

Mass Spectrometer

The mass spectrometer was evaluated before analysis of each set of samples to ensure proper operating performance, and the results were recorded in a binder. The daily system evaluation examined the following:

1. The presence of power to the system, the vacuum pump, and adequate pressure in the helium- and nitrogen-gas cylinders.
2. The GC and transfer line was cooled so the injection port septum and liner could be replaced, then warmed to normal operating temperatures to continue evaluation.
3. The amount of air, water, hydrocarbons, high-mass noise, and column bleed was acceptable. In the air/water mass range (10–45), the 100-percent scale of the chromatogram should be less than 500 and the total ion count (TIC) should be less than 2,000. In the hydrocarbon range (50–200), the 100-percent scale of the chromatogram should be less than 200 and the TIC should be less than 1,000. In the high mass range (200–650), the 100-percent scale of the chromatogram should be less than 200 and the TIC less than 1,000. In the column bleed range (205–210), the 100-percent scale of the chromatogram should be less than 100 and the TIC less than 300.
4. All ions of the calibration gas, perfluorotributhylamine (FC-43) were present and noted the 100-percent scale of the chromatogram, (TIC), and the ion time.
5. The calibration gas 502 ion had 100-percent scale of at least 50 and the TIC was at least 300.
6. The resolution of the 131 and 132 mass. The height of the 132 mass should be at least twice the height of the valley between the 131 and 132 masses.

If any of the elements failed to meet the criteria, the source of the problem was immediately determined and corrected.

Maintenance Program

Maintenance of the GC/MS was done at least quarterly if indicated by the daily performance evaluation. Maintenance involved changing the oil in the mechanical pump (vacuum system) and disassembling and cleaning the ion trap. The electron multiplier was changed when the sensitivity had decreased, such that any target pesticide could not be detected at the MDL. The filament was checked routinely for sensitivity by checking the ion gauge reading, which should be approximately 14.4 μ torr, and replaced when necessary.

The ion trap was reassembled, the manifold was baked at 135°C for 12–20 hours and the vacuum system was allowed to pump for 24 hours. The air-water spectrum was checked and if it appeared normal, the instrument was adjusted by running the mass-spectrometry tuning program. If the air-water spectrum did not appear normal, generally there was a small leak that was

found and fixed before continuing. This tuning program used perfluorotributylamine to achieve linear response between the known masses of perfluorotributylamine and the radio frequency voltage ramp for the instrument.

Quality-Control Data

Quality-control data are produced to quantitatively check the measurement process for environmental samples (T.L. Miller, U.S. Geological Survey, written commun., 1993). The types of quality-control data collected included results of the analysis of field equipment blanks, laboratory equipment blanks, replicate samples, matrix-spiked samples, surrogate recovery, and standards analyzed as samples.

Equipment Blanks

Equipment blanks were used to demonstrate that the equipment was cleaned adequately and that no contamination was present. Pesticide-free reagent water was used for the equipment blanks. The organic-free reagent water was poured into the Teflon sampling bottle, filtered, extracted, and eluted. If the cone splitter was used in sampling, the equipment blank included pouring the organic-free reagent water through the cone splitter. Equipment blanks were processed about every 20 samples and at the beginning and end of intensive sampling.

If pesticides were detected at any concentration above the MDL in the equipment blanks, the source of the problem was determined and corrected. The samples analyzed during that time period were then reevaluated for contamination.

Replicate Samples

A minimum of 10 percent of the samples were collected in replicate. The replicates were analyzed concurrently and reanalyzed if agreement of the calculated concentration for any detected pesticide was not within 25 percent, as determined by the relative percent difference.

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100 \qquad (5)$$

where

RPD = relative percent difference,

$|X_1 - X_2|$ = absolute value of the difference between the two values, and

$\bar{X}$ = mean of the two values.

Matrix-Spiked Samples

Recovery of all target compounds was checked for each matrix spike. The matrix spike was an ethyl acetate solution with 1 ng/μL concentration for each of the pesticides. After the water sample was filtered, 100 μL of the matrix spike was added prior to extraction. The recovery of each pesticide was compared with the recovery obtained to validate the corresponding method. If the recovery was greater than 25 percent different from the values obtained to validate

the method, additional matrix spike samples were collected and analyzed. Three samples were spiked and two samples were extracted without the matrix spike to determine the presence of any background pesticide concentration. If compounds were present in the matrix, their calculated concentration was added to the spike concentration to calculate the percent recovery.

Surrogate Recoveries

Recovery of the surrogate, terbuthylazine, was determined for each sample, including all quality-control samples. Control charts for the terbuthylazine recovery were constructed using the mean, the warning limits at ±1.5 standard deviations from the mean, and the control limits at ±2 standard deviations from the mean. The control charts were constructed using all previous sample terbuthylazine recoveries for a particular sampling site. The sample was reanalyzed on the GC/MS if the recovery was outside the control limits. If the terbuthylazine recovery remained outside the control limits, the sample data were not included in the data set.

Calibration Verification

A standard was analyzed after every six sample injections on the GC/MS to verify that the pesticide calibration curves were within operational specifications. Measured concentrations of these standards were entered into a spreadsheet to compare with the expected standard concentrations. If the measured concentrations of the standards differed by more than 25 percent from the expected concentrations, the source of the problem was determined and corrected and the samples were reanalyzed. For example, the injection end of the column might have required cutting because it became dirty with matrix and lowered the recovery for some pesticides.

SUMMARY

This report describes the analytical methods and quality-assurance practices developed to study the fate and transport of pesticides in surface water by the U.S. Geological Survey. The analytical method uses solid-phase extraction and gas chromatography/mass spectrometry for analysis of pesticides in water samples. The method was validated by using three matrices: organic-free (pesticide-free) water, Sacramento-San Joaquin Delta water, and Suisun Bay water. Recoveries for the method ranged from 44 to 140 percent for 25 pesticides fortified at 0.05 and 0.50 micrograms per liter (µg/L), respectively. The method detection limit (MDL) for the method ranged from 0.002 to 0.025 µg/L. The percent recoveries and the MDLs were dependent on sample matrix and the specific pesticide. The estimated holding times on the cartridge ranged from 10 to 257 days.

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PESTICIDE ANALYSIS METHOD AND QUALITY-ASSURANCE PRACTICES

A method for determining pesticides in water and the corresponding quality-assurance practices has been developed by the U.S. Geological Survey (USGS) Toxics Substances Hydrology Program. Pesticides are of concern because of their extensive use in California'a Central Valley. The fate and transport of various pesticides in the Sacramento-San Joaquin Delta and the San Francisco Bay is the focus of the USGS Toxics Substances Hydrology Program. The analytical method and quality-assurance practices used in the detection of pesticides is described in a report just released by the USGS.

As the nation's largest water, earth and biological sciences, and civilian mapping agency, the USGS works in cooperation with more than 2,000 organizations across the country to provide reliable, impartial, scientific information to resource managers, planners, and other customers. This information is gathered in every state by USGS scientists to minimize the loss of life and property from natural disasters; to contribute to the sound conservation, economic and physical development of the nation's natural resources; and to enhance the quality of life by monitoring water, biological, energy, and mineral resources.

Copies of the U.S. Geological Survey Open-File Report 00-229 "Method of Analysis and Quality-Assurance Practices for Determination of Pesticides in Water by Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry at the U.S. Geological Survey California District Organic Chemistry Laboratory, 1996–99," by Kathryn L. Crepeau, Lucian M. Baker, and Kathryn M. Kuivila are available from the U.S. Geological Survey, Earth Science Information Center, Open-File Reports Section, Box 25286, MS 517, Denver Federal Center, Denver, Co 80225. The price of the paper copy is $____; microfiche is $____. When ordering, please mention the report number and complete title of the report. Payment (check, money order, purchase order, Visa or MasterCard information, including expiration date and signature) in the exact amount, plus a $3.50 handling fee, must accompany order. Make all drafts payable to U.S. Geological Survey, Department of Interior. The report is available for inspection at the following offices and libraries:

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