METHODS OF ANALYSIS AND QUALITY-ASSURANCE PRACTICES OF THE U.S. GEOLOGICAL SURVEY ORGANIC LABORATORY, SACRAMENTO, CALIFORNIA–DETERMINATION OF PESTICIDES IN WATER BY SOLID-PHASE EXTRACTION AND CAPILLARY-COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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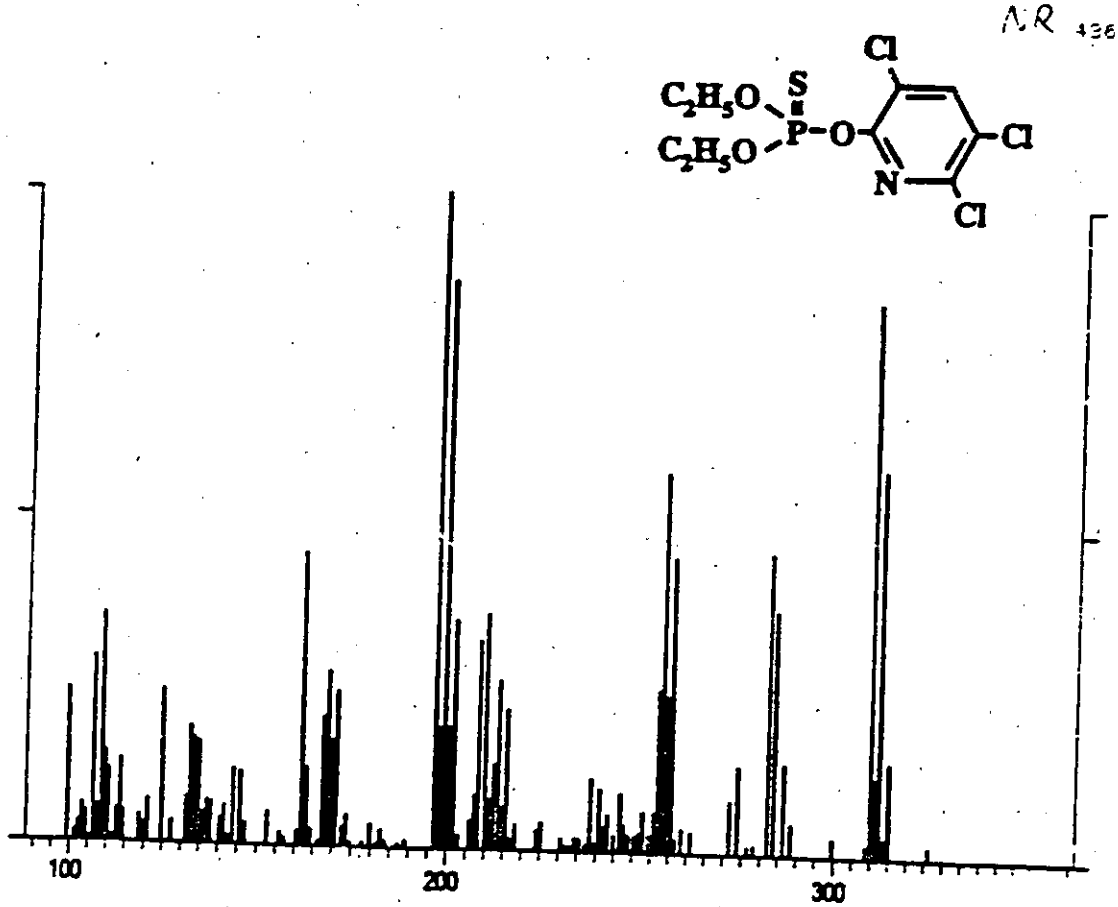

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METHODS OF ANALYSIS AND QUALITY-ASSURANCE PRACTICES OF THE U.S. GEOLOGICAL SURVEY ORGANIC LABORATORY, SACRAMENTO, CALIFORNIA—DETERMINATION OF PESTICIDES IN WATER BY SOLID-PHASE EXTRACTION AND CAPILLARY-COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

By Kathryn L. Crepeau, Joseph L. Domagalski, *and* Kathryn M. Kuivila

Abstract

Analytical method and quality-assurance practices were developed for a study of the fate and transport of pesticides in the Sacramento-San Joaquin Delta and the Sacramento and San Joaquin Rivers. 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 2-milliliter aliquots of hexane: diethyl ether (1:1). The eluants were analyzed using capillary-column gas chromatography/mass spectrometry in full-scan mode. Method detection limits for analytes determined per 1500-milliliter samples ranged from 0.006 to 0.047 microgram per liter. Recoveries ranged from 47 to 89 percent for 12 pesticides in organic-free, Sacramento River and San Joaquin River water samples fortified at 0.05 and 0.26 microgram per liter. The method was modified to improve the pesticide recovery by reducing the sample volume to 1,000 milliliters. Internal standards were added to improve quantitative precision and accuracy. The analysis also was expanded to include a total of 21 pesticides. The method detection limits for 1,000-milliliter samples ranged from 0.022 to 0.129 microgram per liter. Recoveries ranged from 38 to 128 percent for 21 pesticides in organic-free, Sacramento River and San Joaquin River water samples fortified at 0.10 and 0.75 microgram per liter.

INTRODUCTION

In 1990, the U.S. Geological Survey (USGS), as part of the Toxic Contaminants and Hydrology program, began a study to determine the fate and transport of pesticides in the Sacramento-San Joaquin Delta and San Francisco Bay. Although a great variety of crops are grown in the Central Valley of California, the study has focused on pesticides applied to stonefruit orchards, alfalfa, and rice. In the Central Valley, nearly 900,000 acres of stonefruit orchards are harvested annually (U.S. Department of Commerce, 1987); about 1,100,000 lb of dormant spray pesticides were applied during the winter of 1990 (California Department of Pesticide Regulation, 1990). Alfalfa is harvested on 367,000 acres throughout the Central Valley (California Department of Water Resources, 1993); about 348,500 lb of pesticides were applied in 1990, primarily during March and April (California Department of Pesticide Regulation, 1990). Rice is grown primarily in the Sacramento Valley, with as many as 500,000 acres harvested each year (California Regional Water Quality Control Board, Central Valley Region, 1991); about 1,650,000 lb of pesticides were applied during April, May, and June of 1990 (California Department of Pesticide Regulation, 1990).

The study area includes the Central Valley of California: Sacramento Valley, San Joaquin Valley, and the Sacramento-San Joaquin Delta. The two primary river systems in the valley, the Sacramento and San Joaquin Rivers, converge to form the delta. Samples were collected primarily in the Sacramento

and San Joaquin Rivers and the Sacramento-San Joaquin Delta and were analyzed for pesticides using the method described in this report. Because most of the water samples came from the Sacramento and San Joaquin Rivers, the method was validated by using samples from these rivers along with organic-free water samples.

PURPOSE AND SCOPE

This report describes the analytical method and quality-assurance practices of the organic-chemistry laboratory at the California District Office of the U.S. Geological Survey. The analytical method includes field sampling, sample processing, and instrument calibration. The method involves using solid-phase extraction (SPE) cartridges to isolate pesticides from water samples and the gas chromatograph/mass spectrometry (GC/MS) to identify and quantify these pesticides. The quality-assurance practices include quality control, instrument performance evaluation, and corrective action.

MODIFICATIONS TO ANALYTICAL METHOD

The analytical method was modified to improve the pesticide recovery by reducing the sample volume to 1,000 mL because of breakthrough problems with the larger sample volume, which lowered the recovery of some pesticides. Internal standards were added to improve quantitative precision and accuracy. The internal standards are d-10 acenapthene, d-10 phenanthrene, and d-10 pyrene. The pesticides are quantified using the internal standard with the closest retention time. Nine pesticides were added to the analysis because they were detected in the Sacramento River and San Joaquin River water samples by the California Department of Pesticide Regulation or the California Regional Water-Quality Control Board. The data on accuracy and precision and method detection limits (MDL's) for the analytical method and for the modified method are presented.

ANALYTICAL METHOD

SCOPE AND APPLICATION

The analytical method is suitable for determining triazine, organophosphate, and carbamate pesticides in natural-water samples containing at least 0.05 µg/L of each pesticide. Water samples are filtered to remove suspended particulate matter; therefore, this method can detect only dissolved-phase pesticides or pesticides on particulate matter that passes through the filter. The recovery of pesticides from water samples are more complete if the compounds partition efficiently from the water phase to the C-8 phase that is chemically bonded to silica. The compounds must be sufficiently volatile and thermally stable to be analyzed by gas chromatography. The method was developed to determine the concentration of 12 pesticides in river water and later expanded to include a total of 21 pesticides. These pesticides, along with their water solubility, vapor pressure, and Chemical Abstracts Service registry numbers, are listed in table 1.

Table 1. Water solubility, vapor pressure, and Chemical Abstract Service registry numbers for the pesticides studied

[Data referenced from Worthing and Walker, 1987, except where noted; CAS, Chemical Abstract Service; °C, degrees Celsius; mg/L, milligram per liter; mPa, millipascal; <, less than; --, no data]

Pesticide	Water solubility [mg/L(°C)]	Vapor pressure [mPa(°C)]	CAS number
Eptam[1]	375(24°C)	4,500(25°C)	759-94-4
Butylate[1]	46(20°C)	170(25°C)	2008-41-5
Pebulate[1]	60(20°C)	4,700(25°C)	1114-71-2
Ethalfluralin[1]	.2(25°C)	0.11(25°C)	55283-68-6
Molinate	880(20°C)	746(25°C)	2212-67-1
Trifluralin	<1(27°C)	13.7(25°C)	1582-09-8
Simazine	5(20°C)	0.00081(20°C)	122-34-9
Carbofuran	700(25°C)	2.7(33°C)	1563-66-2
Atrazine	30(20°C)	0.04(20°C)	1912-24-9
Fonofos	13(25°C)	28(25°C)	944-22-9
Diazinon	40(20°C)	0.097(20°C)	333-41-5
Carbaryl[2]	32(20°C)	0.181(25°C)	63-25-2
Alachlor[1]	242(25°C)	2.9(25°C)	15972-60-8
Thiobencarb	30(20°C)	--	28249-77-6
Malathion	145(25°C)	5.3(30°C)	121-75-5
Metolalchlor[1]	530(20°C)	1.7(20°C)	51218-45-2
Cyanazine[1]	171(25°C)	0.00020(20°C)	21725-46-2
Chlorpyrifos	2(25°C)	2.5(25°C)	2921-88-2
Dacthal[1,3]	.5(25°C)	0.333(25°C)	1861-32-1
Methidathion	250(20°C)	0.186(20°C)	950-37-8
Napropamide[1]	73(20°C)	0.53(25°C)	41643-35-0

[1]Added later as part of modified method.
[2]Howard, 1991.
[3]Wauchope and others, 1991.

The USGS National Water Quality Laboratory (NWQL) developed a similar method for determining organonitrogen herbicides in water samples (Sandstrom and others, 1991). NWQL uses C-18 bonded phase with hexane:isopropanol (3:1) for elution and a quadruple mass spectrometer 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.

SUMMARY OF METHOD

The analytical method developed for the project incorporates various standard USGS water-sampling procedures (Edwards and Glysson, 1988). SPE is used to recover pesticides for analysis on a GC/MS. A flow chart outlining the method is given in figure 1 and a more detailed summary is given below.

1. Filter the water sample into 1-L bottle with a glass-fiber, 0.7-µm, nominal pore-diameter filter to remove suspended particulate matter.
2. Add surrogate, terbuthylazine, to the filtered water sample.
3. Pump the filtered water sample through disposable, polypropylene SPE cartridges containing C-8 chemically bonded to 0.5 g of porous silica.
4. Dry the SPE cartridges by centrifuging for 2 minutes at 1,500 r/min (revolutions per minute), and then remove any interstitial water with a gentle stream of carbon dioxide.
5. Elute the pesticides with three 2 mL aliquots of hexane:diethyl ether (1:1).

NOTE: If the modified method is not used, omit step 6.

6. Add 200 µL of internal standards at 0.25 ng/µL.
7. Concentrate the eluant with nitrogen to a final volume of about 200 µL.
8. Analyze the eluant using a capillary-column GC/MS in full scan mode.

EQUIPMENT AND MATERIALS

The equipment and supplies required for this method are listed in table 2. The specific sources and models used for this method are included where applicable.

The stock solutions were prepared by weighing an appropriate amount of the pesticide for a solution of 200 ng/µL in ethyl acetate. A series of eight calibration standard solutions with concentrations ranging from 0.032 to 4.17 ng/µL was prepared from a standard solution of the pesticides of interest at 8.33 ng/µL.

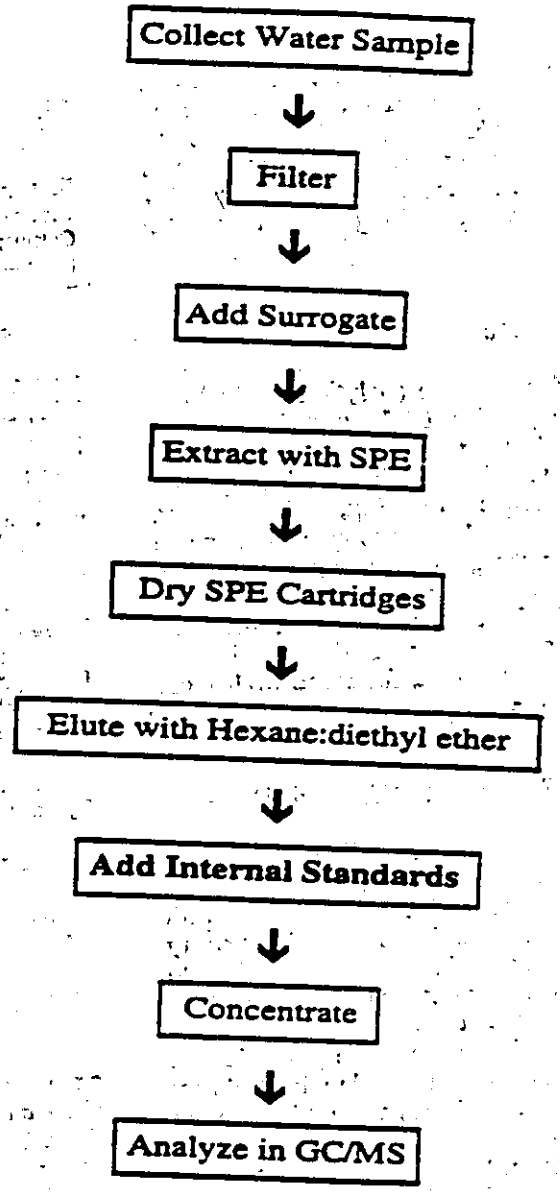

Figure 1. Flow chart of analytical method. (Bolded area is used only in modified method.)

FIELD SAMPLING

SAMPLE COLLECTION AND STORAGE

Water samples from the San Joaquin River at Vernalis, California, were collected at a point that provided a representative sample of the average suspended-sediment concentration for the cross section of the river (Porterfield, 1992). Water sam-

Table 2. List of equipment and supplies required for sampling and analysis

[Sources for some items are listed to maintain quality standards or when volume discounts are available. m, meter; mL, milliliter; mm, millimeter; µm, micrometer; mg, milligram; r/min, revolutions per minute]

Sampling

- D-74 sampler, depth-integrating
- D-77 sampler, depth-integrating
- Bottle, Teflon perfluoroalkoxy (PFA), 3,000 mL, cap and adaptor (Geotech Environmental Equipment, Inc.)
- Nozzle, Teflon-TFE (tetrafluoroethylene) (U.S. Geological Survey Hydrologic Instrumentation Facility)
- Bottle, amber glass, 1,000 mL, Teflon-lined screw caps (NWQL)

Filtering

- Filtration unit, aluminum, 142-mm diameter (Geotech Environmental Equipment, Inc.)
- Pump, Teflon-diaphragm pump head (Cole-Parmer Model 07090-42), masterflex drive (Cole-Parmer Model 07553-50)
- Filters, glass fiber (GF/F grade), 142-mm diameter, 0.7-µm pore diameter (Whatman, Inc.)

Extraction

- SPE (solid-phase extraction) cartridges, 500 mg of silica coated with a chemically bonded C-8 hydrocarbon phase (Varian, Bon-Elut No. 1212-4026)
- Terbuthylazine, surrogate, purity 99 percent (Chem Service, Inc.)
- Metering pump, ceramic piston, valveless, 1/8-inch outside-diameter tubing (Fluid Metering Inc., Model RHB-1CKC 12 V pump)
- Tubing, Teflon-PFA, 1/8-inch outside diameter (Cole-Parmer Instrument Company)
- Tubing, Teflon-FEP (fluorinated ethylene polypropylene), corrugated, 1/4-inch outside diameter (Cole-Parmer Instrument Company, Model L-06407-60)

Drying

- Centrifuge-,1,500 r/min IEC HN-SII cartridge, (Damon IEC Division)
- Carbon-dioxide gas, coleman grade 5
- Manifold (Supleco)

Elution/Concentration

- Hexane:diethyl ether 1:1
- Nitrogen gas, prepurified
- Internal standard -d-10 acenepthene, purity 99 percent (Cambridge Isotope Labratories, Inc.)
  - d-10 phenanthinene, purity 99 percent (Cambridge Isotope Laboratories, Inc.)
  - d-10 pyrene, purity 98 percent (Cambridge Isotope Laboratories, Inc.)

Analysis

- Gas chromatograph, (Varian, model 3400)
- Column, 5 percent phenyl-methylsilicone, DB-5, 30 m, 0.25-mm inner diameter, 0.25-µm film thickness (J & W Scientific)
- Ion-trap, mass spectrometer (Finnigan Corporation)

Solvents--high-purity pesticide quality (B & J Brand)

- Methanol
- Hexane
- Diethyl ether
- Ethyl acetate
- Acetone
- Organic-free water produced in the laboratory by pumping dionized water through a PICTEC H² system with an ultra-violet unit and an activated carbon unit (Hydro Service and Supplies, Inc.)

Pesticides-standard materials from commercial vendors such as Chem Service, Inc.

ples were collected using a D-74 sampler designed to obtain suspended-sediment samples. The sampler is constructed of glass or Teflon parts that make it compatible for organic sample analyses. Depth-integrated samples of approximately 1 L were collected daily and stored in 1-L amber bottles (baked at 450°C). The bottles were labeled for date, time of collection, water temperature, and stage height of the river. Samples were then placed in a refrigerator and stored at 4°C. The storage time prior to extraction was 1 week or less; the effect of this storage time on analyte degradation is being investigated in a separate study. Samples from 2 consecutive days were combined for extraction.

Water samples from the Sacramento River at Tower Bridge in Sacramento were collected three times a week at a point near the center of flow, which under normal flow conditions is representative of a cross section. Depth-integrated samples were collected with a D-77 sampler equipped with a Teflon bottle and nozzle. The samples were stored in the refrigerator at 4°C in amber bottles until extracted.

CLEANING PROCEDURES

Sampling containers and equipment, aluminum filtration unit, and metering pump for SPE were cleaned with a phosphate-free detergent and then rinsed with distilled water, organic-free water, pesticide-residue grade methanol, and organic-free water, in that order. The sample containers were air dried before they were capped and stored in the cabinet. The Teflon tubing on the equipment and aluminum filtration unit was covered with aluminum foil to prevent contamination between use. SPE cartridges were precleaned with 6 mL of hexane:diethyl ether (1:1).

SAMPLE PROCESSING

FILTRATION

Water samples were filtered either in the field or within 24 hours of their arrival at the laboratory. The samples were pumped through a Teflon line into an aluminum filter holder that holds a glass-fiber filter. Filters were prebaked at 450°C for 4 hours to remove any organic contaminants. The pump was equipped with a masterflex variable-speed drive and a Teflon diaphragm head. The filtered sample was collected in a 1-L baked (450°C) amber glass bottle.

EXTRACTION

SPE cartridges were precleaned with three 2-mL aliquots of the eluting solvent (hexane:diethyl ether 1:1). The cartridges were allowed to drip dry before each was wrapped in foil and placed in a glass jar.

The SPE cartridges were conditioned by adding 3 mL of methanol followed by 3 mL of organic-free water just before extracting the sample. The silica in the cartridge must not become dry during the extraction process. Prior to extraction, 100 µL of the surrogate standard solution of terbuthylazine (2 ng/µL) in acetone was added to the filtered sample and mixed thoroughly. The measured recovery of the surrogate provided quantitative data on the efficiency of the extraction. The sample was pumped at 20 mL/min through an SPE cartridge containing C-8 chemically bonded phase. The amount of extracted water was measured with a graduated cylinder and the volume was recorded. The pump and Teflon tubing were rinsed with methanol and then with organic-free water. The cartridges were placed on a manifold and dried with carbon dioxide or nitrogen gas at 70 kPa for about 1 hour or until dry.

ELUTION

The analytes were eluted by adding three separate 2-mL aliquots of hexane:diethyl ether (1:1) to the cartridge and allowing the solvent to drip into an 8-mL vial. Nitrogen can be used to force any remaining solvent into the vial. The eluant was concentrated to approximately 200 µL using nitrogen and transferred to an auto-sample vial for GC/MS analysis. For the modified method, the internal standards were added during the concentration of the sample.

GAS CHROMATOGRAPH/MASS SPECTROMETER CALIBRATION

An initial calibration of the GC/MS using standard solutions containing all the target pesticides was acquired before the samples were analyzed. The calibration was checked by injecting a calibration standard solution at least every 8 hours during sample analysis. The computer software generates linear regression equations for the analyte calibration over a concentration range of 0.033 to 4.17 ng/µL. If the correlation coefficients were greater than 0.99, the calibration was accepted and the software quantified

Table 3. Retention time and quantitation ions for pesticides and surrogate compound for original analytical method

[S, surrogate compound; min:s, minute:second; m/z, mass per unit charged; --, not applicable]

Compound	Compound type or number	Retention time (min:s)	Quantitation ion (m/z)	Second confirmation ion	Third confirmation ion
Molinate	1	11:25	187	126	188
Trifluralin	2	14:08	306	264	--
Simazine	3	15:09	201	186	173
Carbofuran	4	15:14	164	149	--
Atrazine	5	15:22	215	200	173
Terbuthylazine	S	15:53	214	229	173
Fonofos	6	16:01	246	109	137
Diazinon	7	16:21	304	179	137
Carbaryl	8	18:04	144	115	116
Thiobencarb	9	19:13	257	125	100
Malathion	10	19:14	173	127	125
Chlorpyrifos	11	19:36	314	199	197
Methidathion	12	21:29	145	125	--

the compounds detected in the samples. The conditions used for GC/MS are as follows:

Carrier gas and flow rate:	Helium, 1 mL/min at 250°C
Injector temperature:	250°C
Detector temperature:	205°C
GC column oven temperature:	90°C for 1 minute (20°C per minute) to 120°C for 1 minute (6°C per minute) to 250°C for 1 minute (12°C per minute) to 275°C for 0.2 minute
Injection mode and volume:	Splitless, 1 µL

Calculation of the relative retention time for each target compound and the surrogate compound (RRT_c) in the standard solution or in a sample is as follows:

$$RRT_c = RT_c / RT_i \quad (1)$$

where RT_c is the uncorrected retention time of the target compound or surrogate compound and RT_i is the uncorrected retention time of the internal standard with retention time closest to that of the target or surrogate compound.

Table 3 lists the retention time and quantitation ions for each of the pesticides and the surrogate for the original method. Table 4 lists the retention time, relative retention time, and quantitation ions for each of the pesticides, surrogate, and internal standards for the modified method.

QUALITY-ASSURANCE PRACTICES

Quality assurance is based on collecting quality-control data and assessing those data. Quality-control data are produced to quantitatively control the measurement process for environmental samples (T.L. Miller, U.S. Geological Survey, written commun., 1993). The types of quality-control data collected included equipment blanks, replicate samples, matrix spikes, surrogate recovery, and standards analyzed as samples. Instrument performance evaluation and maintenance are part of the quality-assurance process to optimize the instrument performance. Corrective action was taken if required after the quality assessment of the data had been made.

QUALITY-CONTROL DATA

EQUIPMENT BLANKS

Equipment blanks were used to demonstrate that the equipment was adequately cleaned and no contamination was present. Organic-free water (pesticide free) was used for the equipment blanks. The organic-freewater was poured into the Teflon

Table 4. Retention time, relative retention time, and quantitation ions for pesticides, surrogate compound, and internal standards for modified analytical method

[The pesticides are grouped with the internal standard used for quantitation. S, surrogate compound; IS, internal standard; min:s, minute:second; m/z, mass per unit charged; —, not applicable]

Compound	Compound type or number	Retention time (min:s)	Relative retention time	Quantitation ion (m/z)	Second confirmation ion	Third confirmation ion
Eptam	1	8:02	0.771	190	160	128
Butylate	2	9:23	0.901	174	156	146
Pebulate	3	9:57	0.955	160	204	128
Acenapthene d-10	IS	10:25	1.000	162	—	—
Molinate	4	11:25	1.096	187	126	188
Ethalfluralin	5	13:47	1.323	316	276	292
Trifluralin	6	14:08	0.885	306	264	—
Simazine	7	15:09	0.950	201	186	173
Carbofuran	8	15:14	0.955	164	149	—
Atrazine	9	15:22	0.963	215	200	173
Terbuthylazine	S	15:53	0.995	214	229	173
Phenanthrene d-10	IS	15:57	1.000	188	—	—
Fonofos	10	16:01	1.004	246	109	137
Diazinon d-10	S	16:14	1.018	314	183	138
Diazinon	11	16:21	1.025	304	179	137
Carbaryl	12	18:04	1.133	144	115	116
Alachlor	13	18:12	1.141	160	188	238
Thiobencarb	14	19:13	0.890	257	125	100
Malathion	15	19:14	0.891	173	127	125
Metolalchlor	16	19:26	0.900	162	238	240
Cyanazine	17	19:31	0.904	225	198	173
Chlorpyrifos	18	19:34	0.908	314	139	197
Dacthal	19	19:45	0.915	301	332	303
Methidathion	20	21:29	0.995	145	125	—
Pyrene d-10	IS	21:35	1.000	212	—	—
Napropamide	21	22:14	1.030	271	171	128

sampling bottle, filtered, extracted, and eluted using the procedure described for a sample. If the cone splitter was used in sampling, the equipment blank included pouring the organic-free water through the cone splitter. Equipment blanks were collected about every 20 samples and at the beginning and end of intensive sampling.

If analytes were detected in the equipment blanks, the source of the problem had to be determined and corrected. The samples analyzed during that time period were then evaluated for contamination.

REPLICATE SAMPLES

A minimum of 10 percent of the samples were collected in duplicate. The duplicates and samples were analyzed concurrently and reanalyzed if agreement of the calculated concentration for any detected analyte was not within 25 percent as determined by the relative percent difference (RPD).

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100, \qquad (2)$$

where

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

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

MATRIX SPIKES

Recovery of all target compounds was checked for each matrix on a regular basis. The matrix spike was an acetone solution with 1 ng/µL concentration for each of the analytes. After the water sample was

filtered, 100 µL of the matrix spike was added prior to extraction. The recovery of each analyte was compared to the recovery obtained to validate the method. Three samples were spiked, and two samples were extracted without the matrix spike to determine any background analyte concentration.

SURROGATE RECOVERIES

Recovery of the surrogate compound, terbuthylazine, was checked for each sample. 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 ±3 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 limit. If the terbuthylazine recovery remained outside the control limit, the sample data were not included in the data set.

VERIFICATION OF CALIBRATION

A standard was analyzed after every set of three samples on the GC/MS to verify that the analyte calibration curves were within operational specifications. The concentrations of these standards were entered into a spreadsheet to compare with the expected standard concentrations. If the calculated concentrations of the standards differed by more than 25 percent from the target value and the analytes were detected in the associated samples, the samples were reanalyzed. The source of the problem needed to be determined and corrected before the samples were reanalyzed. For example, the glass insert might need to be changed, the injection end of the column cut, or the column changed.

EVALUATION AND MAINTENANCE OF INSTRUMENT PERFORMANCE

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 and initialed each time the balance was calibrated. Balances were professionally serviced when the calibrating weight varied by more than 0.1 percent from its established weight or annually, whichever came first (Makita and Fujii, 1992).

GAS CHROMATOGRAPH

The performance of the gas chromatograph was indicated by the peak shape and by changes in the peak areas compared to those obtained with a new capillary column and new standards. The glass injection-port liners were changed on a weekly basis. The liners also were changed if initial calibration or continuing calibration criteria were not met. In addition, if the peak shape or peak area appeared to have deteriorated, the capillary column could be cut on the injection-port side. The column was replaced if the chromatographic performance did not improve.

MASS SPECTROMETER

The mass spectrometer was checked daily to ensure proper operating performance. Results of this daily check were recorded and kept in a binder.

The daily system evaluation examined the following:

1. Instrument background noise (between 0.5 and 1.0)
2. Operating temperatures (250°C for transfer line, 205°C for ion trap)
3. Radio frequency (steady ramp)
4. Amount of air and water in the ion-trap manifold (isotopic ratios can be affected by a high water content and should be less than 200 area counts)
5. Voltage required by the electron multiplier to achieve a gain of 100,000
6. Mass spectrum of the perfluorotributylamine (FC-43) standard is obtained and checked for isotopic ratios of carbon-12 and carbon-13.

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

MAINTENANCE PROGRAM

Maintenance of the GC/MS was done quarterly and whenever the daily performance evaluation indicated the necessity. Maintenance involved changing

the oil in the mechanical and turbo-molecular pumps (vacuum system) and cleaning the ion-trap manifold. The electron multiplier was changed when the voltage to achieve a gain of 100,000 was greater than 1,800 and the sensitivity had decreased such that any target analyte could not be detected at its method detection limit. The filament also was checked routinely for sensitivity and replaced when necessary.

The ion trap was reassembled, and the vacuum system was allowed to pump down 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. This tuning program used perfluorotributylamine (FC-43) to achieve optimum resolution and sensitivity for the instrument.

CALCULATION AND REPORTING OF RESULTS

SAMPLE ANALYSIS AND DATA VALIDATION

The samples were analyzed on the GC/MS immediately after the initial calibration had been evaluated. The GC/MS conditions must remain the same for analysis of the target compounds and the calibration standards. Data validation consisted of assessing the regression lines of standards, assessing the recovery of the surrogate compound, and verifying the presence or absence of targeted compounds. 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. The recovery of the analytes was verified using the matrix spike samples, and the results of the replicate samples were compared.

Individual standards must be detectable throughout the range of injected amounts. The method detection limit varies with individual compounds according to their chromatographic properties. 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. Sample data were eliminated from the data set if poor performance was reproduced upon reinjection of the sample extract.

Each chromatogram was examined to verify the presence or absence of targeted analytes. Initial verification of the presence of analytes was determined by the quantitation routine of the ion-trap software. The analyst then searched the chromatogram at the expected retention time (equation 1) of the analyte and, by examining the mass spectrum, confirmed or denied the presence of the compound. The mass spectrum was compared to the mass-spectral library acquired on the ion-trap detector. The analyst verified the presence and relative abundance of the major fragment ions for the analyte of interest. If the fragments were not consistent with the library spectrum, the data for that analyte were rejected as a false positive. The analyst then scannedthe chromatogram for the presence or absence of remaining analytes; analytes were not always recorded automatically by the quantitation routine of the ion-trap software. If additional analytes were detected, the analyst manually used the quantitation routine to quantify the compound.

DATA REPORTING

Data were stored in a Lotus 1-2-3 spreadsheet format. The data included sample-site identification, date, nanograms per liter calculated by quantitation routine for sample compounds, and percent recovery of the quality-assurance surrogate. The concentration of each pesticide detected was reported to two significant figures.

METHOD VALIDATION

The analytic method was validated by using three matrices: organic-free, Sacramento River, and San Joaquin River water. The samples were split into subsamples for blanks and low- and high-spike concentrations of each pesticide. The low- and high-spike concentrations for the original method were 0.05 µg/L and 0.26 µg/L; concentrations for the modified method were 0.10 µg/L and 0.75 µg/L. The concentration changes were made because the original low concentration was too close to the MDL's for the analytes, and the high concentration was lower than some sample data. Accuracy and precision data are presented in tables 5 through 7 (at back of report) for the original method and tables 8 through 10 (at back of report) for the modified method. The MDL's for both methods are listed in table 11 (at back of report).

ACCURACY AND PRECISION

Accuracy was assessed using recovery of spiked samples for the method validation. Mean accuracy is calculated as follows:

$$Acc=[X/M+B]\times 100, \quad (3)$$

where

- Acc = mean accuracy (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).

Precision is expressed in terms of the relative standard deviation of the seven 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 accuracies (recoveries) of analytes depended on the sample matrix and the concentration. Atrazine, diazinon, and simazine were present in the San Joaquin River water. The background concentration (table 7) was added to the matrix spike concentration to determine the mean accuracy for these three compounds as described in equation 3. Mean accuracies for the original method ranged from 46 to 89 percent for 12 pesticides fortified at 0.05 and 0.26 µg/L. The mean accuracy for the compounds at 0.26 µg/L was generally less than that at 0.05 µg/L (tables 5, 6, and 7).

The river water used for the modified method contained background concentrations for some of the analytes. Molinate was present in the Sacramento River water; eptam, simazine, diazinon, and metolachlor were present in the San Joaquin River water. The background concentration was added to the matrix-spike concentration (tables 9 and 10) to determine the mean accuracy for these compounds (equation 3).

The modified method improved the accuracy of the original 12 compounds, except trifluralin; however, a strict comparison could not be made because the value of the low and high concentration was increased. The primary reason for this improvement is the smaller volume of water extracted and the resulting reduction in breakthrough. Mean accuracies for the modified method ranged from 38 to 128 percent for 21 pesticides fortified at levels of 0.10 and 0.75 µg/L. The mean accuracy for the compounds at 0.75 µg/L generally was greater than at 0.10 µg/L (tables 8, 9, and 10). The precision of the original 12 compounds did not improve except for the San Joaquin River water samples at the low concentrations. The accuracy and precision data obtained from both methods adequately addressed the data-quality objectives.

METHOD DETECTION LIMIT

An MDL was calculated for each analyte using the formula

$$MDL=S\times t(n-1,1-\alpha=0.99), \quad (4)$$

where

- MDL = Method detection limit
- S = standard deviation of replicate analyses (microgram per liter) at the lowest concentration,
- n = number of replicate analyses, and $t(n-1,1-\alpha=0.99)$ is the student's t value for the 99-percent confidence level with n-1 degrees of freedom (Eichelberger and others, 1988).

MDL's are compound and matrix dependent. MDL's calculated for organic-free water range from 0.006 to 0.028 µg/L for the original analytical method and from 0.022 to 0.060 µg/L for the modified method (table 11). MDL's calculated for Sacramento River water ranged from 0.013 to 0.047 µg/L for the original method and from 0.028 to 0.110 µg/L for the modified method. MDL's calculated for San Joaquin River water ranged from 0.022 to 0.044 µg/L for the original method and from 0.019 to 0.129 µg/L for the modified method. Only the MDL's for the San Joaquin River water improved for the 12 original compounds under the modified method.

SUMMARY

This report describes the analytical methods and quality-assurance practices developed to study the fate and transport of pesticides in the Sacramento-San Joaquin Delta and Sacramento and San Joaquin Rivers. The analytical method uses solid-phase extraction and gas chromatograph/mass spectrometry for analysis of pesticides in water samples. The method was validated by using three matrices: organic-free water and Sacramento and San Joaquin Rivers water. Recoveries for the original method

ranged from 47 to 89 percent for 12 pesticides fortified at 0.05 and 0.26 microgram per liter. The method detection limits for the original method ranged from 0.006 to 0.047 microgram per liter. The method was modified by reducing sample volume to 1,000 milliliters of the pesticides and by using internal standards to improve quantitative precision and ac- curacy. The modified method improved the accuracy of the original 12 compounds, except trifluralin. Recoveries for the modified method ranged from 38 to 128 percent for 21 pesticides fortified at levels of 0.10 and 0.75 microgram per liter. The method detection limits for the modified method ranged from 0.022 to 0.129 microgram per liter. The precision and method detection limit of the original 12 compounds did not improve, except for the San Joaquin River water samples. The percent recoveries and the method detection limits were dependent on sample matrix and the specific pesticide.

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Table 5. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.26-microgram-per-liter concentrations in spiked organic-free water for original analytical method

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

Compound	0.05 microgram per liter					0.26 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Molinate	0.042	0.05	0.009	21	82	0.155	0.26	0.047	30	60
Trifluralin	.031	.05	.004	13	60	.142	.26	.023	16	55
Simazine	.028	.05	.004	14	55	.119	.26	.019	16	46
Carbofuran	.032	.05	.004	13	62	.140	.26	.022	16	55
Atrazine	.037	.05	.004	11	72	.174	.26	.027	16	68
Terbuthylazine[1]	.041	.05	.007	17	79	.178	.26	.032	18	70
Fenofos	.032	.05	.004	13	62	.153	.26	.029	19	60
Diazinon	.033	.05	.005	15	65	.162	.26	.028	17	63
Carbaryl	.030	.05	.003	10	58	.135	.26	.018	13	53
Thiobencarb	.042	.05	.008	19	81	.173	.26	.034	20	68
Malathion	.036	.05	.003	8	70	.171	.26	.025	15	67
Chlorpyrifos	.030	.05	.004	13	59	.150	.26	.026	17	59
Methidathion	.028	.05	.002	7	55	.141	.26	.018	13	55

[1]Surrogate compound.

Table 6. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.26-microgram-per-liter concentrations in spiked Sacramento River water for original analytical method

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

Compound	0.05 microgram per liter					0.26 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Molinate	0.036	0.05	0.008	22	70	0.160	0.26	0.069	43	63
Trifluralin	.027	.05	.006	22	53	.141	.26	.046	33	55
Simazine	.041	.05	.015	37	79	.149	.26	.052	35	58
Carbofuran	.037	.05	.013	35	72	.144	.26	.051	35	56
Atrazine	.036	.05	.007	19	70	.156	.26	.044	28	61
Terbuthylazine[1]	.035	.05	.004	11	68	.162	.26	.053	33	63
Fenofos	.029	.05	.006	21	57	.150	.26	.045	30	59
Diazinon	.032	.05	.006	19	63	.154	.26	.055	36	60
Carbaryl	.045	.05	.013	29	89	.180	.26	.069	38	70
Thiobencarb	.029	.05	.005	17	56	.153	.26	.048	31	60
Malathion	.039	.05	.006	15	76	.171	.26	.057	33	67
Chlorpyrifos	.027	.05	.009	33	53	.146	.26	.050	34	57
Methidathion	.043	.05	.010	23	83	.172	.26	.061	36	67

[1]Surrogate compound.

Table 7. Accuracy and precision data from seven determinations of the method analytes at 0.05- and 0.26-microgram-per-liter concentrations in spiked San Joaquin River water for original analytical method

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

Compound	0.05 microgram per liter					0.26 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Molinate	0.038	0.050	0.012	32	75	0.143	0.260	0.040	28	61
Trifluralin	.038	.050	.009	24	74	.222	.260	.018	8	84
Simazine	.056	.095	.026	46	59	.187	.297	.035	19	63
Carbofuran	.029	.050	.010	35	56	.133	.260	.023	17	52
Atrazine	.047	.068	.011	23	69	.199	.273	.042	21	73
Terbuthylazine[1]	.039	.050	.009	23	76	.201	.260	.033	16	78
Fonofos	.037	.050	.007	19	72	.203	.260	.022	11	79
Diazinon	.067	.092	.012	18	73	.262	.298	.022	8	88
Carbaryl	.037	.050	.014	38	72	.181	.260	.030	17	70
Thiobencarb	.043	.050	.012	28	83	.224	.260	.024	11	88
Malathion	.044	.050	.010	23	85	.214	.260	.019	83	83
Chlorpyrifos	.030	.050	.009	30	58	.175	.260	.036	68	68
Methidathion	.037	.050	.009	24	72	.195	.260	.029	76	75

[1]Surrogate compound.

Table 6. Accuracy and precision data from seven determinations of the method analytes at 0.10- and 0.75-microgram-per-liter concentrations in spiked organic-free water for modified analytical method

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

Compound	0.10 microgram per liter					0.75 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Eptam	0.060	0.100	0.014	23	60	0.671	0.750	0.123	18	89
Butylate	.076	.100	.012	16	76	.611	.750	.117	19	82
Pebulate	.076	.100	.014	18	76	.536	.750	.061	11	71
Molinate	.089	.100	.019	21	89	.652	.750	.065	10	87
Ethalfluralin	.080	.100	.019	24	80	.416	.750	.112	27	55
Trifluralin	.071	.100	.018	25	71	.386	.750	.118	31	51
Simazine	.074	.100	.007	9	74	.441	.750	.060	14	59
Carbofuran	.082	.100	.010	12	82	.462	.750	.080	17	62
Atrazine	.085	.100	.012	14	85	.672	.750	.114	17	90
Terbuthylazine[1]	.182	.100	.010	5	91	.182	.750	.021	12	91
Fonofos	.084	.100	.013	15	84	.527	.750	.070	13	70
Diazinon d-10[1]	.067	.100	.009	13	67	.060	.750	.013	22	60
Diazinon	.074	.100	.009	12	74	.525	.750	.083	16	70
Carbaryl	.085	.100	.013	15	85	.394	.750	.092	23	53
Alachlor	.096	.100	.009	9	96	.657	.750	.063	10	88
Thiobencarb	.084	.100	.012	14	84	.678	.750	.083	12	90
Malathion	.094	.100	.018	19	94	.582	.750	.055	8	91
Metolachlor	.106	.100	.014	13	106	.733	.750	.043	6	98
Cyanazine	.070	.100	.013	19	70	.572	.750	.163	28	76
Chlorpyrifos	.080	.100	.008	10	80	.651	.750	.076	12	87
Dacthal	.112	.100	.008	7	112	.754	.750	.082	11	101
Methidathion	.075	.100	.012	16	75	.571	.750	.063	11	76
Napropamide	.107	.100	.019	18	107	.696	.750	.079	11	93

[1]Surrogate compound.

Table 9. Accuracy and precision data from seven determinations of the method analytes at 0.10- and 0.75-microgram-per-liter concentrations in spiked Sacramento River water for modified analytical method

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

Compound	0.10 microgram per liter					0.75 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Eptam	0.062	0.100	0.012	19	62	0.743	0.750	0.111	15	99
Butylate	.075	.100	.014	19	76	.648	.750	.085	13	87
Pebulate	.070	.100	.016	23	70	.561	.750	.083	15	75
Molinate	.133	.140	.035	26	95	.719	.790	.048	7	91
Ethalfluralin	.063	.100	.024	38	63	.537	.750	.179	33	72
Trifluralin	.053	.100	.027	51	53	.519	.750	.146	28	69
Simazine	.083	.100	.019	23	83	.579	.750	.062	11	77
Carbofuran	.101	.100	.014	14	101	.631	.750	.072	11	84
Atrazine	.095	.100	.015	16	95	.744	.750	.097	13	99
Terbuthylazine[1]	.189	.100	.016	8	94	.196	.750	.018	9	98
Fonofos	.086	.100	.009	10	86	.599	.750	.067	11	80
Diazinon d-10[1]	.072	.100	.014	19	72	.071	.750	.014	20	71
Diazinon	.085	.100	.012	14	85	.622	.750	.094	15	83
Carbaryl	.103	.100	.016	16	103	.614	.750	.077	13	82
Alachlor	.091	.100	.011	12	91	.685	.750	.054	8	91
Thiobencarb	.098	.100	.013	13	99	.770	.750	.136	18	103
Malathion	.092	.100	.011	12	92	.812	.750	.086	11	108
Metolachlor	.104	.100	.011	11	104	.816	.750	.065	8	109
Cyanazine	.087	.100	.016	18	87	.663	.750	.145	22	89
Chlorpyrifos	.089	.100	.014	16	89	.761	.750	.109	14	102
Dacthal	.111	.100	.014	13	111	.835	.750	.107	13	111
Methidathion	.085	.100	.010	12	85	.701	.750	.038	5	93
Napropamide	.104	.100	.015	14	104	.700	.750	.056	8	93

[1]Surrogate compound.

Table 10. Accuracy and precision data from seven determinations of the method analytes at 0.10- and 0.75-microgram-per-liter concentrations in spiked San Joaquin River water for modified analytical method

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

Compound	0.10 microgram per liter					0.75 microgram per liter				
	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Mean observed conc. (µg/L)	Matrix plus background (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Eptam	0.125	0.149	0.041	33	84	0.676	0.799	0.145	21	85
Butylate	.074	.100	.006	8	74	.617	.750	.117	19	82
Pebulate	.074	.100	.014	19	74	.604	.750	.098	16	81
Molinate	.105	.100	.017	16	105	.733	.750	.101	14	98
Ethalfluralin	.038	.100	.010	26	38	.354	.750	.095	27	47
Trifluralin	.059	.100	.019	32	59	.315	.750	.057	18	42
Simazine	.157	.171	.020	13	92	.685	.821	.061	9	83
Carbofuran	.097	.100	.009	9	97	.662	.750	.062	9	88
Atrazine	.091	.100	.009	10	91	.748	.750	.050	7	100
Terbuthylazine[1]	.180	.100	.013	7	90	.196	750	.019	10	98
Fonofos	.085	.100	.008	9	85	.617	.750	.058	9	82
Diazinon d-10[1]	.079	.100	.012	15	79	.075	.750	.008	11	75
Diazinon	.102	.120	.010	10	85	.711	.770	.077	11	92
Carbaryl	.094	.100	.010	11	94	.567	.750	.062	11	76
Alachlor	.090	.100	.007	8	90	.713	.750	.049	7	95
Thiobencarb	.110	.100	.019	17	110	.801	.750	.137	17	107
Malathion	.122	.100	.014	11	122	.897	.750	.151	17	120
Metolachlor	.135	.115	.015	11	117	.953	.765	.157	16	125
Cyanazine	.097	.100	.016	16	97	.728	.750	.123	17	97
Chlorpyrifos	.101	.100	.011	11	101	.858	.750	.141	16	114
Dacthal	.120	.100	.020	17	120	.960	.750	.159	17	128
Methidathion	.090	.100	.009	10	90	.722	.750	.072	10	96
Napropamide	.097	.100	.009	9	97	.788	.750	.048	6	105

[1]Surrogate compound.

Table 11. Method detection limits for the original analytical method calculated at the 0.05-microgram-per-liter concentration and for the modified analytical method calculated at the 0.10-microgram-per-liter concentration

[Values in microgram per liter. —, not included in original method]

	Organic-free water		Sacramento River water		San Joaquin River water	
	Original	Modified	Original	Modified	Original	Modified
Eptam	—	0.044	—	0.038	—	0.129
Butylate	—	.038	—	.044	—	.019
Pebulate	—	.044	—	.050	—	.044
Molinate	0.028	.060	0.025	.110	0.038	.053
Ethalfluralin	—	.060	—	.075	—	.031
Trifluralin	.013	.057	.019	.085	.028	.060
Simazine	.013	.022	.047	.060	.082	.063
Carbofuran	.013	.031	.041	.044	.031	.028
Atrazine	.013	.038	.022	.047	.035	.028
Terbuthylazine[1]	.022	.031	.013	.050	.028	.041
Fonofos	.013	.041	.019	.028	.022	.025
Diazinon d-10[1]	—	.028	—	.044	—	.038
Diazinon	.016	.028	.019	.038	.038	.031
Carbaryl	.009	.041	.041	.050	.044	.031
Alachlor	—	.028	—	.035	—	.022
Thiobencarb	.025	.038	.016	.041	.038	.060
Malathion	.009	.057	.019	.035	.031	.044
Metolachor	—	.044	—	.035	—	.047
Cyanazine	—	.041	—	.050	—	.050
Chlorpyrifos	.013	.025	.028	.044	.028	.035
Dacthal	—	.025	—	.044	—	.063
Methidathion	.006	.038	.031	.031	.028	.028
Napropamide	—	.060	—	.047	—	.028

[1]Surrogate compound.