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Quantitative Determination of Pyrethroids, Pyrethrins, and Piperonyl Butoxide in Surface Water by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry

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A new method for determination of pyrethroids, pyrethrins, and piperonyl butoxide (PBO) by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) was developed for surface water samples. The method is based on sampling 100 L of ambient surface water with a solid phase extraction (SPE) technique that uses both wound glass fiber filters for collecting the particulate-associated chemicals and XAD-2 resin for collecting the dissolved chemicals. The method detection limits of the analytes ranged from 0.58 to 8.16 ng/sample, which is equivalent to a detection limit range of 0.0058−0.082 ng/L for a 100 L water sample collected by the SPE technique. The SPE when coupled with HRGC/HRMS was a suitable match for detecting these chemicals at subnanogram per liter ranges that are toxicologically significant to aquatic organisms. To confirm the utility of this method for environmental applications, pyrethroids and PBO were found at subnanogram per liter concentrations in surface water samples collected from five tributaries (primarily urban creeks) of the San Francisco Bay, California.

KEYWORDS: Pyrethroids; pesticides; XAD-2; HRGC/HRMS; San Francisco Bay

INTRODUCTION

The decision of the U.S. Environmental Protection Agency (EPA) to phase out certain uses of the organophosphate (OP) insecticides because of their potential for causing toxicity in humans, especially children, has led to their gradual replacement with another class of insecticides, pyrethroids. Pyrethroids are synthetic derivatives of pyrethrins, which are natural insecticides that are produced by certain species of chrysanthemum (*1*). Pyrethroids act as neurotoxins and target insects' central nervous system (*2*). They have been applied primarily for insect control in agricultural areas and can be transported into surface waters by agricultural runoff from rainstorms (*3*), drift from aerial or ground-based spraying (*4*), and release of agricultural tailwaters (*5*). These insecticides are also applied in urban areas for structural pest control, landscape maintenance, public health pest control, and rights of way (*6*), where their major transport pathway into surface waters is stormwater runoff. Once in receiving waters, these insecticides can potentially induce toxicity on aquatic organisms (*7*, *8*). In addition, piperonyl butoxide (PBO) is commonly added to pyrethroid and pyrethrin pesticide formulations where it can act as a synergist by enhancing the toxic effects of the active ingredient. It functions by inhibiting a group of enzymes (mixed-function oxidases) that are involved in pyrethroid detoxification, which as a result enhances the toxicity of pyrethroids by 10−150 times (*9*).

Measurement and positive identification of pesticides at the concentrations (sub-ng/L range) that might be found in the surface water samples would be difficult if the chemical analysis was limited to the use of conventional sample collection and concentration methods combined with gas chromatography-electron capture detection (GC-ECD) or high-performance liquid chromatography with ultraviolet absorbance detection (HPLC-UV). These methods are prone to interferences that normally occur when analyzing environmental samples.

There is a need for developing new methods of sample preparation and handling and using new and different types of analytical instruments, such as high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), for measuring chemicals in environmental samples. This instrument provides high selectivity and mass resolution to reduce potential interferences and, when combined with large volume sampling, enables the method to routinely achieve very low levels of chemical detection. Furthermore, the level of confidence in data collected is much greater than for any data collected by conventional mass spectrometric methods (*10*).

A new method for determination of pyrethroids, pyrethrins, and PBO by HRGC/HRMS was developed for ambient surface

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Table 1. Analyte Ions Monitored, Ion Ratios, and Quantification Standards Used

analyte	retention time (min)	quantification ion (m1)	confirmation ions (m2)	expected ion ratio (m1/m2)	lock
allethrin-A	23:05	136.0888 (123.1174)	137.0922 (124.1208)	9.8	130.9920
allethrin-B	23:16	136.0888 (123.1174)	137.0922 (124.1208)	9.8	130.9920
prallethrin-A	23:45	133.0653 (123.1174)	134.0732 (124.1208)	0.77	130.9920
prallethrin-B	23:54	133.0653 (123.1174)	134.0732 (124.1208)	0.77	130.9920
cinerin-I	26:11	123.1174	124.1208 (150.1045)	10	130.9920
jasmolin-I	28:05	123.1174	124.1208 (164.1201)	10	130.9920
pyrethrin-I	28:14	123.1174	124.1208 (162.1045)	10	130.9920
cinerin-II	36:06	167.1072	NA	NA	130.9920
jasmolin-II	38:30	167.1072	NA	NA	130.9920
pyrethrin-II	38:38	167.1072	NA	NA	130.9920
resmethrin-A	31:11	171.0810	172.0844	4.2	218.9856
bioresmethrin	31:33	171.0810	172.0844	4.2	218.9856
PBO	31:20	176.0837	177.0871	5.7	218.9856
tetramethrin-A	33:05	164.0712	165.0743	8.5	180.9888
tetramethrin-B	33:30	164.0712	165.0743	8.5	180.9888
bifenthrin	33:32	197.0345	199.0316	3.4	180.9888
fenpropathrin	33:55	208.0762	209.0795	0.27	180.9888
phenothrin-A	34:58	183.0810	184.0844	3.5	180.9888
phenothrin-B	35:23	183.0810	184.0844	3.5	180.9888
permethrin-A	40:06	183.0810	184.0844	5.4	180.9888
permethrin-B	40:37	183.0810	184.0844	5.4	180.9888
L-cyhalothrin-A	36:43	197.0345	199.0316	3.1	180.9888
L-cyhalothrin-B	37:28	197.0345	199.0316	3.1	180.9888
cyfluthrin-A	42:28	199.0559	200.0593	6.8	180.9888
cyfluthrin-B	42:51	199.0559	200.0593	6.8	180.9888
cyfluthrin-C	43:07	199.0559	200.0593	6.8	180.9888
cyfluthrin-D	43:17	199.0559	200.0593	6.8	180.9888
cypermethrin-A	43:36	181.0653	182.0687	6.8	180.9888
cypermethrin-B	44:00	181.0653	182.0687	6.8	180.9888
cypermethrin-C	44:15	181.0653	182.0687	6.8	180.9888
cypermethrin-D	44:26	181.0653	182.0687	6.8	180.9888
flucythrinate-A	44:27	199.0934 (181.0653)	200.0968 (182.0687)	7.6	180.9888
flucythrinate-B	45:11	199.0934 (181.0653)	200.0968 (182.0687)	7.6	180.9888
fenvalerate-A	46:53	167.0628	169.0600	1.9	180.9888
fenvalerate-B	47:39	167.0628	169.0600	1.9	180.9888
delta/tralomethrin-A	48:50	250.9071	252.9051	0.51	242.9856
delta/tralomethrin-B	49:33	250.9071	252.9051	0.51	242.9856
^{13}C-cypermethrin[a]	44:05	187.0857	188.0891	11.7	180.9888
^{13}C-Cl$_6$-PCB-138[b]	29:57	230.0093	232.0000	1.55	242.9856
^{13}C-cyfluthrin[c]	42:50	232.0063	206.0797	11.1	180.9888

[a] ^{13}C-Cypermthrin is the labeled quantification standard. [b] ^{13}C-Cl$_6$-PCB-138 is the recovery (injection) standard. [c] ^{13}C-Cyfluthrin is the field standard. Abbreviations: NA, not applicable, single ion monitored.

water samples. This work was conducted primarily because there are a limited number of published analytical methods for measuring these chemicals at the subnanogram per liter range that are expected in surface water samples (*11*−*13*). To confirm the utility of this method for environmental applications, this method was further tested in the field by analyzing high volume (100 L) surface water samples collected from five tributaries (primarily urban creeks) of the San Francisco Bay, California.

MATERIALS AND METHODS

Reagents and Analytical Standards. Solvents included pesticide residue grade dichloromethane (DCM) and hexane and HPLC grade acetonitrile and ethyl acetate. High-purity water (reagent grade; Seastar Chemicals, Sidney, B.C., Canada) was used. Pyrethroid, pyrethrin, and PBO standards were obtained from AccuStandards (New Haven, CT). Labeled standard cypermethrin, mix of stereoisomers (phenoxy-$^{13}C_6$), and cyfluthrin, mix of stereoisomers (phenoxy-$^{13}C_6$), were obtained from Cambridge Isotope Laboratories (Andover, MA). 2,2′,3,4,4′,5′-Hexachlorobiphenyl ($^{13}C_{12}$-PCB 138) was obtained from Wellington Laboratories (Guelph, Ontario, Canada).

Field Sampling Equipment. Water samples were collected using an AXYS Infiltrex high volume water sampler (AXYS Technologies, Sidney, B.C.). The XAD-2 columns were constructed of Teflon pipe (32 cm length, 18 mm width), which were packed with Supelco XAD-2 resin (300 μm diameter). The wound glass fiber filter cartridges used were 4 in. in size with a 1 μm nominal particle retention (obtained from General Filtration, Concord, Ontario). All XAD-2 used in this project was cleaned by Soxhlet extraction using the following solvents: 16 h with acetone, followed by 48 h with methanol, and then 96 h with DCM. Similarly, all wound filters were cleaned by Soxhlext extraction with acetone for 16 h and DCM for 16 h.

Working Solutions. A labeled standard solution, containing $^{13}C_6$-labeled cypermethrin, was prepared in methanol at a concentration of 1000 ng/mL. An aliquot containing 20 ng of the labeled standard was added to each sample prior to analysis. A recovery (internal) standard solution containing $^{13}C_{12}$-labeled PCB 138 was prepared in isooctane at a concentration of 2000 ng/mL. An aliquot containing 10 ng of the recovery standard was added to each extract prior to instrumental analysis. A native (unlabeled) analyte spiking solution containing the native analytes listed in **Table 1** was prepared in methanol from prime stock solutions. Typically, a 10 μL aliquot (equivalent to 20−40 ng of each analyte) was added to each laboratory control sample prior to analysis.

Extraction of XAD-2. XAD-2 resin (140 g) samples were spiked with 20 ng of quantification standard solution containing $^{13}C_6$-cypermethrin. The samples were then Soxhlet extracted with DCM for 16 h. The DCM extract containing residual water was reduced by rotary evaporation to the residual water level. The volume was adjusted to 100 mL with reagent water and then liquid−liquid extracted 3× with 50 mL of DCM. The extract was dried with granular sodium sulfate and reduced to 1 mL by rotary evaporation. The resulting extract was

transferred from the round-bottom flask and filtered through a glass wool-plugged pipet into a centrifuge tube. The resulting extract was gravimetrically split for multiple analyses. The portion of the extract used for pyrethroid analysis (one-fourth of the original extract) was solvent exchanged to hexane and cleaned up as described below.

Extraction of Filters. Wound glass fiber filter samples were placed in a narrow body 700 mL beaker and soaked in 300 mL of 1 M sodium acetate buffer at pH 4 (to allow for carbamates and pyrethroid analyte extraction) and spiked with 20 ng of quantification standard solution containing $^{13}C_6$-cypermethrin in methanol. Ultrasonic extraction of the filters was conducted 3× with 300 mL of acetonitrile. The extracts were combined, and the acetonitrile was removed by rotary evaporation. The resulting aqueous extract was made to 1 L with reagent water and liquid−liquid extracted with 3 × 100 mL of DCM. The combined extract was dried with granular sodium sulfate and reduced in volume to 50 μL and solvent exchanged to hexane for clean up.

Extract Cleanup with Florisil. Florisil (pesticide grade, 60/100 mesh; U.S. Silica, Berkeley Springs, WV) was used. Florisil was first activated by heating at 450 °C for a minimum of 8 h and then deactivated with ultrapure water (2.1% by weight), allowed to cool to room temperature under nitrogen, and allowed to sit for 24 h. A Florisil column was prepared by filling a glass column (25 cm length × 1 cm i.d. with 100 mL reservoir) with hexane. The column was then packed with 8 g of 2.1% deactivated Florisil. Elution profiles for the analytes of interest were identified on the Florisil column, and suitable elution cut points were determined. Approximately 1 mL of the hexane sample extract was loaded onto the Florisil column. The column was first eluted with 50 mL of 15% DCM in hexane, and the eluate was discarded. The column was then eluted with 75 mL of 1:1 DCM:ethylacetate. The DCM:ethylacetate eluate was concentrated by rotary evaporation, solvent exchanged to 1 mL of acetonitrile, and then cleaned up with an aminopropyl bonded silica solid phase extraction (SPE) column.

Extract Cleanup with NH_2 SPE Column. The aminopropyl SPE column (NH_2 column, 1 g, 6 mL; Varian, Palo Alto, CA) was initially conditioned with 2 column volumes of acetonitrile, followed by 2 column volumes of DCM, and then 2 column volumes of acetonitrile. The 1 mL sample extract was loaded onto the SPE column and then eluted with 6 mL of acetonitrile. Both the extract loading and the elution solvents were collected, reduced in volume, solvent exchanged to hexane, and then transferred to a microvial. The final extract volume was adjusted to 95 μL and spiked with 5 μL of the recovery standard ($^{13}C_{12}$-labeled PCB 138) just prior to instrumental analysis.

HRGC/HRMS Conditions. HRGC/HRMS analysis was conducted using an AutoSpec Ultima (Micromass, Wythenshawe, United Kingdom) HRMS equipped with a HP 6890 GC (Agilent Technologies), a CTC autosampler (CTC Analytics, Zwingen, Switzerland), and an Alpha data system running on Micromass Opus software. A DB-5 (Agilent, CA) capillary chromatography column (60 m, 0.25 mm i.d., and 0.1 μm film thickness) was coupled directly to the MS source. Immediately prior to running samples, the mass spectrometer was tuned to a static mass resolution of at least 8000 and operated in the electron impact ionization mode using voltage-selected ion mode (V-SIR) with perfluorokerosene lock masses, acquiring the ions listed in **Table 1**.

GC operating conditions included the following oven temperature program for analyte separation: initial temperature 50 °C hold for 0.5 min, ramp at a rate of 20−150 °C; ramp at a rate of 4−230 °C and hold for 6 min, ramp at a rate of 3−300 °C and hold for 1 min. Injection temperatures and interface temperatures were set at 220 and 290 °C, respectively.

Surface Water Collection. Water samples were collected during the spring season (April 2005) from five tributaries of the San Francisco Bay, CA, including Coyote Creek, San Lorenzo Creek, San Mateo Creek, Suisun Creek, and Petaluma River. This period was after the major winter rains and coincided with the resumption of fresh pesticide applications in urban and agricultural settings. Samples were collected upstream above the region of tidal influence. Water was sampled at depths of just below the water surface down to 1 m below the surface through Teflon tubing that was attached to an aluminum pole oriented up-current and upwind from equipment and personnel by pumping through a customized AXYS Infiltrex sampler. Water was pulled first through a wound glass fiber filter (1.0 μm nominal pore size) to obtain a separate particulate fraction and then through two XAD-2 resin (70 g each)-filled Teflon columns mounted in parallel to obtain the dissolved fraction. For quality assurance purposes, the XAD-2 columns were spiked in the laboratory with $^{13}C_6$-cyfluthrin to account for efficiency of analyte retention in the field and analyte losses that may occur during sample workup. The water samples collected were approximately 100 L pulled at a flow rate of 1.5 L/min. Caution was taken to minimize contamination at all levels of sample collection and handling. Samples were shipped to the laboratory on ice; filters were stored frozen, and XAD-2 columns were maintained at 2−4 °C until analysis.

RESULTS AND DISCUSSION

Coelution of Pyrethroids. Gas chromatographic conditions were optimized to achieve separation of the different pyrethroids, the six pyrethrins, and PBO. Under the experimental conditions described, all of the observed isomers of the various pyrethroids, pyrethrins, and PBO were separated with the exception of the first eluting isomer of flucythrinate (flucythrinate A), which coelutes at the same retention time as the last-eluting isomer of cypermethrin (cypermethrin D). This problem was overcome by monitoring an additional ion (181.0653) for flucythrinate in the channel for cypermethrin. The contribution of flucythrinate A to cypermthrin D was determined from the ratio of flucythrinate A and B in the quantification mass ion channels (199.0934 and 181.0653).

Analyte Transformation in the Analytical System. Under the GC conditions described, the pyrethroid tralomethrin was observed to transform into deltamethrin in a reproducible and quantitative manner. This is possibly due to the debromination of tralomethrin while it is in the GC injector. Similar phenomenon has also been observed previously (*14*). As a result, deltamethrin and tralomethrin concentrations were reported here as their combined sum from the GC/MS method described.

Method Detection Limits (MDLs). A MDL study was conducted for XAD-2 samples following U.S. EPA MDL protocol (*15*), and the results are shown in **Table 2**. The MDLs for pyrethroids, pyrethrins, and PBO ranged from 0.58 to 8.16 ng/sample, which is equivalent to a detection limit range of 0.0058−0.082 ng/L for a 100 L water sample collected using the XAD-2 SPE technique.

To reflect variations in detection limits as a result of chromatographic noise from matrix coextractives, sample specific detection limits (SDL) were calculated. The SDL values were determined from the analysis data by converting three times the representative chromatographic noise to concentration following the same procedure used to convert target peak responses to concentration. The SDL value was used as a detection qualifier for reporting field sample data.

Quantification Method. Target concentrations were determined with respect to the labeled quantification standard, $^{13}C_6$-cypermethrin, as indicated in **Table 1**. The concentration of each pyrethroid was determined by summing the concentration of the observed individual isomers. Recovery values of the labeled quantification standard were determined with respect to the labeled recovery (internal) standard, $^{13}C_{12}$-PCB 138, added just prior to instrumental analysis. Instrument linearity was determined by running a five-point linearity series prior to analysis of sample extracts. Mean relative response factors, determined from a calibration solution run at the beginning and end of the analysis run, were used to convert raw peak areas in sample chromatograms to final concentrations using standard procedure.

Retention of Pyrethroids on XAD-2 Resin. The retention of pyrethroids on the XAD-2 column was examined, and the percent recovery values for the analytes are shown in **Table 3**. To mimic a large volume water sample, 20 L of reagent water

Table 2. MDL Determination Based On Nine Replicates[a]

native analyte	spiking level (ng/sample)	observations	mean (ng/sample)	SD	Student's *t*-value	MDL (ng/sample)[b]
allethrin	9	9	12.4	2.57	2.896	7.45
bifenthrin	10	9	10.1	1.85	2.896	5.36
cyfluthrin	10	9	10.1	0.28	2.896	0.80
cypermethrin	10	9	9.20	0.20	2.896	0.58
delta/tralomethrin[c]	10	9	7.43	0.3	2.896	0.88
fenpropathrin	10	9	9.14	1.06	2.896	3.06
fenvalerate	10	9	9.04	0.23	2.896	0.67
flucythrinate	11	9	10.4	0.28	2.896	0.81
L-cyhalothrin	10	9	7.31	0.75	2.896	2.16
permethrin	12	9	14.7	2.82	2.896	8.16
phenothrin	5	9	5.71	1.11	2.896	3.20
prallethrin	9	9	12.8	2.27	2.896	6.57
pyrethrin[d]	10	9	10.9	2.80	2.896	8.11
resmethrin	9	9	9.33	1.48	2.896	4.29
tetramethrin	5	9	8.63	1.18	2.896	3.43
PBO	5	8	4.71	0.54	2.889	1.55

[a] Abbreviations: SD, standard deviation. [b] To determine the detection limit based on a 100 L water sample, the MDL values should be divided by 100. [c] Deltamethrin and tralomethrin are reported as sums. [d] Partial sum; data represent the sum of cinerin I, jasmolin I, and pyrethrin I.

Table 3. Percent Recovery for Target Analytes From a 20 L Spiked Reagent Water Sample[a]

analytes	spike (5 ng/L)	spike duplicate (5 ng/L)	high level spike (100 ng/L)
allethrin	116	123	96
bifenthrin	100	89	84
bioresnethrin	86	81	77
cyfluthrin	NA	NA	NA
cypermethrin	165	149	118
esfenvalerate	122	118	86
fenpropathrin	73	69	100
flucythrinate	125	117	98
L-cyhalothrin	NA	NA	NA
permethrin	96	97	85
phenothrin	115	117	89
prallethrin	135	150	110
pyrethrins[b]	125	121	92
resmethrin	103	104	76
tetramethrin	85	66	49
PBO	113	111	104

[a] NA, result not available. [b] Partial sum; the data represent the sum of cinerin I, jasmolin I, and pyrethrin I. The reported % recovery values in this table are not recovery corrected.

was spiked with the pyrethroids at the two different spiking levels (5 and 100 ng/L). The solution was then passed through a column containing 70 g of XAD at a rate of 200 mL/min. The resulting XAD was extracted and analyzed. The percent recoveries for the analytes in the low spike (5 ng/L) test ranged from 73 to 165%, while in the high spike test they ranged from 49 to 118%. Overall, the XAD-2 spiked analyte recoveries were good.

Adsorption on Florisil Columns. Analyte retention and elution were characterized on the Florisil column, and the elution patterns are shown in **Table 4**. Analytes were spiked into hexane and loaded on the Florisil column as described in the Materials and Methods. The column was sequentially eluted with the following solvents: 50 mL of hexane, 50 mL of 15% DCM/hexane, 50 mL of 50% DCM/hexane, 50 mL of DCM, 50 mL of 50% DCM/ethyl acetate, and 50 mL of ethylacetate. None of the analytes was eluted in the first 50 mL of hexane and 15% DCM in hexane. All of the analytes were recovered split in the fractions with the 50 mL of 50% DCM/hexane, 50 mL of DCM, and 50 mL of 50% DCM/ethyl acetate. From this, a suitable discard solvent was determined to be 50 mL of 15% DCM in hexane and the elution solvent was determined to be 75 mL of 1:1 DCM:ethylacetate.

Table 4. Elution Patterns and Percent Recoveries of the Analytes from Florisil Column

analyte	50 mL of Hex	50 mL, 15% DCM/Hex	50 mL, 50% DCM/Hex	50 mL of DCM	50 mL, 50% DCM/EtAc	50 mL of EtAc	total % recovery
allethrin	ND	ND	ND	ND	93.6	ND	93.6
bifenthrin	ND	ND	86.0	ND	ND	ND	86.0
cyfluthrin	ND	ND	3.3	79.4	0.40	ND	83.3
cypermethrin	ND	ND	2.9	84.5	0.37	ND	88.0
delta/tralomethrin[b]	ND	ND	4.30	82.1	0.25	ND	86.5
esfenvalerate	ND	ND	0.5	89.1	0.35	ND	90.0
fenpropathrin	ND	ND	0.7	68.8	0.70	ND	70.0
flucythrinate	ND	ND	ND	95.1	1.45	ND	96.5
L-cyhalothrin	ND	ND	14.2	54.4	0.10	ND	69.0
permethrin	ND	ND	66.5	7.3	ND	ND	74.0
phenothrin	ND	ND	23.8	39.0	0.90	ND	63.5
prallethrin	ND	ND	ND	ND	101	0.1	100
pyrethrin[c]	ND	ND	ND	ND	72.8	ND	72.8
resmethrin	ND	ND	20.2	27.9	0.60	ND	49.0
tetramethrin	ND	ND	ND	ND	88.0	0.30	88.0
PBO	ND	ND	ND	ND	92.4	1.00	92.0

[a] Abbreviations: Hex, hexane; EtAC, ethylacetate; and ND, not detected. [b] Deltamethrin and tralomethrin are reported as sums. [c] Partial sum; the data represent the sum of cinerin I, jasmolin I, and pyrethrin I. The reported % recovery values are not recovery corrected.

Table 5. Accuracy and Precision for Analysis of Pyrethrins, Pyrethroids, and PBO from XAD-2 and Filters

		XAD matrix		filter matrix	
	spiked amount (ng/sample)	average % recovery, $n = 6$	%RSD, $n = 6$	average % recovery, $n = 6$	%RSD, $n = 6$
allethrin	100	109	27	121	4.6
bifenthrin	100	100	12	98.2	6.3
cyfluthrin	100	112	2.2	128	2.7
cypermthrin	100	107	1.9	112	2.0
delta/tralomethrin[a]	100	101	4.1	109	2.0
fenpropathrin	100	123	9.8	116	3.2
fenvalerate	100	114	6.8	120	2.7
flucythrinate	100	108	4.7	129	3.6
L-cyhalothrin	100	121	4.1	127	2.5
permethrin	50	119	11	120	2.7
phenothrin	50	112	12	120	4.0
prallethrin	100	110	27	125	4.0
pyrethrin[b]	63	137	22	126	6.1
resmethrin	100	100	17	38.9	23
tetramethrin	50	129	30	152	4.3
PBO	50	136	32	148	4.2

[a] Deltamethrin and tralomethrin are reported as sums. [b] Partial sum; the data represent the sum of cinerin I, jasmolin I, cinerin II, and jasmolin II.

Cleanup Using NH_2 Columns. The usefulness of aminopropyl column in removing acidic interferences such as humic and fluvic acids, fatty acids, and phenolic interferences from various environmental matrices has been previously documented (*16*−*18*). The behavior of the pyrethroids was studied using a 1 g NH_2 column. The initial elution study, which used hexane as the elution solvent, showed strong retention for pyrethroids containing a nitrile functional group. This was remedied when the loading solvent was replaced with acetonitrile. The combination of Florisil and aminopropyl cleanup produced extracts that were suitable for analysis by the HRGC/HRMS instrument.

Precision and Accuracy. Replicate measurements of spiked XAD and filter samples were conducted to demonstrate precision and recovery of the analytical procedure. These results are shown in **Table 5**. The observed results demonstrated that the analytical method produced complete recovery of the analytes and good precision. The pyrethroid resmethrin showed the lowest recovery (38.9%) from the filter matrix. Recovery values for the labeled quantification standard, $^{13}C_6$-cypermethrin, from the six replicate measurements averaged at 67.4 and 78.0% for the XAD and filter samples with %RSD values of 17.4 and 3.4%, respectively.

Field Sampling Results. The dissolved (XAD-2 associated components), particulate (filter associated components), and total (dissolved plus filtered components) concentrations of pyrethroids, pyrethrins, and PBO detected in the five San Francisco Bay tributary surface water samples are shown in **Table 6**. The pyrethroids that were detected included bifenthrin, permethrin, and deltamethrin/tralomethrin. Permethrin and deltamethrin/tralomethrin were detected at all of the sampling sites except Suisun Creek, while bifenthrin was detected only in Coyote Creek. The synergist PBO was also detected at all of the sampling sites except Suisun Creek. The total concentrations for these analytes were in the subnanogram per liter range. To our knowledge, these are the first reported measurements of these analytes in water samples from these San Francisco Bay urban creeks. Pyrethroids have been previously detected in several San Francisco Bay creeks; however, only sediment concentrations were reported (*19*).

Quality Assurance Results of XAD-2 and Filter Samples. Laboratory background levels were monitored by analysis of a

Table 6. Field Sample Analysis Results For San Francisco Bay Tributary Water Samples[a]

	Coyote Creek			Petaluma River			Petaluma River Field Duplicate			San Mateo Creek			San Lorenzo Creek			Suisun Creek		
analyte	XAD	filter	total[b]	XAD	filter	total[b]	XAD	filter	total[b]	XAD	filter	total[b]	XAD	filter	total[b]	XAD	filter	total[b]
allethrin	<0.159	<0.121	ND	<0.454	<0.082	ND	<0.487	<0.057	ND	<0.143	<0.053	ND	<0.237	<0.078	ND	<0.091	<0.053	ND
bifenthrin	<0.163	0.188	ND	<0.156	<0.026	ND	<0.292	<0.024	ND	<0.083	<0.024	ND	<0.095	<0.024	ND	<0.048	<0.026	ND
cyfluthrin	<0.064	<0.321	ND	<0.138	<0.112	ND	<0.130	<0.121	ND	<0.065	<0.083	ND	<0.052	<0.103	ND	<0.030	<0.119	ND
cypermethrin	<0.064	<0.090	ND	<0.094	<0.039	ND	<0.111	<0.039	ND	<0.093	<0.026	ND	<0.061	<0.037	ND	<0.029	<0.036	ND
delta/tralomethrin[c]	**0.006**	**0.057**	**0.063**	**0.001**	**0.007**	**0.008**	**0.001**	**0.009**	**0.010**	**0.019**	**0.023**	**0.042**	**0.001**	<0.004	**0.001**	<0.001	<0.004	ND
fenpropathrin	<0.029	<0.024	ND	<0.019	<0.015	ND	<0.040	<0.015	ND	<0.022	<0.014	ND	<0.020	<0.013	ND	<0.006	<0.011	ND
fenvalerate	<0.013	<0.077	ND	<0.009	<0.026	ND	<0.012	<0.032	ND	<0.008	<0.016	ND	<0.013	<0.022	ND	<0.005	<0.030	ND
flucythrinate	<0.003	<0.016	ND	<0.004	<0.011	ND	<0.006	<0.013	ND	<0.007	<0.011	ND	<0.004	<0.009	ND	<0.002	<0.012	ND
L-cyhalothrin	<0.009	<0.060	ND	<0.011	<0.018	ND	<0.014	<0.027	ND	<0.009	<0.021	ND	<0.004	<0.020	ND	<0.002	<0.024	ND
permethrin	**0.078**	**0.180**	**0.258**	**0.025**	**0.011**	**0.036**	**0.027**	**0.010**	**0.037**	**0.064**	**0.013**	**0.077**	**0.018**	<0.006	**0.018**	<0.003	<0.010	ND
phenothrin	<0.021	<0.024	ND	<0.033	<0.017	ND	<0.042	<0.017	ND	<0.022	<0.013	ND	<0.016	<0.013	ND	<0.006	<0.019	ND
prallethrin	<0.998	<0.137	ND	<1.13	<0.089	ND	<1.20	<0.102	ND	<0.512	<0.088	ND	<0.869	<0.079	ND	<0.462	<0.071	ND
pyrethrin[d]	<1.18	<1.64	ND	<1.88	<1.23	ND	<2.56	<3.06	ND	<1.21	<0.700	ND	<1.13	<0.855	ND	<0.638	<8.96	ND
resmethrin	<0.060	<0.105	ND	<0.084	<0.040	ND	<0.079	<0.044	ND	<0.096	<0.024	ND	<0.092	<0.029	ND	<0.045	<0.032	ND
tetramethrin	<0.050	<0.113	ND	<0.093	<0.061	ND	<0.080	<0.062	ND	<0.050	<0.082	ND	<0.050	<0.069	ND	<0.015	<0.083	ND
PBO	**0.174**	<0.014	**0.174**	**2.59**	<0.011	**2.59**	**3.00**	<0.012	**3.00**	**0.330**	<0.009	**0.330**	**0.205**	<0.011	**0.205**	<0.021	<0.010	ND
^{13}C-cyfluthrin[e]	**105**	**88.2**		**91.5**	**99.5**		**98.5**	**82.8**		**114**	**99.4**		**106**	**101**		**84**	**89.6**	

[a] Concentrations are all ng/L; <, analyte not detected and value represents the detection limit; ND, analyte not detected. [b] Total concentrations are the summed concentrations of the analytes in the dissolved (XAD-2) and suspended (filter) portions of the sample. [c] Deltamethrin and tralomethrin are reported as a sum. [d] Partial sum; represents sum of cinerin-I, jasmolin-I, and pyrethrin-I. [e] Values represent percent recovery of the field standard for XAD samples and extraction standard for the filter samples.

laboratory blank using clean XAD-2 and wound filter sample matrix. Analysis of the laboratory blank conducted along with the field samples demonstrated no detectable background levels. The recovery of analytes spiked into clean XAD-2 and wound filter samples ranged from 81.1 to 128% for the XAD-2 and from 74.8 to 108% for the filters, which demonstrates excellent recovery for these two matrices. In addition, the recoveries of analytes through the sampling and analytical procedure were demonstrated by spiking a labeled field standard solution containing $^{13}C_6$-cyfluthrin into the XAD-2 prior to shipping of the sampling media for field sample collection. Recovery values for labeled cyfluthrin from XAD-2 ranged from 84 to 114% for the field samples, which demonstrated very good efficiency of the sampling and analytical procedure.

Field duplicate samples were analyzed to demonstrate analytical precision through the sampling and analysis procedure. The relative percent difference (RPD) for the ^{13}C-cyfluthrin standard in the Petaluma River sample and its field duplicate was 7.37% for the XAD-2, which demonstrates excellent precision. The RPD values for the detected analytes between the field duplicate samples were the following: deltamethrin/tralomethrin (XAD-2 = 0%, filters = 25%), permethrin (XAD-2 = 7.69%, filters = 9.5%), and PBO (XAD-2 = 14.5% and was not detected on the filter samples).

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