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Pyrethroids, pyrethrins, and piperonyl butoxide in sediments by high-resolution gas chromatography/high-resolution mass spectrometry

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Abstract

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 aquatic sediments. The method detection limits for pyrethroids (15 compounds), pyrethrins, and PBO ranged from 0.16 to 1.50 ng/g sediment, which was suitable for detecting these chemicals at environmentally relevant concentrations (low ng/L range) that are toxicologically significant to benthic organisms. Recovery of the analytes from a low level spiked sediment ranged from 89.7% to 135%. Resmethrin showed the lowest recovery at 23.5% and pyrethrins showed the highest recovery at 154%. To confirm the utility of this new method for environmental applications, sediment samples collected from five tributaries of the San Francisco Bay, California were analyzed. Individual pyrethroids were detected in concentrations of up to 17.6 ng/g, while PBO was detected in all sediment samples in concentrations of 0.010–0.215 ng/g. Pyrethrins were not found in the sediment samples.

Keywords: Pyrethroids; Pesticides; HRGC/HRMS; San Francisco Bay

1. Introduction

The decision of the US Environmental Protection Agency (EPA) to phase out/eliminate 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. Pyrethroids act as neurotoxins and target insects' central nervous system [1]. When applied in agricultural areas these insecticides can be transported into surface waters by agricultural runoff from rainstorms [2], drift from aerial or ground-based spraying [3], and by release of agricultural tail waters [4]. In urban areas (residential and industrial), pyrethroids are used for structural pest control, landscape maintenance, public health pest control, and rights of way [5] and their major transport pathway into surface waters is generally by storm water drainage [6]. Once in receiving waters, these insecticides can potentially induce toxicity on aquatic organisms such as benthic invertebrates and fish [7]. Piperonyl butoxide (PBO), which can act as a synergist by enhancing the toxic effects of the active ingredient when added to pyrethrin and pyrethroid pesticide formulations, can also potentially be found in receiving waters and their sediments. PBO 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 [8].

There is a need for developing new methods that use new and different types of analytical instruments for measuring these chemicals in environmental samples. High-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) provides high selectivity and mass resolution to reduce potential interferences and achieve low levels of chemical detection. Furthermore, the level of confidence in data collected is much greater than for any data collected by conventional liquid chromatography/mass spectrometry (LC/MS) and gas chromatography/mass spectrometry (GC/MS) methods, which are routinely used by analytical laboratories.

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A new method for determination of pyrethroids, pyrethrins, and PBO by HRGC/HRMS was developed for aquatic sediments. This work was conducted because there are a limited number of published analytical methods for measuring these chemicals at the environmentally relevant concentrations (low ng/L range) that are expected in aquatic system sediments [9]. To confirm the utility of this method for environmental applications, this method was further tested in the field by analyzing sediment samples collected from five tributaries, primarily urban creeks, of the San Francisco Bay, California.

2. Experimental

2.1. Reagents and analytical standards

The solvents used included pesticide residue grade dichloromethane (DCM) and *n*-hexane and HPLC grade acetonitrile and ethyl acetate. High purity water (reagent grade; Seastar Chemicals, Sidney, Canada), was used. Pyrethroid, pyrethrin, and piperonyl butoxide standards were obtained from AccuStandards (New Haven, CT, USA). Labeled standard cypermethrin, mix of stereoisomers (phenoxy-$^{13}C_6$), was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). 2,2′,3,4,4′,5′-hexachlorobiphenyl ($^{13}C_{12}$-PCB 138) was obtained from Wellington Laboratories (Guelph, Canada).

2.2. Working solutions

A labeled standard solution, containing [$^{13}C_6$] 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, [$^{13}C_{12}$] 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 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) is added to each laboratory control sample (LCS) prior to analysis. In this study it was observed that standard solutions containing pyrethrin analytes degrade rapidly. As a result fresh calibration and LCS spiking solutions were prepared every week or with every batch of samples, whichever came later, for these analytes. These solutions were also stored in dark at 0 °C.

2.3. HRGC/HRMS conditions

High-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) was conducted using an Autospec Ultima high-resolution MS equipped with a HP 6890 GC, a CTC auto-sampler, and an Alpha data system running on Micromass Opus software. A DB-5 capillary chromatography column (60 m, 0.25 mm i.d., and 0.1 μm film thickness) was coupled directly to the MS source. The carrier gas was helium and the GC was operated at a constant head pressure of 200 kPa. When GC columns age the head pressure was slightly adjusted to maintain the retention times shown in Table 1. 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 (EI) ionization mode using voltage selected ion mode (V-SIR) with perfluorokerosene (PFK) 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 temperature and interface temperatures were set at 220 °C and 290 °C, respectively.

2.4. Field sample collection and preparation

Sediment samples were collected during the spring season (April 2005) from five tributaries of the San Francisco Bay, California 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. The top 5 cm layer of sediment was collected using Teflon lined scoops and buckets. The sediment at each site was thoroughly homogenized, placed in cleaned 500 mL wide mouth jars, and then stored at −20 °C prior to extraction and analysis.

2.4.1. Extraction of sediments

Ten grams (dry weight) of each sediment sample was mixed with 75 g of baked powdered sodium sulfate and spiked with 20 ng of quantification standard solution containing cypermethrin, mix of stereoisomers (phenoxy-$^{13}C_6$) and mixed with spatula. The resulting mixture was left for 0.5 h for equilibration prior to extraction. The samples were then Soxhlet extracted with DCM for 16 h. The extract was dried with granular sodium sulfate and reduced to 1 mL by rotary evaporation. The extract was then solvent exchanged to *n*-hexane and cleaned up as described below. To minimize breakdown of pyrethrin analytes due to exposure to light, all materials containing the sample and QC sample extracts were wrapped and covered with aluminium foil.

2.4.2. Extract cleanup with Florisil

Florisil (pesticide grade, 60/100 mesh; US Silica, Berkeley Springs, WV) was used. Florisil was first activated by heating at 450 °C for a minimum of 8 h then deactivated with ultra pure water (2.1% by weight), flushed with 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 *n*-hexane. The column was then dry packed with 8 g 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 *n*-hexane sample extract was loaded onto the Florisil column. The column was first eluted with 50 mL of 15% DCM in *n*-hexane and the

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
Piperonyl butoxide	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
13C-Cypermethrin[a]	44:05	187.0857	188.0891	11.7	180.9888
13C-Cl6-PCB-138[b]	29:57	230.0093	232.0000	1.55	242.9856
13C-Cyfluthrin[c]	42:50	232.0063	206.0797	11.1	180.9888

Abbreviations: NA = not applicable, single ion monitored.
[a] 13C-Cypermthrin is the labeled quantification standard.
[b] 13C-Cl6-PCB-138 is the recovery (injection) standard.
[c] 13C-Cyfluthrin is the field standard.

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 acetonitrile, and then cleaned up with an aminopropyl bonded silica solid phase extraction (SPE) column.

2.4.3. 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 *n*-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 ([$^{13}C_{12}$] PCB 138) just prior to instrumental analysis.

3. Results and discussion

3.1. Co-elution 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 eluted

isomer of flucythrinate (flucythrinate A), which coelutes at the same retention time as the last eluted isomer of cypermethrin (cypermethrin D), see Table 1. 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).

3.2. 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 [10]. As a result deltamethrin and tralomethrin concentrations were reported here as their combined sum from the GC/MS method described.

3.3. Quantification method

Target concentrations were determined with respect to the labelled quantification standard (cypermethrin, mix of stereoisomers (phenoxy-$^{13}C_6$)) 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 labelled quantification standard were determined with respect to the labelled 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, see Table 2. Mean relative response factors (RRF), 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. During this study it was observed that standard solutions containing pyrethrin analytes degrade rapidly. As a result fresh calibration and LCS spiking solutions were prepared every week or with every batch of samples for these analytes.

Table 2
Method linear calibration data

Analytes	Concentration range (ng/mL)	Mean RR, $n=5$	%RSD
Allethrin	50 – 1000	1.11	12.5
Bifenthrin	50 – 1000	0.03	17.8
Cyfluthrin	50 – 1000	0.36	17.2
Cypermethrin	50 – 1000	1.18	3.66
Delta/tralomethrin	50 – 1000	0.56	10.8
Fenpropathrin	50 – 1000	0.58	6.52
Fenvalerate	50 – 1000	1.43	4.67
Flucythrinate	50 – 1000	1.52	8.18
L-Cyhalothrin	50 – 1000	1.76	6.85
Permethrin	25 – 500	6.47	4.93
Phenothrin	25 – 500	2.7	5.8
Prallethrin	50 – 1000	0.58	17.6
Pyrethrin	50 1000	NA	NA
Resmethrin	50 1000	1.26	7.81
Tetramethrin	25 500	1.83	26.8
Piperonyl butoxide	25 200	2.02	24.3

RR = relative response, NA = not applicable, Pyrethrin is a total of six analytes the mean RR for each analyte was measured separately and ranged between 0.01% and 0.31 and %RSD ranged between 0.89% and 29%.

3.4. Method detection limits

A method detection limit (MDL) study was conducted for sediment samples following US EPA MDL protocol *Federal Register 40CFR Part 136, Appendix B* and the results are shown in Table 3. The range of MDLs for pyrethroids (15 analytes) and pyrethrins (reported as the sum of cinerin I, jasmolin I, and pyrethrin I) was 0.16–1.36 ng/g of sediment, while the MDL for PBO was 1.50 ng/g of sediment.

Table 3
MDL determination based on nine replicates for sediment samples

Native analyte	Spiking level (ng/g)	Observations	Mean (ng/g)	SD	Student's *t*-value	MDL (ng/g)
Allethrin	4	9	3.93	0.25	2.896	0.74
Bifenthrin	4	9	3.01	0.21	2.896	0.60
Cyfluthrin	4	9	2.68	0.12	2.896	0.34
Cypermethrin	4	9	3.14	0.24	2.896	0.68
Delta/tralomethrin[a]	4	9	2.42	0.09	2.896	0.27
Fenpropathrin	4	9	2.97	0.14	2.896	0.40
Fenvalerate	4	9	3.00	0.11	2.896	0.31
Flucythrinate	4	9	3.22	0.12	2.896	0.34
L-Cyhalothrin	4	9	2.75	0.13	2.896	0.37
Permethrin	2	9	1.44	0.06	2.896	0.16
Phenothrin	2	9	1.46	0.06	2.896	0.17
Prallethrin	4	9	4.31	0.47	2.896	1.36
Pyrethrin[b]	2	9	2.36	0.34	2.896	0.98
Resmethrin	4	9	2.72	0.15	2.896	0.45
Tetramethrin	2	9	2.55	0.24	2.896	0.71
Piperonyl butoxide	2	8	2.06	0.52	2.889	1.50

Abbreviations: MDL = method detection limit, SD = standard deviation. Sample size was 10 g dry weight.
[a] Deltamethrin and tralomethrin are reported as sum.
[b] Partial sum, data represents sum of cinerin I, jasmolin I and pyrethrin I.

Table 4
Elution patterns and percent recoveries of the analytes from Florisil column

Analyte	50 mL Hexane	50 mL, 15% DCM/hexane	50 mL, 50% DCM/hexane	50 mL DCM	50 mL, 50% DCM/EtAc	50 mL 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[a]	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[b]	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
Piperonyl butoxide	ND	ND	ND	ND	92.4	1.00	92.0

Abbreviations: Hex = hexane, DCM = dichloromethane, EtAC = ethylacetate, ND = not detected.
[a] Deltamethrin and tralomethrin are reported as sum.
[b] Partial sum, data represents sum of cinerin I, jasmolin I and pyrethrin I. The reported % recovery values are not recovery corrected.

To reflect variations in detection limits based on the characteristics of the sample matrix, sample specific detection limits (SDL) were calculated. The SDL values were determined from the analysis data by converting three times the representative 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.

3.5. Adsorption of Florisil columns

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

3.6. 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 [11–13]. The behavior of the pyrethroids was studied using a 1 g NH_2 column. The initial elution study, which used *n*-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.

3.7. Precision and accuracy

Replicate measurements of spiked sediment were conducted to demonstrate precision and recovery of the analytical procedure. These results are shown in Table 5. Analyte recoveries ranged between 89.7% and 135%. Resmethrin showed the lowest recovery (25.3%) and pyrethrins showed the highest

Table 5
Accuracy and precision for analysis of pyrethrins, pyrethroids and PBO from 10 g (dry weight basis) sediment sample

	Spiked amount (ng/g)	Average % recovery, $n=5$	%RSD, $n=5$
Allethrin	10	113	3.0
Bifenthrin	10	89.7	11
Cyfluthrin	10	112	4.2
Cypermthrin	10	105	2.7
Delta/tralomethrin[a]	10	115	2.8
Fenpropathrin	10	135	6.8
Fenvalerate	10	110	3.0
Flucythrinate	10	120	3.2
L-Cyhalothrin	10	116	3.8
Permethrin	5	127	4.5
Phenothrin	5	101	5.4
Prallethrin	10	107	8.2
Pyrethrin[b]	10	154	29
Resmethrin	10	25.3	47
Tetramethrin	5	119	3.1
Piperonyl-butoxide	5	114	6.1

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

Table 6
Field sample analysis results for San Francisco bay tributary sediment samples

Analyte	Coyote Creek (ng/g)	Coyote Creek Duplicate (ng/g)	Petaluma River (ng/g)	San Mateo Creek (ng/g)	San Lorenzo Creek (ng/g)	Suisun Creek (ng/g)
Allethrin	<0.912	<1.07	<1.38	<20.4	<2.24	<0.544
Bifenthrin	**1.48**	**1.87**	<1.84	**9.24**	**3.99**	<0.232
Cyfluthrin	<0.573	<0.490	<1.45	**17.6**	<2.19	<0.182
Cypermethrin	<0.461	<0.300	<0.494	**4.57**	<0.768	<0.121
Delta/tralomethrin[a]	**0.370**	**0.247**	**0.146**	**2.73**	**0.725**	<0.005
Fenpropathrin	<0.117	<0.0980	<0.165	<0.284	<0.183	<0.027
Fenvalerate	<0.335	<0.184	<0.368	<1.51	<0.396	<0.114
Flucythrinate	**0.347**	**0.050**	<0.063	<0.089	<0.072	<0.012
L-Cyhalothrin	**0.454**	**0.307**	<0.100	**1.71**	**0.221**	<0.015
Permethrin	**2.06**	**2.08**	**0.940**	**9.12**	**2.90**	<0.018
Phenothrin	<0.072	<0.067	<0.145	<0.180	**0.395**	<0.017
Prallethrin	<1.07	<0.924	**<1.09**	<4.81	<2.64	**<1.18**
Pyrethrin[b]	<59.7	<20.5	<32.7	<160	<99.3	<5.71
Resmethrin	<0.220	<0.220	<0.494	<0.592	<0.564	<0.050
Tetramethrin	<0.438	<0.245	<0.621	<0.922	<0.740	<0.109
Piperonyl butoxide	**0.102**	**0.098**	**0.035**	**0.215**	**0.056**	**0.010**

All results are on a dry weight basis. <Analyte not detected value represents the detection limit.
[a] Deltamethrin and tralomethrin are reported as a sum.
[b] Partial sum; represents sum of cinerin-I, jasmolin-I and pyrethrin-I.

recovery at 154%. Relative standard deviation (RSD) values of less than 11% were observed between the replicate measurements. Relatively high RSD values were observed for resmethrin and pyrethrins. Generally, the observed results demonstrated that the analytical method produced complete recovery of the analytes and acceptable precision.

3.8. Field sample results

The concentrations of pyrethroids, pyrethrins, and PBO detected in the five San Francisco Bay tributary sediment samples are shown in Table 6. The pyrethroids that were found above their SDLs included allethrin, bifenthrin, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, fenvalerate, flucythrinate, L-cyhalothrin, permethrin, and prallethrin. Individual analyte concentrations ranged from <SDL to 17.6 ng/g of sediment. San Mateo Creek total pyrethroid concentrations were much higher than the other sampling sites. The synergist PBO was found at all of the sampling sites at concentrations ranging from 0.010 to 0.215 ng/g of sediment. The highest PBO concentration was found in San Mateo Creek.

3.9. Quality assurance

Laboratory background levels were monitored by analysis of a laboratory blank containing clean sediment matrix. Analysis of the laboratory blank conducted along with the field samples demonstrated no detectable background levels. Recovery of analytes from spiked (spiked with 2 ng/g for permethrin, phenothrin, tetramethrin, and piperonyl butoxide and 4 ng/g for all other analytes) sediment sample known to contain no pyrethroids, pyrethrin or PBO ranged between 51% and 128%.

To demonstrate analytical precision and recovery duplicate field samples were analyzed. Relative percent difference (RPD) values of less than 20% against the mean were observed between the duplicate samples. RPD value of above 20% was observed for flucythrinate. This may be related to the characteristic of the sample matrix such as level of sediment homogeneity.

In addition matrix spike and matrix spike duplicate samples were analyzed along with the field sediment samples. Matrix spike recoveries ranged between 53.3% and 145%, while matrix spike duplicate recoveries ranged between 52.4% and 136%. RPD values of less than 18% were observed between the matrix spike and matrix spike duplicate pairs against the mean. The lowest recovery was observed for resmethrin in both the matrix spike (30%) and matrix spike duplicate (23.1%) samples.

Pyrethrin analytes were observed to degrade rapidly during sample preparation and storage. This was observed both in standard solutions and in LCS extracts. As a result these analytes were reported by summing the analytes that were observed to be recovered in the LCS extract.

4. Conclusions

A method for determination of pyrethroids, pyrethrins, and piperonyl butoxide by HRGC/HRMS in sediments was developed. The method detection limits obtained were low enough for measuring these important chemicals at the environmentally relevant concentrations (low ng/L range) that are generally expected in contaminated sediments.

Pyrethroids and PBO were found at low levels in sediment samples collected from five tributaries (primarily urban creeks) of the San Francisco Bay, California, which further confirmed the utility of this method for environmental applications. Individual pyrethroid concentrations in the tributary sediments ranged from <SDL to 17.6 ng/g, while PBO concentrations ranged from 0.010 to 0.215 ng/g.

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