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Analytical method development for the determination of synthetic pyrethroid insecticides in soil by gas chromatography–mass spectrometry operated in negative-ion chemical-ionization mode

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Abstract

An effective analytical method for the simultaneous determination of five synthetic pyrethroid insecticides in soil is developed and method performance data presented. The pyrethroid residues were extracted with hexane–dichloromethane in an ultrasonic bath. The extract was cleaned up on a Florisil column prior to determination by gas chromatography–negative-ion chemical ionization mass spectrometry (GC–NICI-MS) in selected-ion monitoring (SIM) mode. The highest detection sensitivities were achieved in the SIM mode where the instrument was adjusted to collect only a few ions which were indicative for the compound to be searched for, instead of scanning the entire spectrum over the whole mass range. The gain in sensitivity was the result of longer specific sampling times for each of the ions selected. Recovery studies were performed at 10, 50 and 100 ppb fortification levels of each pyrethroid and of the internal standard, mirex, and the percentage recoveries ranged from 81.7±4.2 to 108.2±2.6%. Four determinations were made at each concentration level along with a procedural blank. The quantification limit of the method was in the range of 0.012 to 4.4 ppb, depending on the compound. This method was also applied to sediment samples collected from the environment of a River Catchment being currently monitored for the presence of target pyrethroids.

Keywords: Soil; Environmental analysis; Sample preparation; Pesticides; Pyrethroids

1. Introduction

The pyrethroids are now broadly recognized as the fourth major class of synthetic organic insecticides. Since the commercial production of the first photostable pyrethroid in 1976, this group of compounds has achieved world-wide use, with widespread agriculture and environmental health applications. Of the major insecticide classes, the pyrethroids as a group are among the most potent as insecticides but have been considered to exhibit comparatively low toxicity to mammals [1].

Permethrin, cyfluthrin, cypermethrin, deltamethrin and fenvalerate are broad spectrum synthetic pyrethroid insecticides with greater photostability, enhanced insecticidal activity and low mammalian toxicity. Their effectiveness against a wide range of insects at extremely low dosages and limited persistence in the environment stimulates interest for use in agriculture around the world. At the same time, many countries have conducted research on the residual effects of these compounds on the environment after use. Contamination of fresh water ecosystems by pyrethroids occurs either due to the direct

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discharge of industrial and agricultural effluents or through the effluents of sewage treatment works where it is accumulated by the surrounding biosphere. The concentrations that have been measured in the soil suggest that this may be a serious problem in the areas to which such effluent is discharged. In the UK, recommendations have been issued for the safe use of some pyrethroids [2]. The Food and Agriculture Organisation and World Health Organisation have prescribed residue limits for some pyrethroids in the area of agricultural and livestock products [3].

Methods for analysis of pyrethroid in a variety of matrices have been presented and reviewed recently. Most of these analytical procedures use GC–electron-capture detection (ECD) or HPLC. Sukul [4] has reported a method for the determination of permethrin, cypermethrin, deltamethrin and fenvalerate in crops by GC–ECD and clean-up using different column adsorbents. Bolygo and Zakar [5] developed a method for the simultaneous determination of six pyrethroids and clean-up on active carbon–magnesia–diatomaceous earth followed by alumina. A method for the determination of cypermethrin in various crops has been described by Chapman and Harris [6]. Fenvalerate is a non-cyclopropane carboxylate pyrethroid shown to be very effective against several vegetable pests. Lee et al. [7] described the determination of fenvalerate by GC–ECD and clean-up on partially deactivated Florisil.

Much work has been conducted on the pyrethroid residue analysis in water, crops and vegetables by GC–ECD and GC–MS. The present study focuses on pyrethroid analysis in soil by GC–negative-ion chemical ionization (NICI) MS, and in particular, centres on the analytical methodology developed which permits the simultaneous determination of permethrin, cypermethrin, cyfluthrin, deltamethrin and fenvalerate at concentration levels ranging from 1 ppb to 0.5 ppm. Ultrasonic extraction using a hexane–dichloromethane solvent mixture to extract selectively the pyrethroid residues gave very good recoveries and detection levels. In addition, the method reported in this paper is successfully applied to the determination of pyrethroids in samples obtained from a contaminated ecosystem.

2. Experimental

2.1. Materials

Permethrin (24.6% *cis*, 73.4% *trans*)[3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], cypermethrin [(*R*,*S*)-α-cyano-3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], cyfluthrin [(*R*,*S*)-α-cyano-4-fluoro-3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl-(1*R*)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylate] and fenvalerate [(*R*,*S*)-α-cyano-3-phenoxybenzyl-(*R*,*S*)-2-(4-chlorophenyl)-3-methylbutyrate] were all purchased from Promochem UK. Decachlorobiphenyl (DCBP) and mirex were obtained from British Greyhound. All substances were of >94% purity. HPLC-grade hexane and dichloromethane and analytical reagent-grade acetone and diethyl ether were used. Anhydrous sodium sulphate was obtained from Fisons. Florisil (20–100 mesh) was obtained from Kodak. About 50 g of Florisil was activated by heating at 200°C for 4 h and then cooled down to ambient temperature in a dessicator. It was then deactivated prior to use by mixing with distilled water (8%, w/w) in a closed glass vessel and agitated until an even consistency was obtained.

2.1.1. Chromatographic cleanup column

A 30×2 cm I.D. glass column fitted with a PTFE stopcock was used for the adsorbent.

2.1.2. Florisil column

A small plug of glass wool was placed at the bottom of the column. Then Florisil (6 g) was introduced into the column and the column sides were tapped to produce an even packing. A 1-cm capping layer of anhydrous Na_2SO_4 was added. The column was conditioned with 10 ml of hexane.

2.2. Preparation of calibration curves

A 10-mg portion of each reference standard was dissolved in 100 ml of hexane–acetone (9:1, v/v) to give a 0.1 mg ml^{-1} stock solution. The stock solution was then serially diluted, and the appro-

priate amounts of internal (mirex) and volumetric (DCBP) standard stock solutions were added. The standard solutions then contained 1, 5, 10, 25, 50, 75, 100 and 500 ng ml^{-1} of the internal standard and of each pyrethroid, together with 50 ng ml^{-1} of volumetric standard, DCBP. These solutions were analysed by GC–NICI-MS three times at each concentration level by determining the areas of peaks obtained by mass chromatogram data processing (a computerised plot of specific ions vs. time) at the correct retention times. The resulting calibration curves were used for all calculations. The calibration curves were linear within this concentration range, with correlation coefficients of 0.995 to 0.999 obtained routinely. The mirex data was used as a check for the recovery efficiency of the method but was not used to correct pyrethroid data. The detection limits for all the pyrethroids were calculated from the calibration graph.

3. Instrumentation

A Hewlett-Packard 5980 series II GC equipped with a HP7673A autosampler and a split/splitless capillary column injector coupled to a VG Trio 1000 quadrupole mass spectrometer electron impact (EI) and positive-ion chemical ionization (PICI)/NICI capability was employed with the Lab-Base data system.

3.1. Gas chromatography

A fused-silica capillary column DB5-MS (J and W Scientific; 15 m×0.32 mm I.D., 0.25 mm film thickness) was used with helium (CP grade, purity 99.999%) as the carrier gas with a head pressure of 5 p.s.i. (1 p.s.i.=6894.76 Pa). A 1-μl volume of sample was injected by the autosampler applied splitless injection technique with the split closed for 1 min. The chromatographic temperature conditions were as follows: 100°C held for 1 min, increased at 20°C/min to 230°C, then 10°C/min to 310°C final temperature, held for 2 min. The injector and transfer line temperatures were maintained at 270°C.

3.2. Mass spectrometric acquisition parameters

Mass spectrometric ion source conditions were as follows: Ion source, 250°C; electron voltage, 70 eV; source current, 350 μA. Scanned acquisitions were made over the mass range 60–550 u, with a scan time of 0.9 s. Selected-ion monitoring (SIM) was performed with the most abundant and diagnostic ions of the compound and the dwell time for each channel was 0.02 s, and the mass span was 0.02 u. A high source temperature was used to prevent the condensation of the involatile targets (vapour pressure, vp$<10^{-5}$ mm Hg; 1 mm Hg=133.322 Pa). A higher secondary electron current was used to maintain the stability of the negative ion production over an extended period of operation. Mass calibration was conducted in the positive-ion EI mode with perfluorotributylamine (PFTBA) prior to optimising the tuning using m/z 452 from the calibrant in the NICI mode. This optimisation is particularly valuable when employing SIM, in order to minimise any variation in instrumental response as a function of mass. The selected-ion groups used for identification in the SIM mode are listed in Table 1.

Table 1
Characteristic ions of compounds according to retention time in the SIM mode

Pesticide/standards	Characteristic ions	Quantification ions
Permethrin	171,173,207,209,211	206.98±0.03
Cyfluthrin	171,173,207,209,211	206.98±0.03
Cypermethrin	171,173,207,209,211	206.98±0.03
Deltamethrin	79,81,137	78.98±0.02
Fenvalerate	167,169,211,213	167.03±0.03
Mirex	366,368,370,402,404,406	367.98±0.02
DCBP	496,498,499	497.78±0.04

3.3. Sample collection and processing

Sediment samples were collected from seven sites within the Meltham area of the River Calder Catchment, 7 km southwest of Huddersfield. These samples were collected manually and placed in wide-neck brown glass bottles. Sediments were air dried at room temperature, ground and graded through a metal sieve (20 mesh).

3.4. Extraction procedures

A 10-g sample of sediment was spiked with 1 ml of 50 ppb mirex in acetone as the internal standard and placed on a shaker for 1 h to ensure complete homogeneity. Hexane–dichloromethane (1:1, v/v) solvent mixture (20 ml) was added to each sample. The beaker containing the sample and extraction solvent was submersed in an ultrasonic bath (Dawe Sonicleaner type 644 sonic bath) and sonicated for 30 min [8]. The supernatant was decanted and passed through a glass sinter No. 4 that was capped with 5 g of anhydrous sodium, sulphate which also serves to remove particulate materials from the extracts. The ultrasonic extraction (USE) process was repeated twice more. The combined extract was then evaporated to 5 ml by rotary evaporation under reduced pressure at 40°C.

3.4.1. Chromatographic column clean-up

The concentrated extract with two additional 2 ml washings was transferred to a previously packed Florisil column head and the solution was allowed to percolate into the column. Pyrethroid residues were eluted with 6 ml of hexane–diethyl ether (7:3, v/v). The total eluate from the column was collected in a conical vial with a 1-ml calibration mark, and evaporated just to dryness with a gentle stream of clean dry nitrogen. A 1-ml volume of the volumetric standard, DCBP (50 ppb), in hexane was added to redissolve the residue. The final sample extract was transferred to an autosampler vial with a PTFE-lined crimp cap in which it could be stored in a refrigerator at 4°C for at least two weeks.

3.5. Recovery studies

Recovery studies were performed at 10, 50 and 100 ppb fortification levels of each pyrethroid and internal standard, at least four times in contamination-free sediment. These samples were prepared by spiking 1 ml of an appropriate concentration of pyrethroid composite solution in acetone. The samples were placed on a shaker for 6 h and left overnight to attain homogeneity. They were spiked with mirex, then extracted and analysed as described previously. Recoveries were calculated by the instrument software, where the amounts of each pyrethroid, and of mirex, were calculated from the ratio, area of analyte/area of volumetric standard, using the previously established calibration curves. The volumetric standard was used to correct for small variations in the instrumental response and injection volumes by determining the ratio of all peak measurements to that of a known amount of the volumetric standard.

4. Results and discussion

Preliminary experiments were carried out with hexane, hexane–acetone (1:1, v/v) and hexane–dichloromethane (1:1, v/v) on soil at 10 ppb and the results are shown in Table 2. Hexane gave good recoveries for permethrin and mirex, but cyfluthrin, cypermethrin, deltamethrin and fenvalerate were very poorly recovered. The hexane–dichloromethane solvent system gave good recoveries for all six pyrethroids and mirex and was used in the subsequent studies. Linear calibration graphs were obtained from 1 to 500 ng ml^{-1} for all the pyrethroids and for the internal standard, mirex. Due to functionality differences between the pyrethroids and lack of availability and cost, stable isotope analogues were not employed as internal standards. As an alternative, mirex was used as the internal standard and was shown to be a very useful monitor for the recovery of the target pyrethroids. Mirex shows high percentage recoveries in non-selective and selective solvent mixtures used for extraction employing USE, indicating good reliability for targets having different polarities, such as permethrin, which is relatively non-polar compared with cypermethrin, cyfluthrin fenvalerate and deltamethrin, which are more polar because of CN and F functional groups. A further reason for using mirex is for the data correlation between GC–MS and enzyme-linked immunosorbent assay (ELISA) [9] developed by our group for

Table 2
Recoveries of pyrethroids from soil at a fortification level of 10 ppb with three solvent systems

Compound	Average recovery (%)±S.D. $n=4$		
	Hexane	Hexane–DCM	Hexane–acetone
Permethrin *cis*	114.1 ±5.4	113 ±2.4	117.5 ±3.5
Permethrin *trans*	97.4 ±1.9	101.9±2.4	107.1 ±1.6
Fenvalerate *cis*	20.2 ±3.2	99.1±3.5	116.5 ±3.1
Fenvalerate *trans*	17.9 ±0.7	100.3±2.8	111.5 ±1.8
Cyfluthrin	15.7 ±2.7	103.3±3.1	117.1 ±0.8
Cypermethrin	17.8 ±2.3	106.1±3.5	114.5 ±3.7
Deltamethrin	18.78±4.3	106.8±1.0	119.44±1.8
Mirex	81.5 ±2.8	90.3±3.7	108.1 ±7.6

DCM = Dichloromethane

environmental screening of pyrethroids. A suitable non-pyrethroid internal standard was required as a replacement for stable isotope analogues, to avoid cross-reactivity between molecules having this type of pyrethroid structure.

The results of the recovery experiments of pyrethroid and internal standard at three concentration levels, namely at 10, 50 and 100 ppb are summarised in Table 3. Four fortified samples and one procedural blank were analysed simultaneously. The procedural blanks gave no response for the ions used in quantification of the target compounds analysed. The reproducibility of an analytical method is characterised by standard deviation. Most of the standard deviations reported in Table 3 are below 12%, at all three concentration levels. The means of all the standard deviations (S.D.) of all target compounds at the spike levels are as follows: 10 ppb with ±7.2, 50 ppb with ±6.3 and 100 ppb with ±6.7. The recovery data fully illustrate the reliability of the method for the routine analysis of pyrethroids in soil at low concentrations.

Table 3
Recoveries of pyrethroids and internal standard at three fortification levels

Compound	Average recovery (%)±S.D. $n=4$ Fortification level		
	10 ppb	50 ppb	100 ppb
Permethrin *cis*	96.9± 4.9	98.9±6.4	92.7±11.9
Permethrin *trans*	94.1± 4.2	93.2±7.2	98.6±10.9
Fenvalerate *cis*	92.3± 9.8	88.4±3.9	98.4± 2.9
Fenvalerate *trans*	93.9± 7.8	91.3±8.1	94.6± 4.6
Cyfluthrin	96.8± 8.1	100.5±4.5	102.3±10.1
Cypermethrin	89.4±10.2	98.8±7.7	108.2± 2.6
Deltamethrin	82.6± 6.3	81.7±4.2	84.8± 6.3
Mirex	96.6± 6.2	101.2±9.1	98.8± 4.4

The recovery results show no significant variation between the high and low spiking levels. The recovery of the internal standard used also remained consistent over the spiking levels studied, with a mean recovery of 98.8±2.3%. This compares favourably with the recovery of the internal standard from the environmental samples analysed. The internal standard, mirex was added to the sediment samples before extraction and the results indicate good recoveries of the internal standard from the sample matrices. The spiking procedure, although used as a quality control indicator, may not accurately assess the ability of an organic solvent system to extract the pesticides originally incorporated into the environmental samples [10].

The chemical structures and typical mass chromatograms of the pyrethroids are shown in Fig. 1 Fig. 2, respectively. Permethrin, fenvalerate, deltamethrin, cypermethrin and cyfluthrin consist of 2, 2, 2, 4 and 4 *R,S* isomers, respectively. Under the specified GC–MS conditions, permethrin, fenvalerate and deltamethrin were totally resolved into two diastereoisomers, while cyfluthrin and cypermethrin, which contain a third asymmetric centre, were partially resolved into envelopes of four and three peaks, respectively. Permethrin and fenvalerate, *cis trans* isomers were quantified while the quantification of other pyrethroids was based on their major peaks. The cis isomers of permethrin and fenvalerate eluted in advance of the *trans* isomers [11], which is in keeping with the certified chemical specifications (see Section 2.1. Previous workers have reported that permethrin and fenvalerate are susceptible to thermal

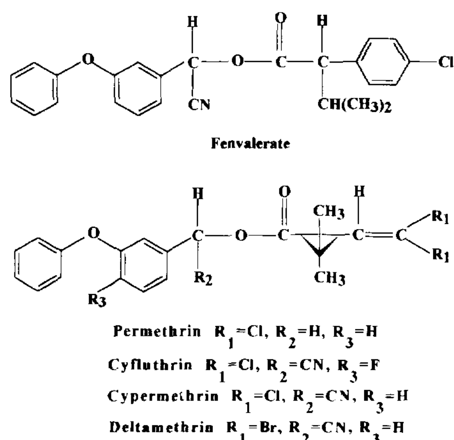

Fig. 1. Chemical structures of pyrethroids.

decomposition on the GC column and that repeated injection with large amounts of the pyrethroids are necessary before peak area reproducibility is acceptable [12]. These difficulties were not observed with the GC–MS conditions specified.

The mass spectra of the pyrethroids are shown in Fig. 3. In the methane negative-ion chemical ionization mode, permethrin, cyfluthrin and cypermethrin [being esters of dichlorovinylcyclopropane carboxylic acid (CPA)] undergo dissociation by electron capture to yield CPA^- anions (Fig. 3A) with m/z 207, 209 and 211, of which m/z 207 was the primary ion selected for quantitation in the SIM mode and m/z 209 and 211 were used for diagnostic purposes. The mass spectrum of fenvalerate showed two potentially useful ion fragments at m/z 167 and 211, corresponding to the portion of the molecule containing the isopropyl group (Fig. 3B). In the case of deltamethrin, the bromide ion was easily recognisable at m/z 79 and 81 in addition to a very characteristic ion at m/z 137 from the cyclopropane carboxylic acid unit after loss of two bromine atoms (Fig. 3C).

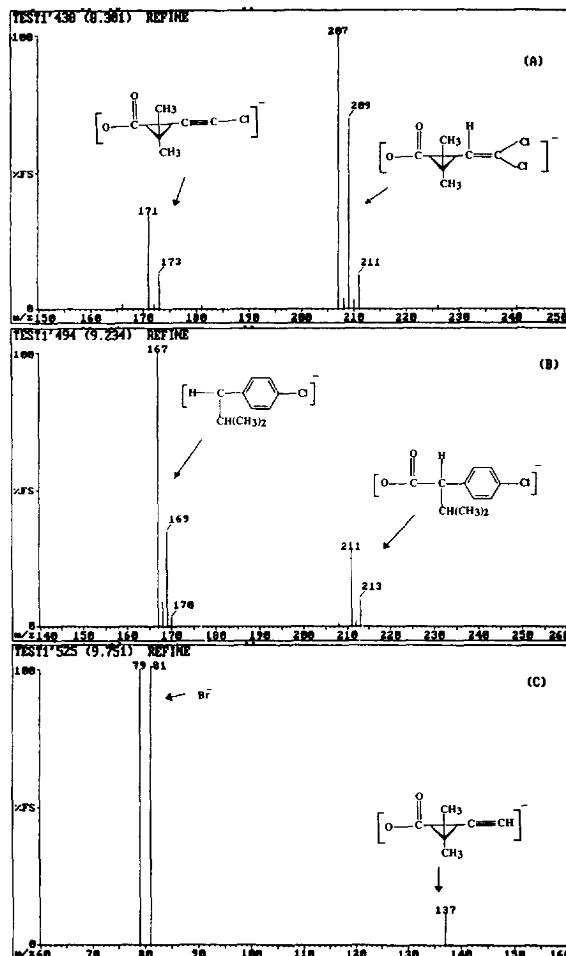

Fig. 3. Negative-ion chemical ionization mass spectra of pyrethroids. (A) Permethrin, cyfluthrin and cypermethrin, (B) fenvalerate and (C) deltamethrin.

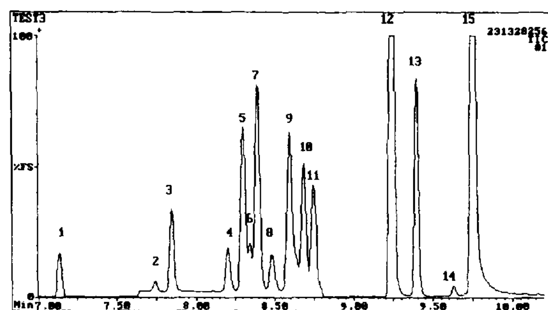

Fig. 2. Total ion chromatograms of pyrethroids and of internal and volumetric standards. 1, Mirex; 2 and 3, Permethrin; 4, 5, 6 and 7, cyfluthrin; 8, 9 and 10, cypermethrin; 11, DCBP; 12 and 13, fenvalerate; 14 and 15, deltamethrin.

One of the principal benefits of using instrumental methods such as GC–MS is that they are capable of detecting and determining much smaller quantities of analyte than classical methods of analysis. These benefits have led to the appreciation of the importance of trace concentrations of materials, for exam-

Table 4
Regression data and limit of detections of pyrethroids and of the internal standard, mirex

Compound	Regression equation	Correlation coefficient	10×LOD Concentration (ppb)
Permethrin *cis*	$y=0.0002x+0.0003$	$r^2=0.999$	0.0123
permethrin *trans*	$y=0.0021x-9\times10^{-5}$	$r^2=0.996$	0.22
Fenvalerate *cis*	$y=0.0517x+0.0237$	$r^2=0.997$	4.4
Fenvalerate *trans*	$y=0.0117x+0.02094$	$r^2=0.998$	0.85
Cyfluthrin	$y=0.01344x-0.0024$	$r^2=0.995$	1.4
Cypermethrin	$y=0.0046x+0.0351$	$r^2=0.998$	0.69
Deltamethrin	$y=0.0718x-0.1909$	$r^2=0.997$	4.3
Mirex	$y=0.02175x-0.4717$	$r^2=0.998$	0.85

ple in environmental samples, and thus to the development of many further techniques in which the limit of detection (LOD) is a major criterion of successful application. It is therefore evident that statistical methods for assessing and comparing limits of detection are of importance. A commonly used definition for the limit of detection is the "analyte concentration giving a signal equal to the blank signal, y_B, plus three standard deviations of the blank, S_B".

$$\text{LOD}=3S_B+y_B$$

$$\text{Limit of quantification}=10\times\text{LOD} \quad (1)$$

The value of a, the calculated intercept, can be used as an estimate of y_B, the blank itself and S_B can be calculated using the following equation [13].

$$S_B=\frac{Sy}{x}=\sqrt{\frac{\sum_i(y_i-\hat{y}_i)^2}{n-2}} \quad (2)$$

where $\hat{y}_i$ values are the points on the calculated regression line corresponding to the individual x-values, i.e. the fitted y-values [13]. Eq. (1) was used to calculate the limits of detection of the pyrethroids and of the internal standard, mirex, with the values of y_B $(=a)$ and S_B $(=Sy/x)$ previously calculated from the regression equations. The data is summarized in Table 4. The detection limits of pyrethroids obtained using GC–NICI-MS in SIM mode are superior to those obtained with GC–ECD [14]. The quantification limits in this work have been presented on the basis of statistical considerations, in order to create confidence in the analytical procedure at low concentration levels.

GC–NICI-MS has been used previously for the analysis of synthetic pyrethroids in water [15,16], fruit, vegetables and grains [14] using different extraction and clean-up procedures. Our group is actively engaged in the environmental monitoring of pyrethroids in soil, moss, water and fish [17] in a liaison with the National River Authority (Yorkshire Division). Results for the environmental sediment samples are shown in Table 5. Only permethrin and cyfluthrin were found in sediments and no other pyrethroid was detected. The highest levels of permethrin, in sediments found at sites 2, 3 and 7, indicate that the major sources of permethrin contamination in the Meltham Catchment area are

Table 5
Levels (μg kg^{-1}) of permethrin and cyfluthrin in sediments from the Meltham Catchment

Sampling site	Permethrin *cis*	Permethrin *trans*	Cyfluthrin	Mirex recovered (%)
Site 1	42.8	19.6	1.5	75.2
Site 2	213.1	82.6	1.3	82.6
Site 3	309.5	108.7	4.6	80.2
Site 4	67.9	24.2	5.8	86.5
Site 5	0.58	0.26	0.086	79.1
Site 6	20.1	4.6	0.45	81.4
Site 7	132.0	22.8	0.56	87.7

Table 6
Levels ($\mu g\ kg^{-1}$) of permethrin and cyfluthrin in sediments originating from site 7 of Meltham Catchment

Sampling time	Permethrin *cis*	Permethrin *trans*	Cyfluthrin	Mirex recovered (%)
July 1994	31.5	6.2	0.34	79.5
August 1994	37.5	37.0	3.7	81.3
October 1994	21.4	6.6	nd	65.5
February 1995	22.7	3.7	0.68	73.8
July 1995	48.4	7.49	nd	68.6

nd = not detected

Meltham Sewage Treatment Works final effluent (site 7) and a source in the vicinity of a Textile Mill (sites 2 and 3). The concentrations found in these samples reflect the extent of the industrial and commercial use of permethrin in that particular area of Meltham Catchment. It is considered unlikely that the occurrence of permethrin within these samples was due to contamination during sample processing or analysis. Procedural blanks confirmed that the method was satisfactory and that the laboratory was not the source of contamination. The greater abundance of *cis* isomer in comparison to the *trans* isomer observed in our samples is comparable to that observed in samples from both terrestrial and aquatic ecosystems. This is due to the *cis* isomer having a greater resistance to bacterial degradation [18]. This finding is not significantly different from that reported on the metabolism of permethrin in soil, where the *trans* isomer was metabolized faster than the *cis* isomer [19].

The work presented indicates that reasonably consistent results were obtained from the sampling, work-up and analytical procedures. However, sediments are complex matrices, the composition of which can vary considerably and this factor is likely to reduce the accuracy and precision of results. An intensive sampling strategy involving frequent sample collections over an extended period would be needed to account for permethrin inputs and such a monitoring scheme would require considerable time and resources. An idea of the regime of sampling required is illustrated by samples of sediment collected from site 7, near to the Meltham Sewage Treatment Works, over a period of twelve months and the concentrations of permethrin and cyfluthrin obtained are given in Table 6. These results indicate that low but consistent levels of permethrin are found, in spite of the changes in the composition of discharged industrial effluents from the Sewage Treatment Works.

In conclusion, the analytical method developed for sediments containing pyrethroids using GC–NICI–MS in detection and quantification is sensitive and reliable analytical quality control has been established for routine analysis.

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