ELSEVIER

Journal of Chromatography A, 707 (1995) 293–302

JOURNAL OF CHROMATOGRAPHY A

Determination of permethrin and cyfluthrin in water and sediment by gas chromatography–mass spectrometry operated in the negative chemical ionization mode

G.A. Bonwick[a], C. Sun[b], P. Abdul-Latif[b], P.J. Baugh[b,*], C.J. Smith[c], R. Armitage[d], D.H. Davies[a]

[a]*Department of Biological Sciences, University of Salford, Salford M5 4WT, UK*
[b]*Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK*
[c]*Cortecs Diagnostics Ltd., Techbase 1, Newtech Square, Deeside Industrial Park, Deeside, Clwyd. CH5 2NT, UK*
[d]*National Rivers Authority (Yorkshire Region), Rivers House, 21 Park Square South, Leeds LS1 2QG, UK*

First received 27 June 1994; revised manuscript received 13 March 1995; accepted 13 March 1995

Abstract

Gas chromatography–mass spectrometry operated in the negative chemical ionization mode (GC–NCI–MS) with selected-ion monitoring (SIM) showed both high sensitivity and excellent specificity for permethrin and cyfluthrin. The detection limit for both permethrin and cyfluthrin was 50 fg, whilst a linear response was observed from 50 fg to 80 pg. A sample extraction method using an ultrasonic bath was developed enabling simultaneous processing of multiple samples. Good percentage recoveries of both permethrin and cyfluthrin from spiked sediments were obtained ($97.3 \pm 4.8\%$ and $93.9 \pm 5.3\%$, respectively) and sample clean-up was avoided. These methods were also successfully applied to samples obtained from a contaminated ecosystem, the highest concentrations recorded in water and sediment samples were 0.048 $\mu g\ l^{-1}$ and 305 $\mu g\ kg^{-1}$, respectively.

1. Introduction

Permethrin and cyfluthrin are both synthetic pyrethroid insecticides. One of the major uses for these pyrethroids is as mothproofing agents for wool and wool-based fabrics by the textile industry. These compounds can enter aquatic ecosystems either by direct discharge, or indirectly within the effluents of sewage treatment works. The toxicity of both permethrin and cyfluthrin to aquatic invertebrates and fish is reflected by the corresponding environmental quality standards (EQS) of 0.01 $\mu g\ l^{-1}$ and 0.001 $\mu g\ l^{-1}$, respectively [1,2]. Thus, there is a need for continuous and accurate monitoring of these pollutants in both effluents and receiving waters if member states are to comply with European Community legislation (76/434/EEC).

Several methods have been previously reported for the determination of permethrin and cyfluthrin residues [3–11]. Most of these are based on either high-performance liquid chromatography (HPLC) or gas–liquid chromatography with electron-capture detection (GC–ECD). These methods are either inefficient or meet with some difficulty when dealing with trace pesticide

* Corresponding author.

0021-9673/95/$09.50
SSDI 0021-9673(95)00362-2

residues in field samples, due to the poor detection limits of the instruments, the presence of background contamination and non-specific chemical interference.

The potential sensitivity of gas chromatography–mass spectrometry operated in the negative chemical ionization mode (GC–NCI–MS) was demonstrated by Hunt et al. [12]. A 10–100 fold increase in sensitivity was obtained over that typically achieved by GC–ECD. A further advantage of GC–NCI–MS is the capability to conduct selected-ion monitoring (SIM), where the instrument is adjusted to collect only ions of one defined mass. Siegel et al. [13] demonstrated a detection limit of 50 pg for permethrin when using GC–SIM–MS. Mattern et al. [14,15] recognized the unique advantage of GC–MS in positive chemical ionization (GC–PCI–MS) and SIM mode. This technique was used successfully for the detection and quantification of pesticides, including permethrin. However, the limits of detection reported for permethrin residues from crop plants (0.10–0.50 $\mu g\ g^{-1}$) indicated that GC–PCI–MS, even when operated in the SIM mode, would not be suitable for the detection of permethrin and cyfluthrin at, or below, the EQS levels.

In this paper, a GC–NCI–MS method is reported which enabled quantitation of both permethrin and cyfluthrin in water at concentrations which ranged from 50 pg l^{-1} to 500 ng l^{-1}. In conjunction with an extraction procedure based on the use of an ultrasonic bath, both permethrin and cyfluthrin were successfully detected in spiked stream sediments at concentrations which ranged from 5 ng kg^{-1} to 200 μg kg^{-1}. In comparison to traditional methods such as Soxhlet extraction, the ultrasonic extraction method was more rapid. Simultaneous processing of multiple samples was also performed whilst the problem of cross-contamination, inherent in methods where an ultrasonic probe tip is inserted directly into the sample, was avoided. Good analyte recoveries and detection levels were achieved following 90 min of sonication. In addition, the analyses of permethrin and cyfluthrin in both water and sediments were achieved without recourse to prior sample clean-up. Through use of the methods reported in this paper, samples obtained from a contaminated aquatic ecosystem were also successfully analysed for both permethrin and cyfluthrin.

2. Experimental

2.1. Materials

Permethrin [3-phenoxybenzyl-3-(2,2-dichlorovinyl) - 2,2 - dimethylcyclopropanecarboxylate], cyfluthrin [α-cyano -3- phenoxy - 4 - fluorobenzyl - 3 - (2,2-dichlorovinyl) - 2,2 - dimethylcyclopropanecarboxylate] and decachlorobiphenyl (DCBP) were of certified purity (British Greyhound, Birkenhead, Merseyside, UK). HPLC grade hexane, analytical reagent grade acetone, dichloromethane, sodium chloride and anhydrous sodium sulphate were obtained from Chem Service (Merck, Lutterworth, Leicestershire, UK).

Clean materials used for recovery and sensitivity studies were previously determined to be free of any of the pesticides in the study. Uncontaminated stream sediments for spiked recovery experiments were obtained from a tributary of the River Tame, Uppermill, Lancashire, UK. Contaminated water and sediment samples were collected from the catchment of the River Calder located at Meltham, Yorkshire, UK. Water samples were collected such that a head space was avoided. Sediment samples were obtained manually as the rocky substrate prevented use of standard sampling apparatus. Glass sample bottles and jars fitted with PTFE-lined caps were used throughout. After collection, samples were transported rapidly to the laboratory where they were stored at 4°C. Extraction of the samples was performed within 48 h of collection.

2.2. Instrumentation

An HP5890 gas chromatograph with a split/splitless injector for capillary columns (Hewlett-Packard, Cheadle Heath, Greater Manchester, UK), combined with a VG TRIO 1000 quadrupole mass spectrometer with EI and PCI/NCI

capability (Fisons Instruments, Wythenshaw, Greater Manchester, UK) was employed.

2.3. Gas chromatography and conditions

A fused-silica column, 20 m × 0.32 mm I.D. DBS-MS (Jones Chromatography, Hengoed, UK) was used with helium (CP grade, purity 99.9995%) as the carrier gas (BOC, Eccles, Greater Manchester, UK). Temperature programme: 1.5 min at 100°C, 12°C/min to 300°C, held for 2 min. A 1-μl volume of sample was injected manually, applying the hot splitless injection technique with the purge off for 1.5 min.

2.4. Mass spectrometric acquisition parameters

Temperature settings: ion source, 250°C; interface line, 250°C. Electron voltage, 70 eV. Scan parameters: scanned mass range, 50–650 a.m.u.; scan rate, 600 a.m.u. in 0.9 s for full scan, 0.2 a.m.u. in 0.08 s for SIM. Solvent delay, 1.5 min. The voltages of the ion repeller, ion focus, ion and electron energies, and the parameters for the quadrupole mass filter were optimised using the negative ion at m/z 452 generated from the calibration compound perfluorotributylamine (PFTBA). Methane (CP grade) was used as the reagent gas (BOC, Eccles, Greater Manchester) at a nominal source pressure of 66.7–133.3 Pa.

2.5. Calibration

For long term storage stock solutions of the reference compounds and the volumetric standard, DCBP, were prepared at concentrations of 100 mg l^{-1}. Short term storage stock solutions containing reference compounds (1 mg l^{-1}) were serially diluted to prepare working standards in the required concentration ranges (0.05 μg l^{-1} to 80 μg l^{-1}) which were dispensed daily or as required for use in calibration.

An appropriate amount of volumetric standard stock solution (0.4–4 mg l^{-1}) was then added to each to give a final DCBP concentration of 4 and 40 μg l^{-1}. The standard solutions were subsequently analyzed by GC–NCI-MS operated in the SIM mode. The ion selected for the detection/quantification of both permethrin and cyfluthrin was m/z 209, whilst for DCBP m/z 498 was chosen. Peak areas were obtained from the mass chromatograms generated for the ions selected for the quantitation of each analyte. For both permethrin and cyfluthrin, calibration curves were obtained from plots of response factor (pesticide peak area/DCBP peak area) against analyte concentration.

Note: The use of DCBP as a volumetric standard is an extension of its use as an external/volumetric standard for analysis by GC–ECD. It is useful in that it elutes at a retention time close to the pyrethroids (narrow retention time window as recommended – US-EPA) and does not interfere chemically – important for pyrethroid specificity and extracts used for ELISA validation. It is also suitably electron affinic and gives therefore a highly reliable and sensitive response (low noise at m/z 498) to MS in NCI-mode operation as with GC–ECD.

DCBP is used for the purpose of correcting for any variation in the sensitivity of the MS instrument and obtaining valid relative response factors.

2.6. Preparation of field samples

Water (1 l) was filtered into a separating funnel. Sodium chloride (20 g) was added and the sample acidified (pH 4.0) by the addition of sulphuric acid. Dichloromethane (50 ml) was added and the funnel shaken vigorously for 3 min. The phases were allowed to separate and the lower fraction transferred into a 250-ml conical flask containing anhydrous sodium sulphate (5 g). This extraction procedure was repeated twice and the extracts combined. The extract was evaporated to dryness using a Kuderna–Danish concentrator and the residue redissolved in hexane. After addition of DCBP, the final extract volume was adjusted to 1.0 ml.

Sediment samples from the field were air dried in the laboratory. After drying, the sediment samples were ground and graded through a metal sieve (20 mesh). Dried sediment (10 g) was placed in a 200-ml glass bottle and dichloro-

methane (20 ml) added. The sample was then sonicated (30 min) in Dawe Sonicleaner Type 644 sonic bath (Dawe Instruments, UK). The solvent was passed through a glass sinter (porosity 4) as a filter containing anhydrous sodium sulphate (5 g) into a 250-ml conical flask. The extraction was repeated twice and the extracts combined. Subsequent concentration of the extract was performed as for the water samples (above).

2.7. Sample analyses

Samples were analyzed by GC–NCI–MS in the SIM mode. At low pesticide concentration, the m/z 209 and 498 ions were selected for use, due to the lower ion background observed for the m/z 209 ion, than for m/z 207. Peak areas were determined manually using the manufacturer software (LabBase). At high concentration of the pesticides the m/z 207 and 498 ions were selected and peak areas were measured by the software automatically. The threshold for manual intervention in peak area determination is considered below. Because of the nature of the detection, NICI, and the consequent large ion background above which the chromatographic peak for the ion selected for quantitation is observed it is not easy to define the instrument detection limit (DL) in terms of the peak response for which the signal-to-noise (S/N) ratio is 2/1. Based on the total ion background valid quantitation can be conducted at signal-to-total ion background ratios considerably less than 2/1 ignoring detector noise which is insignificant for this mode of detection. Here, the DL can be taken as the signal intensity to total ion background intensity ratio in SIM mode obtained for a peak characterised by m/z 207 (cyfluthrin) for a concentration of 50–100 ng l^{-1} (equivalent to 50–100 fg μl^{-1} injected).

Conventionally area determinations are not carried out at the lowest peak responses near to the DL but at a quantitation limit (QL) about $10 \times$ DL. An assumption could be made that the response for a concentration of 50–100 ng l^{-1} at the DL is $3 \times$ S.D. of the background noise ($S/N = 2/1$). Then making a background correction using the mean of the background response an estimate of the instrument QL could be obtained using the following expression:

$$\mathrm{QL} = 10 \times \frac{3\text{S.D.} + \text{Mean background}}{\text{Mean response} - \text{mean background}} \times (\text{analyte}) \simeq 500 \text{ ng } l^{-1} \text{ (fg } \mu l^{-1})$$

Alternatively, the DL could be based on peak precision favoured by the EPA/FDA. However, we favour considering correlation coefficients obtained by linear regression analysis of the calibration data to validate or invalidate quantitative determination and consequently the threshold for manual intervention in peak area determination (see section 3 for the additional linear regression data included for the lowest concentration range).

Note that the analytical method detection limit depends on the concentration factor possible with the matrix, water or sediment, concerned.

For SIM the collection of ions by the MS was set to 30 s before and after the retention time of the analyte. The diagnostic ions used for permethrin and cyfluthrin were m/z 207, 209, 211, 173, and 171 and for DCBP were m/z 496, 498 and 500.

2.8. Recovery studies

Known concentrations of permethrin and cyfluthrin in acetone (0.05–500 ng l^{-1}) were spiked into clean water matrices. Spiked water samples were prepared by adding pesticide solution (1 ml) to distilled water (1 l), and then shaking the samples vigorously to ensure mixing. Sediment samples (10 g) were fortified by the addition of pesticide solution (1 ml), followed by shaking for 10 h with protection from light. Sediment samples were kept in the dark for two days prior to extraction. Extraction and analysis of spiked samples was performed as described for the field samples (above).

3. Results

Representative mass spectra obtained from the GC–NCI-MS analysis of permethrin and cyflu-

thrin are shown in Fig. 1A,B. A chromatogram of permethrin, cyfluthrin and DCBP is shown in Fig. 1C. A total separation of permethrin into the *cis* and *trans* isomers can be observed as well as four isomers of cyfluthrin. Although the molecular ions of permethrin and cyfluthrin were not observed in the NCI mass spectra, the stabilized carboxylate anions at m/z 207 (209, 211) were detected. This suggested that the pyrethroids in the MS chemical ionization source form stabilized anions by loss of the ester substituent as a neutral fragment.

For both analytes the calibration range extended from 0.05 $\mu g\ l^{-1}$ to 80 $\mu g\ l^{-1}$. Peak areas were linearly related to permethrin concentration ($a = 5.14 \cdot 10^3 \pm 3.65 \cdot 10^{-2}$, $b = 1.27 \cdot 10^4 \pm 1.18 \cdot 10^{-3}$, $n = 9$) and cyfluthrin concentrations ($a = 2.09 \cdot 10^4 \pm 4.9 \cdot 10^{-2}$, $b = 5.0 \cdot 10^4 \pm 1.59 \cdot 10^3$, $n = 9$). The correlations recorded for both analytes ($r = 0.999$) were significant ($p < 0.05$). We have determined correlation coefficients close to unity for concentrations of both target compounds approaching the detection limit (0.05 $\mu g\ l^{-1} = 0.05$ pg μl^{-1} injected). The linear regression data for the concentration range, 0.1–0.5 $\mu g\ l^{-1}$ for the two analytes is as follows: (i) permethrin $r^2 = 0.977$, $n = 5$, $F = 0.0001$, $A = 3.026 \cdot 10^3 \pm 1.033 \cdot 10^3$, $B = 1.438 \cdot 10^4 \pm 4.191 \cdot 10^2$; (ii) cyfluthrin $r^2 = 1.000$, $n = 5$, $F = 0$, $A = 5.143 \cdot 10^3 \pm 2.07 \cdot 10^{-1}$, $B = 1.272 \cdot 10^5 \pm 8.45 \cdot 10^{-2}$.

These results demonstrate the validity of linear

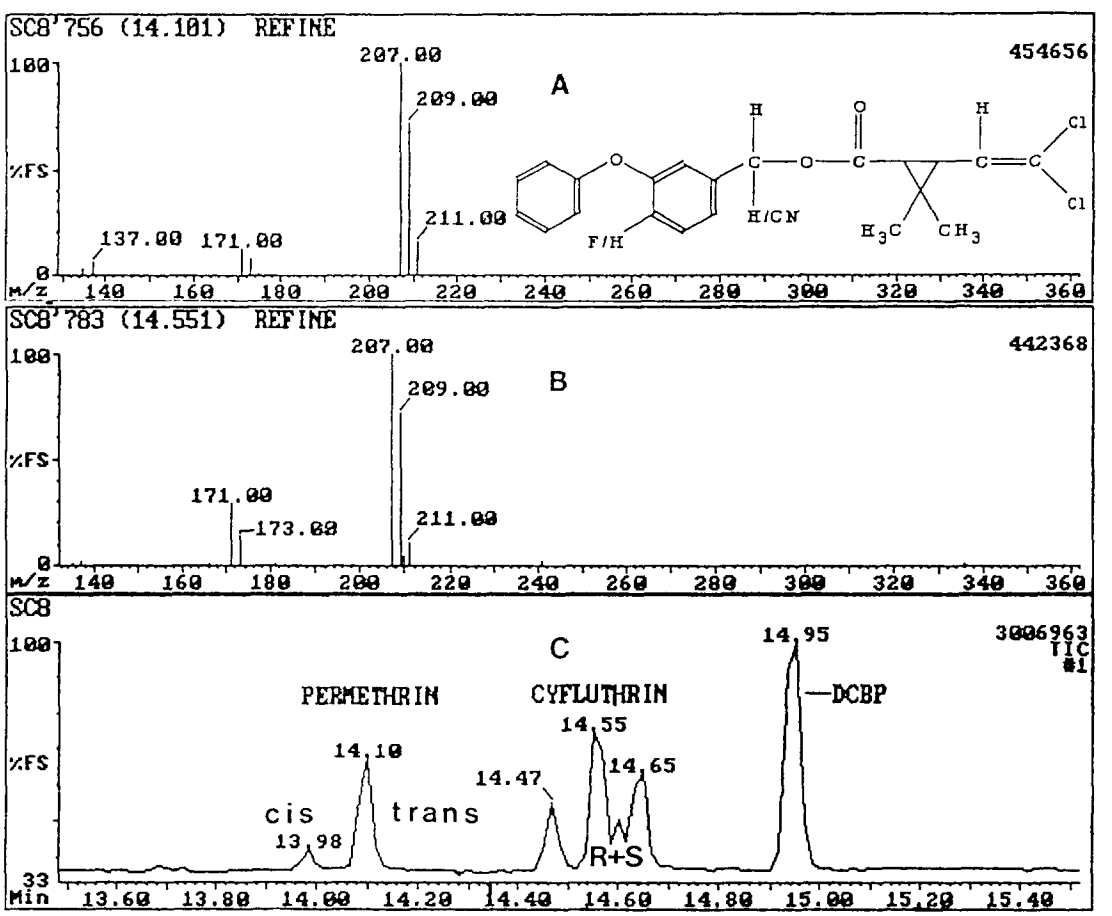

Fig. 1. GC–NCI-MS mass spectra for permethrin (A) and cyfluthrin (B) and the total ion chromatogram (C) of permethrin, cyfluthrin and DCBP indicating *cis/trans* isomers, 2 for permethrin, *R/S* isomers, 4 for cylfluthrin, respectively.

Table 1
Percentage recoveries of permethrin and cyfluthrin from spiked water samples

Concentration range (ng l^{-1})	Permethrin recovery (%)	Cyfluthrin recovery (%)
0.05–0.5	115.5 ± 7.3 (6)	97.0 ± 10.4 (7)
1.0–5.0	98.4 ± 13.1 (5)	98.4 ± 21.6 (5)
10–50	104.1 ± 16.5 (6)	99.5 ± 6.6 (6)
100–500	101.5 ± 17.5 (6)	101.2 ± 14.0 (5)

Values are expressed as mean percentage recovery ± standard deviation. Values in parentheses denote number of observations, $n - 1$ used in computation.

regression analysis of the calibration data over an extremely wide dynamic range and importantly when the data at the low end of the concentration range in particular is focused on.

The percentage recoveries of permethrin and cyfluthrin from water are summarised in Table 1. The concentration range of the pesticides fortified was from 50 pg l^{-1} to 500 ng l^{-1}, a dynamic range over 4 orders of magnitude. The percentage recoveries of permethrin varied from 98.4 ± 13.1% to 115.5 ± 7.3%, and those of cyfluthrin from 97.0 ± 10.4% to 101.2 ± 14.0%.

Table 2 illustrates the percentage recoveries of the pesticides from sediment. The concentration spiked in sediment was from 5 ng kg^{-1} to 200 μg kg^{-1}, a dynamic range of nearly 5 orders of magnitude. The percentage recoveries of permethrin ranged from 88.4 ± 21.5% to 94.7 ± 15.8%, whilst those of cyfluthrin ranged from 90.5 ± 21.4% to 98.4 ± 12.4%.

Table 2
Percentage recoveries of permethrin and cyfluthrin from spiked sediment samples

Concentration range (μg kg^{-1})	Permethrin recovery (%)	Cyfluthrin recovery (%)
0.005–0.05	88.4 ± 21.5 (5)	94.6 ± 7.3 (4)
0.01–0.5	91.5 ± 14.4 (9)	96.3 ± 13.0 (9)
1–5	94.7 ± 15.8 (10)	98.4 ± 12.4 (10)
10–200	82.3 ± 9.7 (10)	90.5 ± 21.4 (10)

Values are expressed as mean percentage recovery ± standard deviation. Values in parentheses denote number of observations. Spiking concentrations expressed in terms of sample dry weights.

These results are an impressive demonstration of the capabilities of this method for the determination of both permethrin and cyfluthrin in water and stream sediments. Overall, the analysis procedure was considered to be effective for these pesticides when present in such environmental matrices. Although the determination of recoveries in this study has been carried out with reference to authentic compounds analysed in the presence of a volumetric or external standard DCBP (NB internal in the sense that it is present at the analysis stage in the extract examined and as such it can be termed a volumetric standard) other closely associated work of the group has employed a combination of internal and external/volumetric standards for QA/QC purposes [16].

To summarise, mirex was employed as the internal (surrogate) standard and deltamethrin as an external/volumetric standard. $\%R$ has been determined for spiked samples of water and sediment. Using ultrasonic extraction several extraction solvent systems have been compared giving comparable results. As examples, the results for sediment spiked at 0.1 and 0.05 mg kg^{-1} are included. The $\%R$ for permethrin, cyfluthrin and mirex are 124.4 ± 19.6 and 93.7 ± 11.5; 106.5 ± 12.6, 69.8 ± 4.8; 105.2 ± 8.7 and 117.4 ± 8.5, respectively for $n = 4$ using the relative retention factor (RRF) calculated from calibration curves derived using deltamethrin (50 μg l^{-1}) as the external/volumetric standard. These results confirm that the recoveries of permethrin and cyfluthrin are consistent and reliable in satisfactory agreement with the recovery of the internal standard, mirex. It is worth noting that the role of mirex and deltamethrin as standards can be reversed with equivalent results.

Mirex was selected in that study as an internal standard because of its elution in close proximity to the target analytes, the low probability of its environmental occurrence, optimal high mass response (m/z 368) and wide dynamic range.

The utilisation of deltamethrin as an external/

volumetric standard has however been discontinued because of its possible interference in extracts made available for the development and assessment of ELISA for which chemical analysis methods are being employed in data correlation and as a monitor. In addition, it is not the most appropriate standard for NCI-MS in SIM mode in spite of its similar pyrethroid structure because of its prominent response in the low mass region resulting from a favoured fragmentation to yield Br^- where the ion background interference is greatest.

This requirement led to the subsequent selection of DCBP as an external/volumetric standard (retention time similar to that of deltamethrin) because of its wide employment and high reliability for sample analysis using ECD, the equivalent conventional GC detection system to NCI-MS. Furthermore, it elutes in a narrow retention window adjacent to the targets, slightly later than cyfluthrin, has maximum response in a high mass region (m/z 498) making it eminently suitable for use in SIM and exhibits a wide linear dynamic range in response. Its use as an external standard has been correlated with that of deltamethrin.

Given the confidence in the $\%R$ obtained in the QC work using mirex and deltamethrin in combination and the fact that control sediment had an integrity compatible with that of environmental sediment it was considered valid to use only an external (volumetric standard) in the current work. It is worth noting that the $\%R$ for spiked sediment demonstrates a low variance and high reliability comparable with those using mirex and deltamethrin in combination.

An additional problem experienced initially was a persistent low-level contamination by permethrin which affected the validity of $\%R$ at low spiking levels. The source of contamination was ultimately traced to the filter paper used for sample preparation. Typically, a single 9-cm diameter filter paper was found to contain approximately 2 ng of permethrin. The use of paper filters during sample preparation was consequently discontinued.

Chemical ionization mass spectrometry often produces only a limited number of ions for each analyte and is important for obtaining the desired sensitivity. Of even greater importance, selected-ion monitoring offers both qualitative and quantitative methods for several targets in the presence of considerable amounts of interference. The analytical method detection limit for GC–MS in both the SIM and NCI mode for water was 50 pg l^{-1} (concentration factor of 1000), whilst for sediment it is thought to be less than 2 ng kg^{-1}. Figs. 2A,B shows chromatograms of the same sample under near identical GC–MS conditions, the only difference being that the former was conducted in the full scan mode whilst the latter was performed in the SIM mode. In the full scan mode the individual analytes are not readily discernible without processing to obtain mass chromatograms for m/z 207 and 209 (211). Conversely, the application of SIM (see Fig. 2B highlighting the retention time region 14.0–14.5 min) enables diagnostic detection of the analyte, both from the TIC and mass chromatograms for m/z 207 and 209. From quantitation in the SIM mode the concentration of permethrin was determined to be 335 μg kg^{-1}.

Field samples from a contaminated freshwater ecosystem were analysed to assess the performance of these methods when extended to real environmental samples. Field samples were collected from three sites; site A (downstream of an active textile mill), site B (downstream of the effluent discharge from a sewage treatment works) and site C (upstream of the textile mill). These were processed and analysed in an identical fashion to the spiked materials and the concentrations of permethrin and cyfluthrin in both water and sediment samples are recorded in Table 3.

Permethrin was detected in both water and sediment samples from sites A and B. This was expected as both sites were known to have received either direct or indirect inputs of mothproofing agents. Cyfluthrin was not detected at these sites, however this is considered to reflect the pattern of mothproofing agent usage by the local industry rather than a failure of the sampling strategy or quantitative technique employed. The failure to detect either of

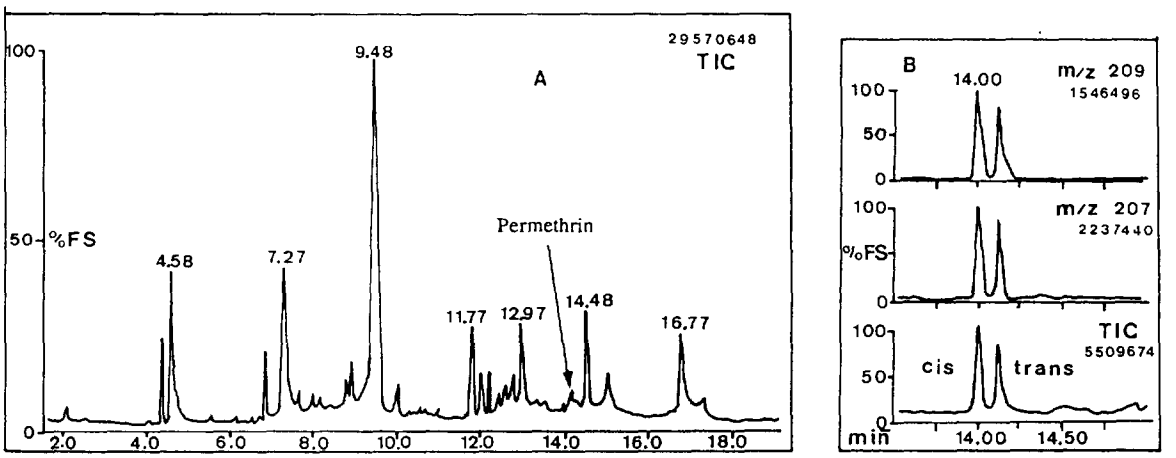

Fig. 2. GC–NCI-MS mass chromatograms of a permethrin contaminated stream sediment. A full scan mode total ion chromatogram (A) fails to show permethrin, the expected position of which is arrowed. Permethrin *cis* and *trans* isomers are revealed in both the total ion chromatogram and mass chromatograms for *m/z* 207 and 209 during operation in the SIM mode (B).

the target analytes at site C was anticipated as this site is not known to have a history of contamination and was therefore expected to be a clean site. This result helped to confirm that the analytical method was not subject to interference and that the prior clean-up of these matrices was unnecessary. Since clean-up can be problematic with losses of analyte it is desirable not to use the extra steps involved in clean-up. The specific quality of the real samples involved allowed us to eliminate clean-up from the procedure. It could be argued that some clean-up is provided by the drying agent anhydrous sodium sulphate which, in addition to removal of water, will remove polar materials which may affect the chromatography. The QC work with spiked samples enables determination of the quality of the results including the chromatography (efficiency reproducibility) and reliability of the response and tuning of the mass spectrometer.

The concentration of permethrin in the water at both sites A and B was in excess of the EQS value (0.01 $\mu g\ l^{-1}$). Sediment values were considerably higher than those recorded for the water samples and indicated that accumulation within the sediment had occurred. Concentration factors for the sediment relative to water at the time of sampling are approximately 10 700 and 7000 for sites A and B, respectively. Although the accumulation of pyrethroids within sediments has been previously demonstrated [17], the concentrations recorded in this study are some of the highest reported for a freshwater ecosystem. EQS values have not been established for

Table 3
Permethrin and cyfluthrin levels in water and sediment samples from the River Calder catchment

Site	Water samples ($\mu g\ l^{-1}$)		Sediment samples ($\mu g\ kg^{-1}$)	
	Permethrin	Cyfluthrin	Permethrin	Cyfluthrin
A	0.020	ND	214.0	ND
B	0.048	ND	335.0	ND
C	ND[a]	ND	ND	ND

Concentrations recorded for sediments expressed in terms of sample dry weights. ND = not detected (lower than the analytical method quantitation limit ~500 pg l^{-1}, 5 ng kg^{-1}).

aquatic sediments, however it is thought likely that the occurrence of permethrin at such high concentrations will be hazardous to the indigenous benthophagic aquatic organisms.

The ratios of the abundance of the *cis*- and *trans*-permethrin isomers in the sediment samples from sites A and B were different from those observed for the standard material: *cis*/*trans* ratios of 34:66 and 53:47 were seen in the sediment samples from sites A and B, respectively, whilst in the analytical standard the ratio was generally 25:75. Both photoisomerisation of *cis*-permethrin to *trans*-permethrin and the preferential biodegradation of *trans*-permethrin isomer have been reported [18,19]. It is thought that both mechanisms will have contributed to the increased abundance of the *cis* isomer relative to the *trans* isomer within the environmental samples. This would appear to be supported by the ratio for the site B sediment, where the analyte would have passed through the treatment works and would thus have experienced a much greater biodegradation influence prior to discharge into the aquatic environment.

4. Discussion and conclusions

It has been shown that GC–NCI-MS in the SIM mode is capable of monitoring at or below the EQS level for both permethrin and cyfluthrin in water. These analytes can also be detected in more complex matrices such as stream sediments at levels below the EQS for water. Preliminary studies have shown that this method is also applicable to other complex matrices such as fish tissues and plants, however clean-up procedures are required to remove extracted fats and pigments (data not shown). The performance of this method in relation to aquatic sediments with a higher clay or humic content is also being studied, whilst an extension to the monitoring of sewage sludges is also under consideration. Although EQS levels have not been set for aquatic sediments, recent EEC legislation (93/57/EEC and 93/58/EEC) has defined maximum residue levels (MRLs) for a range of foods and in most cases an MRL of 0.05 $\mu g\ kg^{-1}$ has been set. It is therefore considered that GC–NCI-MS will also prove suitable for monitoring pyrethroids such as permethrin and cyfluthrin when present at, or below, the MRL in such matrices.

Ultrasonic extraction of stream sediments was not only effective and inexpensive, but also simple and rapid. In particular, the time required to extract the pesticides from sediment was less than two hours when an ultrasonic bath was used. Use of the bath was considered advantageous in comparison to an ultrasonic probe method as eight or more samples could be simultaneously extracted, the final number influenced by bath size and container dimensions. An added advantage of the bath over the sonic probe was that cross-contamination of samples was not possible. It is thought that extraction times can be further reduced and an assessment of this parameter is in progress.

During this study, clean sediments were spiked with pesticide in order to examine the effectiveness of the extraction procedure. Clean stream sediments were used because standard materials were not available. Although it may be argued that pesticide spiking and extraction should have been conducted using a standard soil, the relevance of such material to that of the matrix of interest in terms of pesticide-retaining properties and extractibility is doubtful. It is considered that the use of a material which more closely simulates the properties of the target matrix, as in this study, ultimately provides for greater accuracy.

Immunoassay methods such as the enzyme-linked immunosorbent assay (ELISA) have been reported for pyrethroid insecticides such as permethrin [20–23]. Chemical methods are required to validate ELISA performance and the GC–NCI-MS method reported in this paper has been used successfully to assess the performance of a permethrin ELISA [24]. Although ELISA methods offer considerable advantages for environmental monitoring, such as increased sample throughput and on-site testing, they are less sensitive and less specific than methods such as GC–NCI-MS. Despite the higher costs and operative skills required, GC methods will not be superseded but rather supplemented by

ELISA techniques. GC–NCI-MS would appear to provide a useful means of confirming the identity of analytes within samples testing positive during ELISA screening procedures.

Overall, it has been clearly demonstrated that the methods developed during this study for the analysis of spiked samples are also applicable to environmental samples with similar matrix compositions. The SIM method is specific for retention time as well as for characteristic ions (m/z). This is not only useful as a tool to confirm the analyses, but also increases the sensitivity of the MS, due to the short scan time. GC–NCI-MS in SIM mode could be widely applied to trace organic analysis, especially for the detection of pesticide residues in complex, ill-defined environmental matrices. GC–NCI-MS in SIM mode should provide a useful tool for the monitoring of toxic haloorganics in the environment. However, it is considered that the GC–NCI-MS method requires further study. In particular, generation of a negative chemical ionisation library would be useful for the rapid identification of pesticides in sample extracts.

Acknowledgements

This study was conducted as part of an United Kingdom National Rivers Authority (Yorkshire Region) Research Contract (Mothproofing Agents and Water Quality Management, R & D Project Number 319). The authors would like to thank the NRA for permission to reproduce this data.

References

[1] T.E. Tooby, Ecotoxicological aspects of water pollution by certain mothproofing agents with reference to Eulan, Mitin and permethrin, Report prepared for the Commission of the European Communities – Environment and Consumer Protection Service, 1981.
[2] T.F. Zabel, J. Seager and S.D. Oakley, Proposed Environmental Quality Standards for List II Substances in Water, WRC, Marlowe, Buckinghamshire, UK, 1988.
[3] R.A. Chapman, J. Chromatogr., 258 (1983) 175.
[4] N. Oi, H. Kithara and R. Kira, J. Chromatogr., 515 (1990) 441.
[5] Y. Nakamura, Y. Tonogal, Y. Tsumara and Y. Ito, J. Assoc. Off. Anal. Chem. Int., 76 (1993) 1348.
[6] Y. Nishikawa, Anal. Sci., 9 (1993) 39.
[7] W.L. Reichel, E. Kolbe and C.J. Stafford, J. Assoc. Off. Anal. Chem., 64 (1981) 1196.
[8] K.M.S. Sundaram, Pestic. Sci., 31 (1991) 281.
[9] U. Preiss, P.R. Wallnofer and G. Engelhardt, Pestic. Sci., 23 (1988) 13.
[10] G.P. Rawn, G.R.B. Webster and D.C.G. Muir, J. Environ. Sci. Health B, 17 (1982) 463.
[11] E. Papadopoulou-Mourkidou and T. Tomazou, J. Stored Prod. Res., 27 (1991) 249.
[12] D.F. Hunt, G.C. Stafford, Jr., F.W. Crow and J.W. Russell, Anal. Chem., 48 (1976) 2098.
[13] M.M. Siegel, B.E. Hildebrand and D.R. Hall, Int. J. Environ. Anal. Chem., 8 (1980) 107.
[14] G.C. Mattern, G.M. Singer, J. Louis, M. Robson and J.D. Rosen, J. Agric. Food Chem., 38 (1990) 402.
[15] G.C. Mattern, C.H. Liu, J.B. Louis and J.D. Rosen, J. Agric. Food Chem., 39 (1991) 700.
[16] P. Abdul-Latif, Ph.D. Thesis, University of Salford, 1994.
[17] C.M. Cooper, J. Freshwater Ecol., 6 (1991) 237.
[18] G.P. Rawn, G.R.B. Webster and D.C.G. Muir, J. Environ. Sci. Health B, 17 (1982) 463.
[19] M.S. Sharom and K.R. Solomon, J. Agric. Food Chem., 29 (1981) 1122.
[20] L.H. Stanker, C. Bigbee, J. Van Emon, B. Watkins, R.H. Jensen, C. Morris and M. Vanderlaan, J. Agric. Food Chem., 37 (1989) 834.
[21] J.H. Skerritt, A.S. Hill, D.P. McAdam and L.H. Stanker, J. Agric. Food Chem., 40 (1992) 1287.
[22] A.S. Hill, D.P. McAdam, S.L. Edward and J.H. Skerritt, J. Agric. Food Chem., 41 (1993) 2011.
[23] G.A. Bonwick, M. Putman, P.J. Baugh, C.J. Smith, R. Armitage and D.H. Davies, 2nd International Conference and Industrial Exhibition on Food Safety and Quality Assurance: Use of Antibody Methods, 9–12 September 1993, El Escorial, Spain, Food & Agricultural Immunology, 6 (1994) 341.
[24] G.A. Bonwick, P. Abdul-Latif, C. Sun, P.J. Baugh, C.J. Smith, R. Armitage and D.H. Davies, 2nd International Conference and Industrial Exhibition on Food Safety and Quality Assurance: Use of Antibody Methods, 9–12 September 1993, El Escorial, Spain, Food & Agricultural Immunology, 6 (1994) 276.