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The Interaction between Pesticides and Particles in Rivers

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ABSTRACT

The results of the analysis of river waters and sediments for the pesticides α-BHC, γ-BHC, *p,p'*-DDE, dieldrin, endrin, *p,p'*-TDE, cis and trans-permethrin, cypermethrin, fenvalerate and deltamethrin are presented for 9 samples at four river sites. In most instances the concentration of organochlorine compounds is low with the notable exception of one catchment in which DDT and its metabolites were found. Pyrethroids have been measured in many of the sediments and in some waters. These include permethrin and deltamethrin as well as cis-permethrin in some water samples. The results have enabled a tentative estimate of field distribution coefficients for γ-BHC, DDE, dieldrin and permethrin.

The performance of the extraction and isolation procedure for the analysis of the pyrethroid and organochlorine pesticides in sediments has been evaluated in detail. The results indicate that the procedure is efficient for the pyrethroids and gives reasonable measurements for all the organochlorines studied.

1. Introduction

The interaction between pesticides in freshwater and particles, either in the sediment or suspended in the water, is important in the assessment of their translocation and impact on the fauna and flora in the system. The pesticides may enter the river as a solute in the aqueous phase and subsequently partition between the water and particulate components in the river sediment or they may enter in association with suspended solids via surface or sub-surface run-off from agricultural land or from discrete sewage discharges.

The first stage of this study is the measurement of the concentration of selected compounds at chosen river sites. The pyrethroids were chosen because of their increasing use in the U.K., the lipophilic character of the molecules and reports of their occurrence in rivers. The other pesticides chosen included a group of organochlorine compounds which have been widely used in the past but are less so today. These include α-BHC, Lindane, Heptachlor, Dieldrin, Aldrin, DDT, DDE, TDE and Endrin. Of this group, Lindane is still widely used and will be studied in more detail later. A third group of pesticides, the triazines, will also be studied because they have physical and chemical properties which differ considerably from many of the compounds in the other two groups ie the pyrethroids and organochlorines, both in terms of solubility and sorption behaviour.

The work reported here concerns the second 6 months progress of the project from 30 April 1990 to 1 November 1990. The report is divided into two sections:

(A) The occurrence of synthetic pyrethroids and selected organochlorine pesticides in different river sediments and waters.

(B) The details of the method development and testing for the analysis of lipophilic/neutral pesticides in natural sediments, i.e. simultaneous determination of pyrethroid and selected organochlorine pesticides in natural sediments.

The work is reported in the format of two papers intended for publication. Some of the results of the river survey work have been done in conjunction with project T05053k2: "Organics in the aquatic environment" but are included in this report for convenience.

In the first year of the project the following studies have been completed:

1. The development of methods for the analysis of pyrethroid and selected organochlorine pesticides in sediments with tests of the performance of the methodology (Section B, this report).

2. The development and testing of methods (liquid-liquid extraction and solid-phase extraction) for the analysis of several pesticides in river water (RL/T04053h1/1).

3. Analysis of river sediments and waters from (a) R. Stour in Worcestershire, (b) drainage channels, Wicken Lode and Reach Lode in Cambridgeshire, East Anglia and (c) Bere Stream, a tributary to the R. Piddle in Dorset (Section A, this report; RL/T04053h1/1).

4. Characterisation of the organic content of the sediments by combustion and in some instances surface areas by gas adsorption and inorganic elements by XRF analysis (RL/T04053h1/1 and Section A, this report).

2. Proposed work for the period November 1990 to April 1991

The first year's research on analytical procedures and field studies has been completed. It has been found that the analytical method for the analysis of sediments for pyrethroids and organochlorine compounds also measures other pesticides including the herbicide, simazine. This has been found in the sediments, F and G. It is proposed to evaluate the performance of the method for the analysis of this herbicide using the same procedure adopted for the pyrethroid and organochlorine pesticides (Section B, below). At the same time a surrogate organic compound will be tested as a potential marker for assessing the efficiency of the analytical procedure.

The results obtained in the first year of the project show the presence of a range of pesticides in river sediments. It is proposed to progress to the next stage of the project and examine the release and uptake of selected pesticides from river sediments. This will be started by examining the adsorption-desorption behaviour of simazine in selected sediments. Some of these natural sediments already contain simazine from its application to crops in the catchment. Others will be initially free of simazine. It is intended to examine the partition between the free-pesticide in solution, and that pesticide associated with colloidial material in the solution and with suspended or sediment particulates. This research will involve the development of new techniques to study the distribution of pesticide between the three compartments.

SECTION A

THE OCCURRENCE OF SYNTHETIC PYRETHROID AND SELECTED ORGANOCHLORINE PESTICIDES IN RIVER SEDIMENTS

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ABSTRACT

The concentration of the pesticides α-BHC, γ-BHC, *p,p'*-DDE, dieldrin, endrin, *p,p'*-TDE, *p,p'*-DDT, cis and tran-permethrin, cypermethrin, fenvalerate and deltamethrin have been measured in several river sediments and waters at selected sites in streams in rural areas and an industrial area. The results illustrate varying levels of contamination of the sediments. Field partition coefficients for lindane, DDE, dieldrin and permethrin are estimated.

INTRODUCTION

This research was initiated to evaluate the occurrence of selected lipophilic pesticides in river sediments as an initial phase in the study of the interaction between pesticides and particles in freshwater habitats. Published information on the concentration of pesticides in natural sediments is very limited, partly because of the analytical difficulties associated with the analysis of trace amounts of pesticides in complex matrices and the view that sediments act as an infinite sink without any obvious effects on the sediment biota. Some suspended particles and sediments effectivly scavenge pesticides from the water and so improve water quality and at the same time enhance the degradation of the pesticides in biofilms associated with natural particles. However, it is important to evaluate the ecological implications of the distribution of pesticide mixtures in sediments, particularly on benthic animals and microfauna. It is also desirable to monitor sediments to assess any problems caused by persistence in the sorbed state in particular sediment conditions.

The results presented are an attempt to examine selected river sites for a range of organochlorine and synthetic pyrethroid insecticides. The sites were chosen because of questions arising about the diversity of invertebrate fauna or where known discharges from agricultural or industrial origin occur.

EXPERIMENTAL

Materials

All the pesticides used to prepare standard solutions were used as supplied (Promochem Ltd.,St. Albans) and were specified to the following purities expressed as mass per cent: α-BHC, 99.5%; γ-BHC (lindane), 99.7%; *p,p'*-DDE, 99.8%; *p,p'*-TDE, 99.3%; dieldrin, 99.5%; endrin, 99.0% ; cis-permethrin, 99.1%; trans-permethrin, 99.8%; cypermethrin, 95.7%; fenvalerate, 90% and deltamethrin, 99.0%. Deltamethrin is the single isomer, (S)-α-cyano-3-phenoxybenzyl (1R,3R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate. The cis and trans isomers of permethrin

correspond to 3-phenoxybenzyl-(1RS)-3- (2,2-dichlorovinyl)-2,2- dimethylcyclopropanecarboxylate stereoisomers. Cypermethrin and fenvalerate were only available as racemic mixtures which separated on glc as four and two components respectively. All solvents were pesticide research grade (BDH, Poole).

Table 1. Location of the river sites studied together with the organic carbon content and total pesticide concentration in the sediment. Standard deviation of duplicates in brackets.

Sample code	National grid reference	Organic carbon, OC, content/ % by mass	Total pesticide concentration / $\mu g\ kg^{-1}$ (dry weight)
A	TL555701	23.3 (0.8)	2.2
B	TL548691	20.8 (0.6)	29.9
C	SY858923	1.6 (2.8)	3.5
D	SY858923	11.4 (2.5)	11.3
E	SO555478	8.2 (0.1)	123.2
F	SO555478	11.4 (0.2)	133.4
G	SO555478	9.2 (0.2)	87.0
H	SO822715	0.89 (0.04)	17.8
I	SO822715	0.71 (0.03)	18.7

Sample collection and preparation

The sites chosen for sampling are listed in Table 1. In brief:

Samples A and B were taken on 13.6.90 from drainage channels, Wicken Lode and Reach Lode respectively, on the River Cam in Cambridgeshire. These were selected because of differences in the invertebrate communities at the sites.

Samples C and D were taken on 20.3.90 from a chalk stream, the Bere stream, a tributary to the River Piddle in Dorset. The sampling sites were adjacent, with sample C from a sand bank and D from a darker "organic-rich" sediment which had accumulated in a marginal area. This stream was chosen because of a recorded change in the invertebrate community in recent years.

Samples E, F and G were taken on 12.7.90 from a field drainage ditch on a mixed farm situated in Herefordshire. The catchment has been described in some detail by Matthiessen (1988). This catchment is being used for modelling the transport of pesticides and offers the advantages that records of the use of pesticides on the farm are available.

Samples H and I were obtained on 12.9.88 and 13.9.89 respectively from the River Stour near Stourport in Worcestershire. This was the only site chosen in a predominantly industrial area.

Surface sediments were collected using either a stainless steel scoop or in large agglomerates using a pond net (1 mm mesh). If necessary the sediments were transferred on site through a 5 mm screen into a wide-necked glass jars with tops lined with aluminium foil. The sediments were transported back to the laboratory, further sieved through 1 mm mesh brass sieve as necessary, stored overnight in the dark at 4 ^{o}C and then frozen and freeze-dried until the weight loss was $< 0.1\%$ in $\cong$ 48 h. The sediments were then sieved through a 0.5 mm mesh brass sieve, thoroughly mixed and then stored as necessary in the dark at 4 ^{o}C under a nitrogen gas atmosphere.

The amount of organic matter in the sediments was estimated by combustion at 550°C using duplicate 5 g subsamples of sediment following the method discussed by Vollenweider (1969). Separate experiments were also performed to test the performance of the combustion method using a 1:1 (by mass) mixture of calcium carbonate and quartz. The results showed that the maximum loss of carbon dioxide from the calcium carbonate amounted to < 2% by mass of the calcium carbonate. The results for each of the samples are shown in Table 1. The two samples, E and H, have been characterised in more detail to determine their mineralogy and specific surface area for detailed adsorption-desorption studies.

The water samples were collected at the same time as the sediment samples in 1 litre pyrex bottles fitted with PTFE screw caps. The bottles were not pre-rinsed with river water prior to sampling to avoid any adsorption of pesticides onto the inner glass surface. The samples were stored in the dark at 4°C and analysed as soon as possible after collection.

Analytical methods

The sediments were analysed using a new extraction and isolation procedure developed initially for the analysis of permethrin, but later extended to include the pesticides listed above. This involved a two-stage extraction with acetone, followed by a two-stage isolation procedure using solid-phase extraction with magnesium silicate, Florisil. The details and performance of the method have been discussed by House et al (1990). The method has been found to be suitable for the analysis of complex natural sediments but for the most accurate quantitative work does necessitate the use of recovery trials on individual sediments using different loadings of a pesticide standard mixture. This is a time consuming procedure and is not necessary in semi-quantitative applications eg screening sediments for specific compounds. The results reported here have not been adjusted for losses during analysis. Experiments with sediment I, which was spiked with a multi-pesticide standard to a concentration of 20 $\mu g\ kg^{-1}$, gave recoveries of between 67 and 97% for the synthetic pyrethroids and between 39 and 82% for the organochlorine pesticides. The lowest recoveries of 39% was obtained for *p,p'*-DDT and *p,p'*-DDE (House et al, 1990). In all the extractions a blank was determined alongside the sediment extraction and isolation. For samples H, E, F and G the blanks were prepared using a sample which had been pre-extracted with acetone and for the other samples, the blank extract was prepared following the procedure for the sediment analysis but without any sediment in the extraction phase.

The samples were analysed in the following groups : A,B; C,D; E,F,G; H; I. A blank extract was included in each group. Samples H and I were analysed in triplicate and duplicate respectively and the other samples were analysed without replication. The limits of detection were generally : ca 0.1 $\mu g\ kg^{-1}$ for the organochlorine pesticides and 1.0 $\mu g\ kg^{-1}$ for the synthetic pyrethroid pesticides. In instances when a pesticide occurred in the blank sample, the detection limit was taken as double the concentration in the blank sample.

The one litre water samples were analysed by a two-stage hexane extraction followed by drying the extract with sodium sulphate (heated to 110°C for a minimum of four hours) and Kurdena-Danish concentration to a volume of 2 ml. Recoveries were determined by the addition of a multi-pesticide standard to a concentration in the aqueous phase of 0.2 $\mu g\ dm^{-3}$ in each pesticide. The percentage recoveries were determined as α-BHC, 86%; γ-BHC, 94%; heptachlor, 101%; aldrin, 90%; DDE, 93%; dieldrin, 103%; endrin, 160%; TDE, 100%; DDE, 119%; cis-permethrin, 123%; trans-permethrin,

107%; cypermethrin, 89% and fenvalerate, 103%. A 1 litre sample of distilled water was analysed with each batch of freshwater samples and the results showed that in general the organochlorines were either not detected or only detected in trace amounts ie < 1 ng dm^{-3}. These levels are similar to the limits observed for carry-over from injections following the calibration. Two of the pyrethroids, permethrin and cypermethrin, were detected at concentrations < 7 ng dm^{-3} in the blanks but this varied slightly between extractions and glc determinations. The detection limits were determined as 1 ng dm^{-3} for the organochlorines and 10 ng dm^{-3} for the pyrethroids.

The glc analysis of the extracts was performed using a Perkin-Elmer 8700 instrument with spit-splitless injector, an electron-capture detector, ecd, and fused silica capillary with 5 % phenyl-methyl silicone stationary phase (House et al, 1990). Peak assignments were based on the relative retention times (RRT) with respect to the internal standard, aldrin, and these were confirmed when necessary by mass-spectroscopy using a Hewlett-Packard 5971A glc with a mass-selective detector (MSD). For the assignment of peaks to specific pesticides the RRT's of the organochlorine and pyrethroid pesticides had to be within ±0.001 and ±0.002 of the corresponding calibration values respectively. The calibration was done using a multi-pesticide standard to give a nominal concentration in each pesticide of 0.05 $\mu g\ ml^{-1}$. The linearity of the ecd response was verified over a concentration range of 0.02-0.1 $\mu g\ ml^{-1}$. Prior to every sample analysis the RRT's and response factors were calibrated by an injection of the 0.05 $\mu g\ ml^{-1}$ multi-standard followed by a second injection for confirmation and then a solvent injection to measure any trace carry-over of pesticides from the injector followed by the replica samples. This sequence was repeated for each sample.

RESULTS AND DISCUSSION

Water samples

The results of the analysis are shown in Table 2. The standard deviations quoted are for the duplicate analysis of each extract except for sample G which was not replicated and sample H which was processed in triplicate ie 3 separate litre samples, with the glc analysis done in duplicate. Those compounds that also occurred in the sediment samples are marked with an asterisk. Samples F and G also contained simazine.

Apart from sample C/D, all the waters contained lindane at concentrations between 2 and 38 ng dm^{-3}. In most cases this was confirmed by mass-spectroscopy (EI) using the indicator ions, m/z, 181 and 219. α-BHC was found in the same samples but at concentrations near the limits of detection of the method. Heptachlor and deltamethrin were not detected in any of the samples and fenvalerate, which was detected in sample E, was also at the limits of detection using ecd and could not be detected using the MSD with ions, m/z, 181 and 253. Endrin was only detected in sample B at a concentration near the limits of detection. DDT and its metabolites, DDE and TDE were found in some samples. In particular, sample H contained both DDT and DDE but the results of the analysis of separate 1 litre samples indicated a high variability between samples eg DDT was not detected in one sample but at concentrations of 14 and 259 ng dm^{-3} in the other two samples with a concentration in the blank determined as 2 ng dm^{-3}. The concentration of DDE determined in these samples was also very variable ie 0, 4, 22 ng dm^{-3} with none detected in the blank. Permethrin was detected at a number of sites with the cis isomer the most abundant. The highest concentrations were found at sites A and H with the results from H again showing variations between samples. This probably reflects the heterogeneity in the colloidial content

in the individual samples. It is significant that better reproducibility between samples was obtained for α-BHC and γ-BHC (Table 2) which are more soluble in water then the other pesticides studied. Technical permethrin has a cis:trans isomer ratio of 40:60. The results obtained for sample H indicate a ratio of between 70:30 and 89:11 in the water samples.

TABLE 2. Concentration of pesticides in river waters / ng dm^{-3}. Values in brackets are standard deviations appropriate to glc analysis. C indicates confirmation by MSD.

Name	A	B	C/D	E	G	H^1	H^2	H^3
α-BHC	1(0)	1(0)	-	<1	<1	*11(0.2)	7(0.2)	9(0.3)
γ-BHC	*2(0.1)C	*5(0.1)C	-	*2(0.5)	*12	*41(3)	38(0.2)C	34(7)C
DDE	-	-	-	*5(2)	-	-	*22(0.4)C	4(1)C
Diel'	-	-	-	-	-	*9(0.2)C	8(0.1)C	6(1)C
Endr'	-	2(2)	-	-	-	-	-	-
TDE	-	-	2(0.1)	-	-	-	2(1)	-
DDT	-	-	-	*<1	-	14(1)C	259(6)C	-
c-per	40(1)C	16(2)	*17(12)C	-	-	*468(48)C	323(2)C	191(23)C
t-per	-	-	-	-	-	*67(7)C	39(17)C	82(34)C
cyp'	11(6)	-	-	-	-	10(6)	24(10)	29(18)
fen'	-	-	-	<10	-	-	-	-
total	54	24	19	19	13	620	722	355

Sediment samples

The results of the analysis of samples A,B and C,D are shown in Table 3. The results for sample A indicate negligible concentrations of the pesticides, with the concentration either similar to that in the blank or close to the limits of detection of the method. Although both permethrin and cypermethrin were detected by ecd in the water sample extracts, these were not detected in the corresponding sediments. The concentrations found in sample B were significantly higher than those in sample A with traces of several organochlorine compounds including DDE and TDE. Trans-permethrin was also detected by glc with MSD but could not be quantified using ecd because of the co-elution of another substance close to where the permethrin eluted. The differences in the pesticide contents of the two sediments is not obviously related to differences in the total organic content of the sediment (Table 1) and is not reflected in the pesticide concentrations in the associated waters at the time of sampling. An example of a chromatogram obtained for sample B is shown in Figure 1.

The concentration of pesticides in sample C and D are also low with sample D having higher levels of all the pesticides. Cis-permethrin, although detected in the water (Table 2), was only detected in the sandy sediment, C, and not in sample D. At this site the sediment heterogeneity measured in terms of the organic content does appear to be an important factor in determining the other pesticide distributions.

The results from the farm site ie samples E,F and G, are shown in Table 4. The results indicate much higher concentrations of several pesticides in the sediments at all the sites sampled including lindane, deltamethrin, DDT and its metabolites. The sediments were similar in appearance, texture and organic content. Both DDT and DDE decrease in concentration downstream whilst the concentration of TDE was less variable. Neither DDT or its metabolites were detected in the blank sample. This is the only site at which deltamethrin has been found in the sediments. Difficulties have been experienced in confirming the presence of low concentrations of

fenvalerate and deltamethrin with the MSD in samples including the multi-pesticide standard used in the calibration. However the agreement of the RRT's for samples E,F and G and the standards obtained from the ecd are very good ie within 0.002. As shown in Table 4, significant concentrations of dieldrin and α-BHC were also detected in some of the samples.

TABLE 3. Concentration of pesticides in the river sediments for samples A-D / $\mu g\ kg^{-1}$.† :Quantified using MSD with m/z=163 ion. C indicates confirmation by MSD.

Name	Blank	A	B	Blank	C	D
α-BHC	0.2	-	-	-	-	0.3C
γ-BHC	-	0.2	1.2	-	0.1	0.3
DDE	-	0.4C	3.0C	-	-	2.2C
Diel'	1.0	1.0C	2.0C	0.7	-	-
Endr'	0.3	-	-	-	-	-
TDE	-	-	2.0C	-	-	0.9C
DDT	-	-	-	0.2	0.6	7.6C
c-per'	1.0	-	-	-	<1	-
t-per'	0.3	-	18†	-	-	-
cyp'	-	-	2.7	-	-	-
fen'	0.3	0.6	1.0C	-	2.2	-

FIGURE 1. Example of a chromatogram obtained for sample B with ecd.

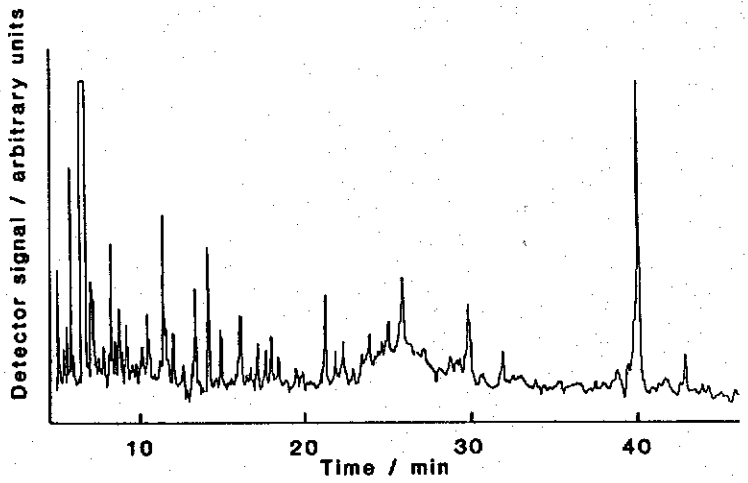

Table 4. Concentration of pesticides in river sediments for samples E-G /μg kg^{-1}. Values in brackets are the standard deviations of glc duplicates. Endrin, trans-permethrin and cypermethrin were not detected. C indicates confirmation by MSD.

Name	Blank	E	F	G
α-BHC	0.12 (0)	-	1.7 (0.5)	-
γ-BHC	0.02 (0.03)	0.4 (0.1)	1.0 (0.1)	0.8 (0.1)
DDE	-	53.6(0.9)C	30.9(1.6)C	12.3(0.9)C
Diel'	0.3 (0.1)	-	6.7(0.2)C	6.0(0.6)C
TDE	-	5.1(0.3)C	28.3(1.5)C	18.4(1.9)C
DDT	-	62.2(1.2)C	47.3(4.3)C	9.4(1.1)C
c-per'	0.6 (0.1)	-	-	-
fen'	-	-	3.6 (0.8)	2.6 (1.3)
del'	-	1.9 (0.4)	14.0 (0.8)	37.5 (2.0)

The results for the two samples H and I are shown in Table 5. The standard deviations given in the table include variation in the triplicate and duplicate analysis of samples H and I respectively together with the variation in the glc duplication. The predominant pesticides were the permethrin isomers and dieldrin probably originating from industrial activity in the area. These were also important components in the associated waters collected at the same time as sample H. The cis:trans isomer ratio is 58:42 for sample H and 74:26 for sample I and as for the water samples, reflects the persistence of the cis compared with the trans isomer, the latter being the major component in the technical product.

The results of the water and sediment analysis can be used to calculate a Henry's law adsorption constant or field distribution coefficient, K_f, in units of dm^3 kg^{-1} ie the concentration of pesticide in the sediment (μg kg^{-1} dry weight) divided by the concentration in solution (μg dm^{-3}). This is only a crude estimate of the distribution coefficient, K_d, because of a number of assumptions implicit in the calculation viz: (a) an equilibrium exists between the freshwater and sediment at the time of sampling and (b) the concentration measured in the water represents a truly soluble fraction and excludes pesticides associated with both colloids and suspended material. In field conditions it is difficult to rigorously evaluate the uncertainties caused by these assumptions because of the dynamic nature of the system and the problems of transferring samples to laboratory for further study without destroying the natural conditions. In spite of these limitations it is worthwhile to record the values of K_f and use the organic contents of the sediments to calculate K_{om} values where $K_{om} = 100\ K_f$ / OC with OC values given in Table 1. This has been done for those pesticides that were detected in both the water and sediment samples (see Table 2).

γ-BHC was in five of the samples and gave log K_{om} values between 2.5 and 3.4 and log K_f between 0.5 and 2.4. These values compare with log K_d reported by Saleh et al (1982) of between 1.8 and 3.4 and the K_{om} values are in reasonable agreement with those predicted from the Collander relationship (Briggs, 1981) :

$$\log K_{om} = 0.52 \log K_{ow} + 0.62 \quad (1)$$

where K_{ow} is the octanol-water coefficient, ie 2.54 obtained using log K_{ow} for lindane of 3.7 (Saleh et al, 1982).

The results for DDE show more variation with values of log K_{om} of 5.1 and 3.1 for samples E and H respectively compared with calculated values from eq(1) of between 3.6 and 4.2 depending on the choice of K_{ow} (Hawker and Connell, 1988).

The results for dieldrin in sample H lead to values of log K_{om} of 3.2 which compares with the calculated value of 3.8 obtained with log K_{ow}=6.2 (Briggs, 1981). The log K_f value is 2.2 and is in the range of the measured values of 2.2 (Bowman et al, 1985) and 2.7 (Sharom et al, 1980).

The results for permethrin obtained for sample H together with the mean water concentrations given in Table 2 leads to log K_d values of 1.5 and 2.0 for the cis and trans isomers and log K_{om} values of 3.50 and 4.1 respectively. These results compare with a log K_d=2.59 for a 40:60 cis-trans mixture (Sharom and Solomon, 1981) and a value of 2.30 given by Hill (1989). Equation (1) predicts a result of between 3.3 and 3.8 depending on the choice of K_{ow}. The values chosen here were 6.2 from Muir et al (1985) and 5.23 from Lockhart et al (1983). The agreement of the calculated log K_{om} results and the values determined here ie 3.5 and 4.1, is no doubt fortuitous.

Table 5. Concentration of pesticides in river sediments for samples H and I /μg kg^{-1}. Values in brackets are the standard deviations described in the text. Endrin, TDE, DDT and deltamethrin were not detected. Sample H was not analysed for the presence of deltamethrin. C indicates confirmation by MSD.

Name	Blank	H	Blank	I
α-BHC	0.1	<0.2	<0.1	<0.1
γ-BHC	0.1	0.1 (0.07)	<0.1	-
DDE	<0.1	0.2 (0.03)	-	-
Diel'	<0.2	1.0(0.2)C	-	2.0(0.3)C
c-per'	-	9.5(1.6)C	-	11.1(2.3)C
t-per'	1.0	6.8(2.2)C	1.0	4.0(0.3)C
cyp'	1.0	-	-	<1
fen'	-	-	-	1.5(0.2)

CONCLUSION

Several pesticides have been determined in different river sediments and their associated waters. In most instances the concentration of organochlorine compounds is low with the notable exception of samples E-G in which DDT and its metabolites were found. Pyrethroids have been measured in many of the sediments and some waters. These include permethrin in samples B,H and I, deltamethrin in samples E-G and cis permethrin in water samples A,B,C/D and H. Further work is needed to evaluate the ecological implications of particle bound pesticide mixtures and to establish criteria for the assessment of sediment contamination.

The results have also enabled a tentative estimate of field distribution coefficients for γ-BHC, DDE, dieldrin and permethrin. The findings appear to be consistent with existing information on the partition behaviour and Collander relationship.

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SECTION B

Simultaneous Determination of Pyrethroid and Selected Organochlorine Pesticides in Natural Sediments

by

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ABSTRACT

The details of a new extraction and isolation procedure developed for the determination of a range of pyrethroid and organochlorine pesticides in natural sediments are presented. The method is evaluated using a river sediment loaded with a multi-pesticide standard. The results indicate that within certain limitations the method may be applied to screening sediments for the occurrence of the pesticides and that detailed recovery trails are needed for individual sediments before accurate concentrations can be determined.

Keywords: Pesticides, Pyrethroids, organochlorine, sediments, gas-liquid chromatography

Introduction

The measurement of trace quantities of toxic organic compounds in various matrices in the aquatic environment is important for the evaluation of their translocation and possible direct or indirect effects on the biota. The partition of lipophilic pesticides between freshwater and the associated sediment may produce situations where a pesticide is at a relatively low concentration in the dissolved state but concentrated through sorption processes to particulate solids in suspension or in the sediment matrix.

The measurement of pesticide concentrations in natural sediments of complex composition is less advanced than for aqueous systems and is generally tedious as it involves both extraction and further isolation stages before separation and detection by gas-liquid chromatography. It is also desirable to develop methods which are suitable for a number of compounds with similar physicochemical properties. The pyrethroids are a group of broad spectrum insecticides of increasing usage (1) whilst the organochlorine insecticides are generally decreasing in usage but are still found at polluted sites. It has been found that an extraction and isolation procedure, originally developed for the determination of the concentration of permethrin in river sediments, may also be used to measure other pyrethroids such as cypermethrin, fenvalerate and deltamethrin as well as some organochlorine compounds viz α-BHC, γ-BHC (lindane), DDT, DDE, TDE, Dieldrin and Endrin. No general method at the moment is available to analyse natural sediments for such a range of compounds using gas-liquid chromatography with a sensor of high sensitivity. The results of the experiments to assess the performance of a new analytical procedure developed in this laboratory are presented here.

Experimental

Materials

All the pesticides were used as supplied (Promochem Ltd, St. Albans) and were specified to the following purities expressed as mass per cent: α-BHC, 99.5%; γ-BHC (lindane), 99.7%; *p,p'*-DDT, 99.8%; *p-p'*-DDE, 99.8%; *p-p'*-TDE, 99.3%; dieldrin, 99.5%; endrin, 99.0%; cis-permethrin, 99.1%; trans-permethrin, 99.8%; cypermethrin, 95.7%; fenvalerate, 90.0% and deltamethrin, 99.0%. Deltamethrin is the single isomer, (S)-α-cyano-3-phenoxybenzyl (1R,3R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate. The configuration of the substituent at the C3 atom of the cyclopropane ring is given as cis or trans relative to the position of the ester group with respect to the plane of the cyclopropane ring. The cis and trans isomers of permethrin correspond to the 3-phenoxybenzyl-(1RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate sterioisomer. Cypermethrin and fenvalerate were only available as racemic mixtures which separated on glc as 4 and 2 components respectively. All solvents were pesticide analysis grade (BDH, Poole).

Analytical Procedure

All glassware was chromic acid cleaned, rinsed in distilled water, acetone and hexane prior to use. A 50 g quantity of freeze-dried sediment, previously sieved through a 0.5 mm mesh brass sieve, was extracted with 150 ml of acetone by shaking for 1 hour. The solids were allowed to settle before filtration through a pre-washed number 4 porosity sintered glass filter and the extract transferred with 2 ml acetone washes to a 250 ml flask. The sediment in the extraction flask was rinsed with 50 ml of acetone, filtered and the residue in the sintered filter leached with a 5 ml aliquot of acetone. The first extract was then rotary evaporated at 45°C to a low volume. The extraction of the sediment was repeated with 150 ml of acetone

and a 50 ml rinse. The extract was finally rotary evaporated to dryness and then redissolved in a 10 ml solution of 5% acetone in dry hexane.

The extracts from natural sediments were usually highly coloured and found to be unsuitable for direct analysis by gas-liguid chromatography using an electron-capture detector (ecd). Further separation of the analytes from other organic material of varied and largely unknown composition was required. The pesticides investigated were neutral compounds and the two-stage procedure outlined below was designed to remove the polar contaminants by normal-phase adsorption chromatography without unacceptable losses of the pesticides. In reality, the high concentration of organic compounds in the extract may include polymeric material which can interfere with the partitioning on the adsorbent column. The procedure involves the use of a magnesium silicate adsorbent, Florisil,to separate the more polar contaminants from the insecticides. This adsorbent has previously been used to purify environmental samples for the analysis of chlorinated hydrocarbons and phthalate esters (2).

The solid phase extraction (SPE) column (Analytichem International, FL694406, 6ml capacity) was preconditioned with 10 ml of dry hexane and 10 ml of 5% acetone in hexane and the extract loaded onto the column.The non-adsorbed solutes were drawn through the column under reduced pressure. The flask containing the extract was then rinsed with six 5 ml aliquots of 5% acetone in hexane and transferred to the adsorption column. The pyrethroids together with several organochlorine insecticides were eluted directly. This eluate was found to be unsuitable for glc analysis because of interferences of compounds in the region of the chromatogram where the organochlorine compounds eluted.

A second stage isolation using Florisil activated to a temperature of 160°C was found to reduce the interference to an acceptable level. Glass columns (5 mm internal diameter, 120 mm in length and fitted with PTFE taps) were filled with dry hexane. A plug of glass wool followed by a 5 mm layer of granular dried sodium sulphate was added. The Florisil (100-200 mesh) activated at 160°C for more than 12 hours was added whilst hot and allowed to settle to give a column of 100 mm depth. This was capped with 10 mm of dry sodium sulphate to protect the magnesium silicate from atmospheric water. The column was further rinsed with 40 ml of dry hexane and the eluate discarded. The sample from the first stage was taken to dryness and dissolved in 10 ml of hexane and loaded onto the adsorption column. The residues were washed from the flask with two 5 ml aliquots of hexane and later with the 5% acetone in hexane mixture in the elution stage. The 20 ml of hexane eluate or column wash, contained much of the interfering organic solutes. It was found that permethrin and some of the organochlorine insecticides required 40 ml or more of hexane before elution. The insecticides were eluted with 20 ml of 5% acetone in hexane mixture, hereafter referred to as the first eluate, followed by a second 20 ml elution with the same solvent, the second eluate. The eluate fractions were retained separately for gas-chromatography.

Gas-liquid chromatography

The concentration of the pesticides was measured using a single method designed to separate the organochlorines including DDE and dieldrin and higher boiling point pyrethroids. The analysis was performed using a Perkin-Elmer 8700 glc instrument with split-splitless injector and an electron capture detector operated at 350°C. The column was a 25 m, 0.25 mm diameter fused silica capillary column with 5% phenyl-methyl silicone stationary phase (DB5). The glc oven was programmed as shown in Table 1. The injector was maintained at 285°C and operated in splitless mode for 30 seconds after each 2 µl injection of sample. The carrier gas was helium with

a septum purge of ≃ 5 ml min^{-1} and make-up nitrogen gas flow to the detector of ≃ 60 ml min^{-1}. Peak assignments were based on the relative retention times with respect to the internal standard, aldrin, and these were confirmed when necessary by mass-spectroscopy using a Hewlett-Packard 5971A glc with a mass-selective detector. The calibration was achieved using a multi-pesticide standard prepared in hexane to give nominal concentrations in each of the compounds as 0.05 mg dm^{-3} ie nominally 0.1 ng of each compound was injected. The linearity of the detector response was determined using a fixed injection of 2 μl of the multi-pesticide standard of nominal concentration of 0.1, 0.05 and 0.02 mg dm^{-3}. The results for two organochlorine compounds and the permethrin isomers are shown in Figure 1. Similar linear calibrations were obtained for the other insecticides used in this study.

Results and Discussion

Analysis of a reference sediment

Preliminary studies indicated that the method was able to detect the pyrethroid and organochlorine pesticides listed above in a range of sediments of complex composition but showed poor recoveries of two other compounds which were tested viz aldrin and heptachlor. As a result of these initial trials, a river sediment was selected for analysis to determine the background concentration of the insecticides. This was found necessary because all the sediments examined in preliminary studies contained one or more of the compounds of interest. The performance of the analytical procedure was evaluated by the addition of a multi-pesticide standard mixture to the sediment at two different concentrations followed by analysis using the method described above.

The sediment was obtained from a batch of material collected from the R. Stour (NGR SO 822715) on 12th September 1989. The organic matter in the sediment was measured by combustion of the sediment at a temperature of 550°C (3). Five sub-samples (1g) were taken for analysis. The organic content of the sediment was found to be 0.71% by mass with a coefficient of variability of 3.9%. This indicates that the sediment was sufficiently homogenous for sub-sampling. The specific surface area of the sediment was determined as 0.94 m^2 g^{-1} by nitrogen gas adsorption at 77.5 K using the B.E.T. method.

Duplicate samples of sediment were analysed and the results of the triplicate glc analysis of the first eluate showed the presence of three insecticides as shown in Table 2. The chromatograms obtained using the ecd detector in the analysis of the first and second eluates are shown in Figure 2 together with a typical chromatogram obtained for the 0.05 mg dm^{-3} multi-pesticide standard. Although the chromatograms are complex, it was possible to achieve the resolution of the pesticide peaks and reasonable base-line determinations for the integrations. The identity of the compounds was confirmed by mass-spectroscopy using the retention times in combination with the indicator ions as shown in the Table. The relative retention times calculated with respect to aldrin for α-BHC, cypermethrin and fenvalerate were within 0.004 of the values calculated from the calibration chromatograms but the presence of these insecticides in the extract could not be confirmed by mass-spectroscopy even after the eluate was concentrated by a factor of approxiametely 13 times. For cypermethrin and fenvalerate, at a concentration in the sediment of ≃ 1 μg kg^{-1}, the additional concentration step led to a final injection of ≃ 60 pg which is well within the detection range of the mass-spectrometer operated in single-ion mode with a scan rate of 1.2 cycles per second. The ratio of the cis/trans isomers of permethrin calculated from the integration of the corresponding ecd peaks and the phenoxyltropylium (m/z = 183) ion peaks were in good agreement ie 2.76 and 2.86 respectively, demonstrating the slower biological degradation of the cis-isomer compared

with the trans-isomer. Although the trans-isomer is the major component in the commercial products, the cis-isomer is more resistant to biodegradation in comparison to the trans-isomer. None of the other insecticides were detected by glc analysis using either detector.

Performance Assessment

The efficiency of the extraction and isolation procedure was evaluated by adding known quantities of the multi-pesticide standard dissolved in 50 ml of acetone to 50 g of freeze-dried dry sediment, mixing and evaporating to dryness with a stream of nitrogen gas. The two concentrations used for the test were nominally 2 and 20 $\mu g\ kg^{-1}$ and were chosen to fall within the range of concentration found in the sediments studied previously. These concentrations are relatively low in comparison with the concentration of other organic compounds that have been found in river sediments eg some groups such as the polyaromatic hydrocarbons may exceed 1000 $\mu g\ kg^{-1}$ (dry weight) in some river sediments (4). The results of the analysis of the first and second eluates from the final isolation stage are shown in Tables 3 and 4 together with the calculation of the percentage recovery of each of the pesticides in the first and total eluate. An account of the initial concentration of the pesticides in the sediment was included in the calculation of the recoveries using the data shown in Table 2 and included those compounds detected by the ecd but not later confirmed by the mass-spectrometer detector. This procedure allowed for the possible interference of co-eluting compounds in the integration of the chromatograms derived from the sediments spiked with the pesticide standard.

As shown in Figure 3, the overall percentage recoveries of the individual pesticides is reasonable with the lowest value of 19 % obtained for γ-BHC at a concentration in the sediment of 2 $\mu g\ kg^{-1}$. The analysis of the blanks ie the extracts obtained using the above analytical method but without the sediment present in the extraction stage, indicated relatively minor interferences (see Table 4). Substantially better recoveries were obtained for the organochlorine insecticides at the higher spike concentration of 20 $\mu g\ kg^{-1}$ eg with γ-BHC a recovery of 67% was achieved. Recoveries of between 30 and 40% for DDE and DDT were determined with little difference between the two spike concentrations. Other compounds such as endrin, TDE and deltamethrin also exhibited similar recoveries at both spike concentrations. All the pyrethroids were recovered efficiently but with some differences between the two levels of spiking. The pyrethroids cypermethrin, fenvalerate and deltamethrin required a second elution to achieve satisfactory recoveries ie a final eluate of 40 ml. For the pyrethroids the percentage of the total recovery in the second eluate increased with increasing retention time of the pesticide on the glc column ie according to the reference number shown in Table 3, and followed a linear trend with the logarithm of the octanol-water partition coefficient (5). The regression coefficient of the 10 points, including the cis and trans isomers of permethrin was determined as 0.92.

The results in Table 3 and 4 also show that the variation in the replicate concentrations obtained from the ecd detector are greater for the pyrethroids than for the organochlorine pesticides. This is because of the lower sensitivity of the detector to the pyrethroids ie lower response factor, and also the broadening of the chromatography peaks associated with the longer retention times on the glc column.

Conclusion

A new method is proposed for the analysis of complex natural sediments involving a relatively simple extraction step followed by a two-stage

isolation procedure using solid-phase extraction techniques with magnesium silicate (Florisil).

The assessment of the performance of the method indicates that it is suitable for the determination of a number of pesticides in natural sediments. The efficiency of the extraction and isolation method varies between the pesticides and in some instances depends on the concentration of the pesticide in the sediment. This limits the use of a single surrogate organic compound to quantify the efficiency of the method. Probably the best method of validating data at the moment is to use a multi-pesticide standard to spike the sediment and to analyse this together with a blank and an untreated sediment. This is a time consuming procedure and is not necessary in all applications eg screening sediments for the occurrence of specific groups of compounds. Future applications include the extension of the method to the analysis of other neutral compounds such as the triazine herbicides and polyaromatic hydrocarbons in natural sediments.

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Legends to Figures

Figure 1 Example of the calibration lines for the glc with the electron-capture detector obtained for: (a) ● , γ-BHC; ○ , dieldrin and (b) ● , trans-permethrin; ○ , cis-permethrin.

Figure 2 Examples of the chromatograms obtained using the electron-capture detector. (a) Multi-pesticide standard containing a nominal 0.05 ng of each compound injected into the glc. The numbers refer to the pesticides listed in Table 3. (b) First 20 ml eluate of 5 % acetone in hexane from the final isolation step. (c) Second 20 ml eluate of 5 % acetone in hexane from the final isolation step.

Figure 3. Overall recoveries of the pesticides obtained after extraction and isolation. The pesticide reference numbers are given in Table 3. ● , 2 $\mu g\ kg^{-1}$ loading of each pesticide; ○ , 20 $\mu g\ kg^{-1}$ loading of each pesticide.

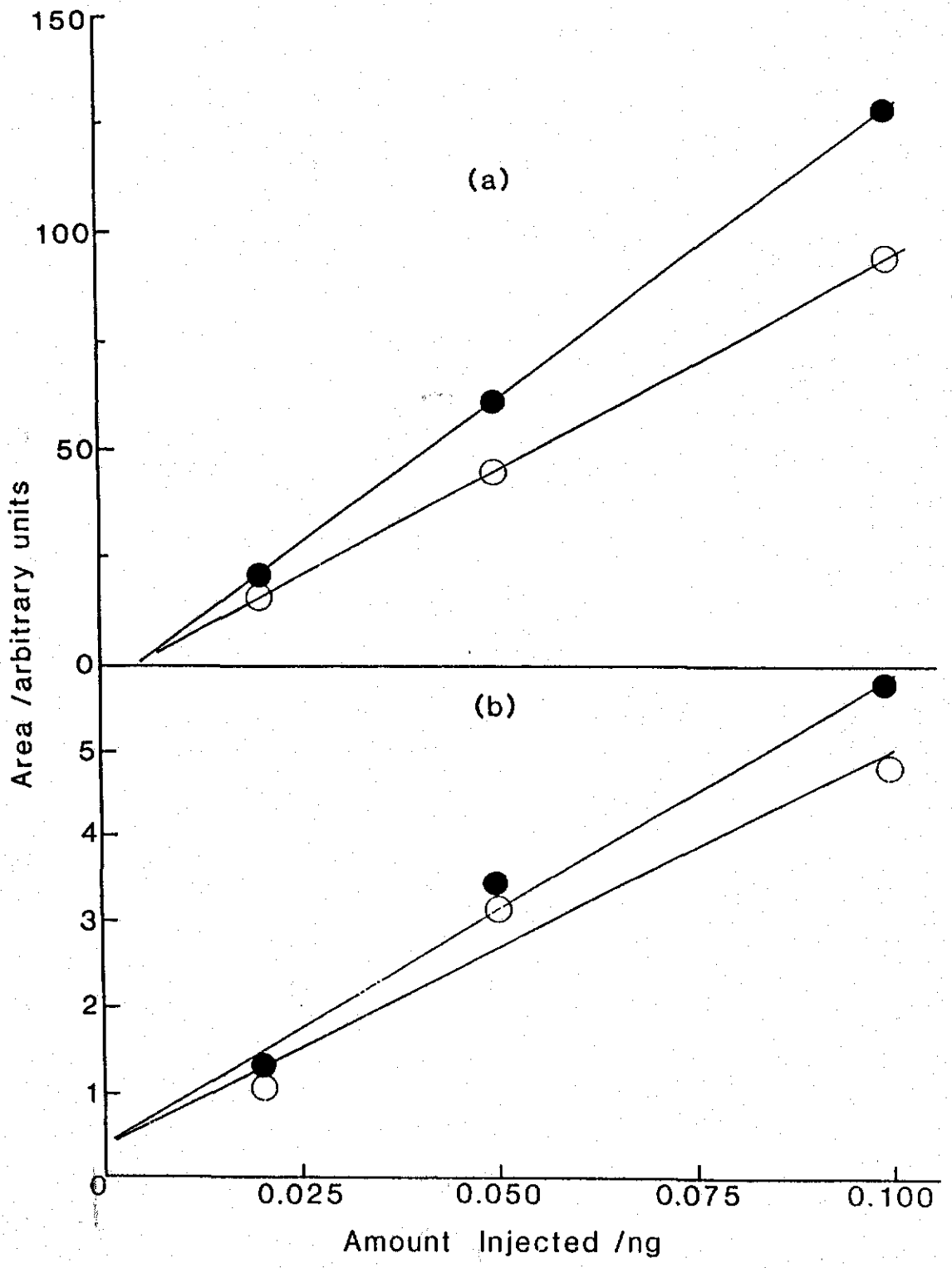
150
100
50
0
(a)
(b)
5
4
3
2
1
0
Area /arbitrary units
0.025
0.050
0.075
0.100
Amount Injected /ng

Figure 1

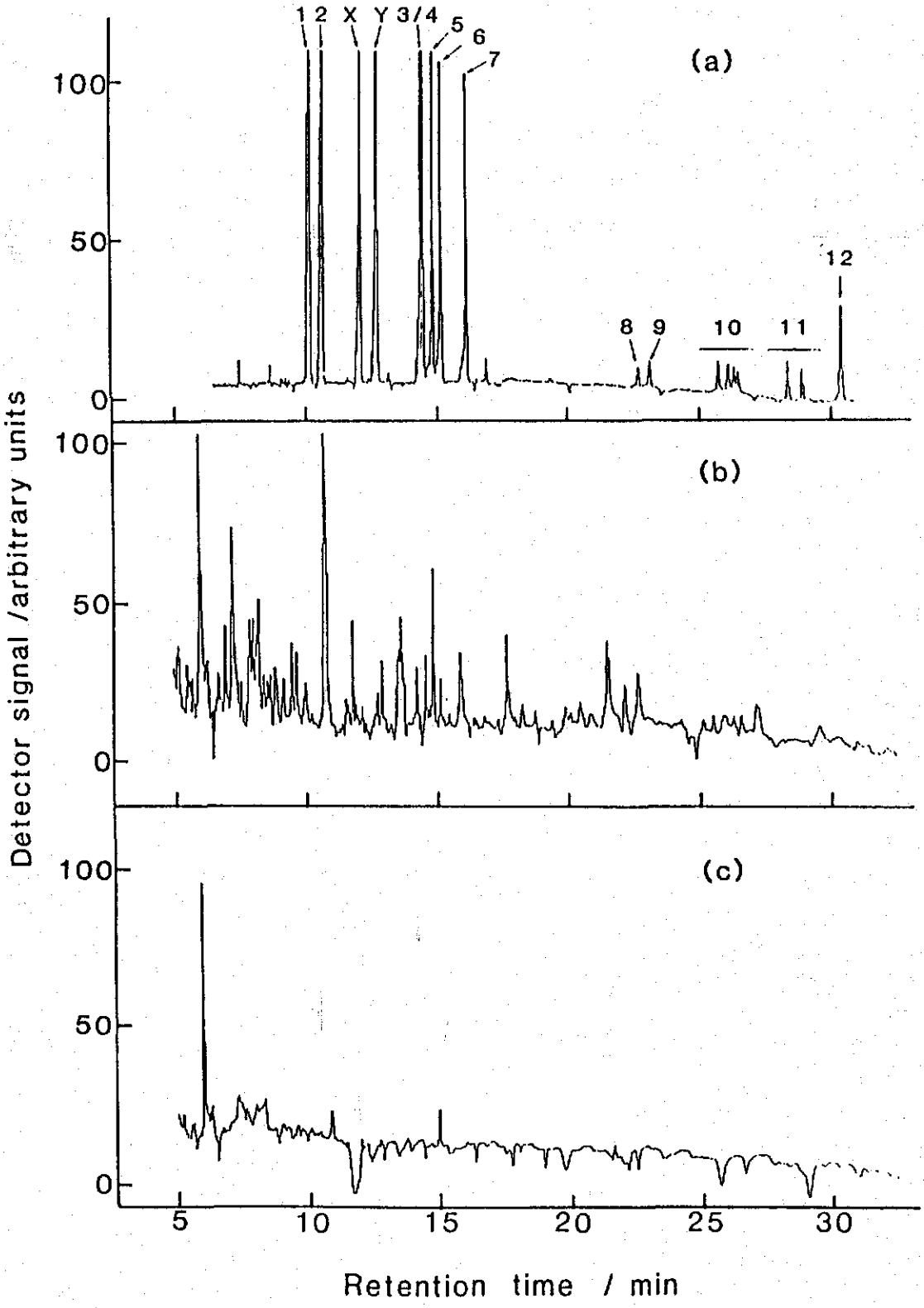
1 2 X Y 3/4 5 6 7
(a)
100
50
0
8 9 10 11 12
(b)
100
50
0
(c)
100
50
0
5 10 15 20 25 30
Detector signal /arbitrary units
Retention time / min

Figure 2

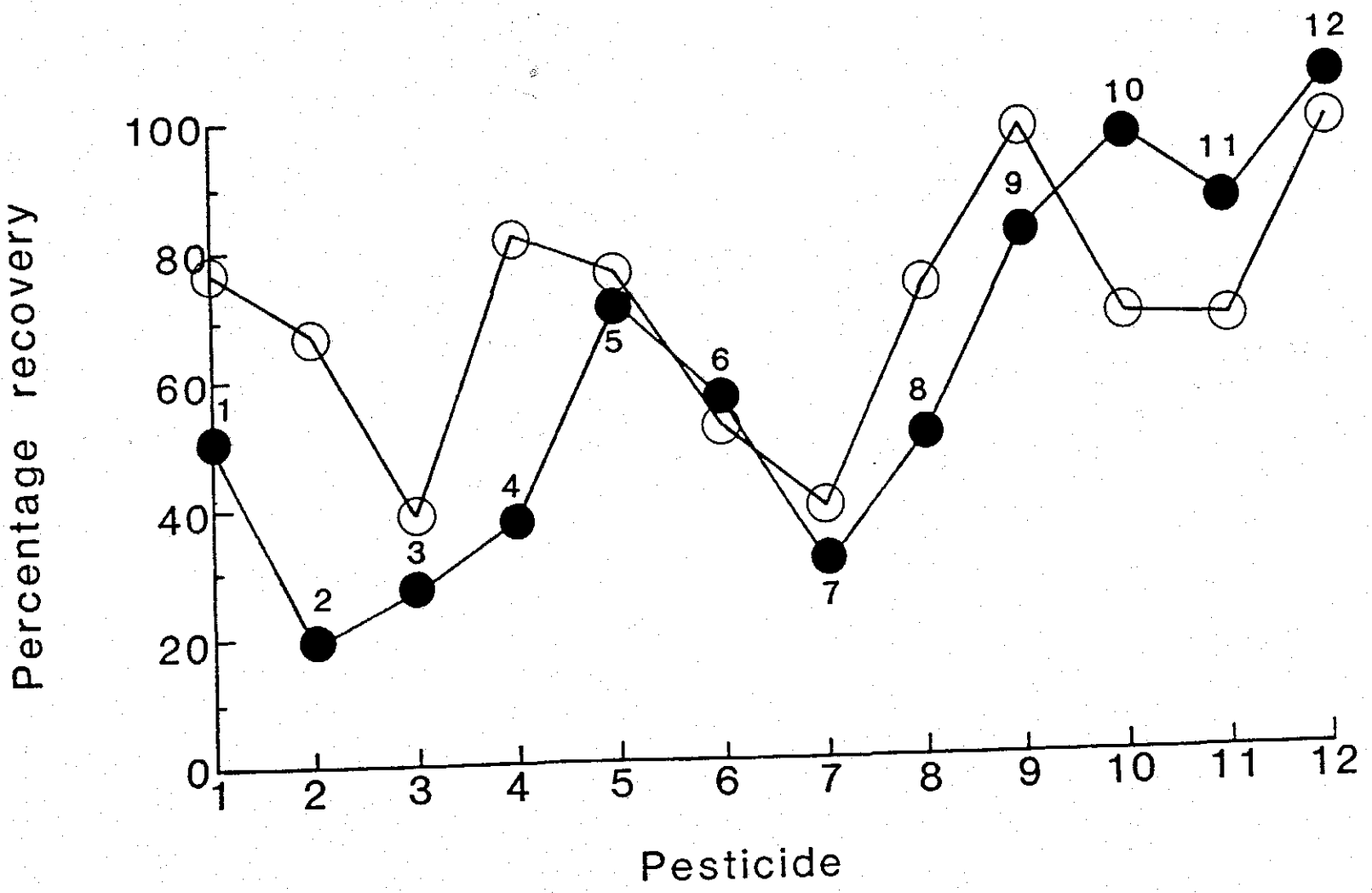
Percentage recovery
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
Pesticide

Figure 3

Table 1. Temperature program for the glc analysis

Oven temperature /°C	50	170	240	260	280
Isothermal time /min	2	0	7	0	5
Ramp rate	30	10	2	10	0

Table 2. Results of the analysis of the reference sediment.

Insecticide	Concentration $\mu g\ kg^{-1}$ (dry wt)	Confirmation by M S	Monitoring ions m/z values
α-BHC	<0.1	NC	181, 219
Dieldrin	1.96 (0.25)	C	79, 263, 277
cis-Permethrin	11.05 (2.25)	C	163, 183
trans-Permethrin	4.01 (0.33)	C	163, 183
Cypermethrin	<1.0	NC	163, 181
Fenvalerate	1.50 (0.2)	NC	125, 152, 167

Key: NC - not confirmed by mass-spectrometry
C - confirmed by mass-spectrometry
* - values in brackets are the standard deviations

Table 3. Results of the analysis of the sediment after the addition of the multi-pesticide standard of nominal concentration of 20 μg kg^{-1}

Pesticide	Ref. No.	Total concentration in sediment /μg kg^{-1}	Concentration calculated from first eluate /μg kg^{-1}	Percentage recovery	Concentration calculated from total eluate /μg kg^{-1}	Final recovery Percentage recovery	Final recovery Coefficient of variation %
α-BHC	1	20.10	15.3	76	15.5	77	0.6
γ-BHC	2	20.68	13.8	67	13.9	67	0.9
DDE	3	20.00	7.6	38	7.9	39	0.6
Dieldrin	4	22.37	18.1	81	18.3	82	1.4
Endrin	5	20.12	15.1	75	15.2	76	1.4
TDE	6	20.00	10.0	50	10.4	52	1.2
DDT	7	23.04	9.0	39	9.1	39	5.3
cis-Permethrin	8	31.48	22.0	70	23.0	73	2.9
trans-Permethrin	9	28.06	26.4	94	27.2	97	1.4
Cypermethrin	10	30.79	16.3	53	21.0	68	6.6
Fenvalerate	11	22.92	10.9	48	15.4	67	18.0
Deltamethrin	12	20.00	12.8	64	19.4	97	16.0

Table 4. Results of the analysis of the sediment after the addition of the multi-pesticide standard of nominal concentration of 2 $\mu g\ kg^{-1}$

Pesticide	Total concentration in sediment /$\mu g\ kg^{-1}$	Concentration calculated from first eluate /$\mu g\ kg^{-1}$	Percentage recovery	Concentration calculated from total eluate /$\mu g\ kg^{-1}$	Concentration in blank /$\mu g\ kg^{-1}$	Final recovery Percentage recovery	Final recovery Coefficient of variation %
α-BHC	2.06	1.0	50	1.0	<0.1	50	0.9
γ-BHC	2.07	0.4	18	0.4	<0.1	19	4.3
DDE	2.00	0.5	26	0.5	ND	27	5.2
Dieldrin	4.37	1.7	38	1.7	ND	38	2.4
Endrin	2.01	1.4	69	1.4	ND	71	3.2
TDE	2.00	1.0	51	1.1	ND	56	1.8
DDT	2.30	0.7	29	0.7	ND	30	2.4
cis-Permethrin	13.44	6.1	45	6.7	ND	50	2.7
trans-Permethrin	7.32	5.7	78	5.9	1.1	81	5.5
Cypermethrin	6.60	6.0	91	6.3	ND	96	10.6
Fenvalerate	3.66	2.4	65	3.1	ND	85	9.7
Deltamethrin	2.00	1.4	70	2.1	ND	104	3.3

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