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Monitoring of pesticides in air by gas chromatography–mass spectrometry and the use of quartz-fibre wool and activated carbon for sampling

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Abstract

A simple monitoring method has been developed to determine the mean concentrations of pesticides in air over a period of one week. The pesticides investigated were buprofezin, edifenphos, ethofenprox, fenitrothion, fenobucarb, fenthion, flutolanil, fthalide, malathion, pencycuron, phentoate, pyridaphenthion, tetrachlorvinphos and tricyclazole. The pesticides were collected using quartz-fibre wool and activated carbon and eluted with acetone and toluene–ethanol (4:1, v/v). The eluate was reduced to a small volume and an acetone solution of the internal standards 1,4-diodobenzene and 9-bromoanthracene was added for gas chromatography–mass spectrometry (GC–MS). Recoveries of the pesticides, indicating the overall performance of this method, ranged from 82.4 to 94.6%. The minimum detectable concentrations ranged from 0.1 ng/m³ to 1 ng/m³. This method has been successfully applied to the monitoring of pesticides in air over a rural area near paddy fields.

1. Introduction

In recent years the effect on human health of pesticide residues in the atmosphere has become of major concern. Although annual variations of atmospheric pesticide concentrations have to be considered when evaluating the impact of pesticides on human health by inhalation, only very few reports have been presented on long-term variations [1,2]. A number of studies have described attempts to collect pesticides in air for gas chromatographic (GC) or gas chromatographic–mass spectrometric (GC–MS) determination using Carbowax 20M [3], Chromosorb 102 [4–6], Porapak C₁₈ [3], polyurethane foam [1,7], Tenax GC [8], XAD-4 [9], glass-fibre

filters [10], quartz-fibre filters and activated-carbon-fibre filters [11–14], etc. However, only a few papers have described simple methods for long-term monitoring of pesticides in air. We have previously reported a simple GC method for this purpose [15] using activated carbon for collection, and have investigated annual variations of two insecticides, fenitrothion (O,O-dimethyl-O-4-nitro-*m*-tolyl phosphorothioate) and fenobucarb (O-*sec*-butylphenyl methylcarbamate), in the atmosphere over some rural and suburban areas near paddy fields [16]. This method, however, has the disadvantage of being limited in multicomponent monitoring, because we adopted GC determination: GC equipped with a flame photometric detector for fenitrothion and a flame thermionic detector for fenobucarb.

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This report presents the results of GC–MS analysis for 14 common pesticides (9 insecticides and 5 fungicides) using quartz-fibre wool and an activated-carbon granule for sampling. The pesticides investigated were buprofezin (2-*tert*-butylimino - 3 - isopropyl - 5 - phenyl - 1,3,5 - thiadiazinan-4-one), edifenphos (O-ethyl-S,S-diphenyl phosphorodithionate), ethofenprox [2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl ether], fenitrothion, fenobucarb, fenthion (O,O-dimethyl-O-3-methyl-4-methylthio-*m*-tolyl phosphorothionate), flutolanil (α,α,α -trifluoro-3'-isopropoxy-*o*-toluanilide), fthalide (4,5,6,7-tetrachlorophthalide), malathion [S-1,2-bis-(ethoxycarbonyl)ethyl-O,O-dimethyl phosphorodithioate], pencycuron [1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea], phenthoate [S-(α -(ethoxycarbonyl)-benzyl)dimethyl phosphorothiolothionate], pyridaphenthion [O,O-diethyl-O-(3-oxo-2-phenyl-2H-pyridazin-6-yl)phosphorothionate], tetrachlorvinphos [2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate] and tricyclazole (5-methyl-1,2,4-triazolo[3,4-*b*]benzothiazole).

2. Materials and methods

2.1. Apparatus and materials

An air pump NS-S2 (Nissei, Tokyo, Japan) and a gas meter DC-2A (Shinagawa, Tokyo, Japan) were used for sample collection. A tube pump TMP-6L (Toyo, Tokyo, Japan) was used for sample elution. A mass spectrometer SX-102A (JEOL, Tokyo, Japan) equipped with a gas chromatograph, HP-5890 II (Hewlett-Packard), was used for quantitative analysis. A fused-silica column HP-5 (0.25 μ m film thickness, 30 m \times 0.32 mm I.D.) was purchased from Hewlett-Packard.

Activated carbon BPL-1 (Calgon) was ground to 0.25–0.42 mm in diameter and was washed with carbon disulfide, methanol, acetone and toluene in a Soxhlet apparatus for 8 h for each solvent. Quartz-fibre wool (fine grade) was purchased from Iuchi (Osaka, Japan). The collection tube used was made of glass (115 \times 18 mm

I.D. with 3 mm I.D. at both ends) and packed with 0.5 g quartz-fibre wool and 5 g of the cleaned activated carbon supported by a small plug of quartz-fibre wool. The tube was pre-conditioned with nitrogen at 150°C for 48 h at a flow-rate of 50 ml/min. The tube was sealed with silicon plugs at both ends, and stored in a glass desiccator with the cleaned activated carbon.

Tricyclazole was purchased from Hayashi (Osaka, Japan). A solution of a mixture of C₁₁–C₃₀ normal alkanes (except for C₂₉), used to measure the programmed temperature retention index (PTRI) [17,18] of each pesticide and as an internal standard, was purchased from Hewlett-Packard. Other pesticides and reagents were purchased from Wako (Osaka, Japan). An acetone solution containing 100 μ g/ml of 1,4-diiodobenzene and 9-bromoanthracene was prepared as an internal standard solution.

2.2. Sample collection and analysis

Air was sampled for 7 days with a collection tube set at a flow-rate of 0.1–0.2 l/min (Fig. 1). The pesticides collected were eluted from the collection tube first with 100 ml of acetone and then with 100 ml of toluene–ethanol (4:1, v/v) at a flow-rate of 0.5 ml/min (Fig. 2). The combined eluates were concentrated first to 5 ml in a Kuderna-Danish apparatus and then to 1 ml under a purified nitrogen gas stream. A volume of 10 μ l of the internal standard solution was

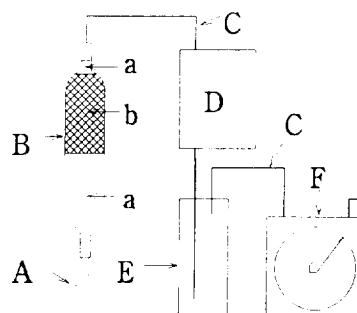


Fig. 1. Apparatus for sampling pesticides in air. A = glass funnel; B = collection tube; C = silicone tube; D = air pump; E = bottle; F = gas meter; a = quartz-fibre wool; b = activated carbon.

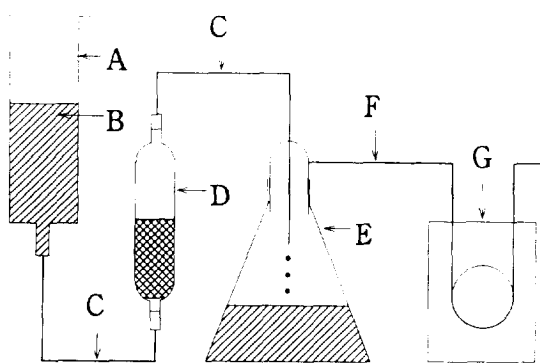


Fig. 2. Apparatus for the elution of pesticides from the collection tube. A = glass syringe; B = elution solvent; C = glass tube; D = collection tube; E = Erlenmeyer flask; F = silicone tube; G = tube pump.

added to the concentrated eluate solution and the resulting mixture was analysed by GC–MS in the selected-ion monitoring mode (SIM). GC–MS conditions were as follows: column temperature programmed from 50°C (held for 1 min) to 280°C (held for 5 min) at a rate of 20°C/min;

injector temperature 200°C; injection mode, splitless; carrier gas pressure from 2 psi to 15 psi (held for 1 min) at a rate of 99 psi/min, then back to 2 psi at the same rate; ionization current 300 μ A; electron energy 70 eV. The ions selected for SIM quantification of the pesticides are listed in Table 1, together with pesticide types and molecular masses [19,20]. PTRIs for the pesticides and the internal standards are also shown in Table 1. PTRIs were calculated using the following equation:

$$\text{PTRI}_A = 100N + 100(\log t_A - \log t_N) / (\log t_{N+1} - \log t_N)$$

where PTRI_A is the PTRI of compound A, t_A is the retention time for compound A, and t_N and t_{N+1} are the retention times for the normal alkanes with carbon number N and $N + 1$ plus compound A [17,18]. The selected ions were divided into three groups according to PTRI data: SIM group No. 1, $\text{PTRI} < 1800$; SIM group No. 2, $1800 \leq \text{PTRI} < 2300$; SIM group No. 3, $\text{PTRI} \geq 2300$.

Table 1
Selected ions for SIM determination of pesticides

Pesticide		M_r^a	m/z	PTRI	SIM group No.
Buprofezin	I ^b	305.4	305	2224	2
Edifenphos	F ^c	310.4	310	2367	3
Ethofenprox	I	376.2	376	2840	3
Fenitrothion	I	277.2	277	1965	2
Fenobucarb	I	207.3	150	1620	1
Fenthion	I	278.3	278	2002	2
Flutolanil	F	323.3	323	2190	2
Fthalide	F	271.9	243	2040	2
Malathion	I	330.3	125	2150	2
Pencycuron	F	328.8	180	1702	1
Phenthoate	I	320.4	274	2106	2
Pyridaphenthion	I	340.3	340	2483	3
Tetrachlorvinphos	I	366.0	329	2152	3
Tricyclazole	F	189.2	189	2209	2
1,4-Diiodobenzene	I.S. ^d	329.9	330	1434	1
9-Bromoanthracene	I.S.	257.1	256	2190	2

^a Cited from Refs. [19,20].

^b Insecticide.

^c Fungicide.

^d Internal standard.

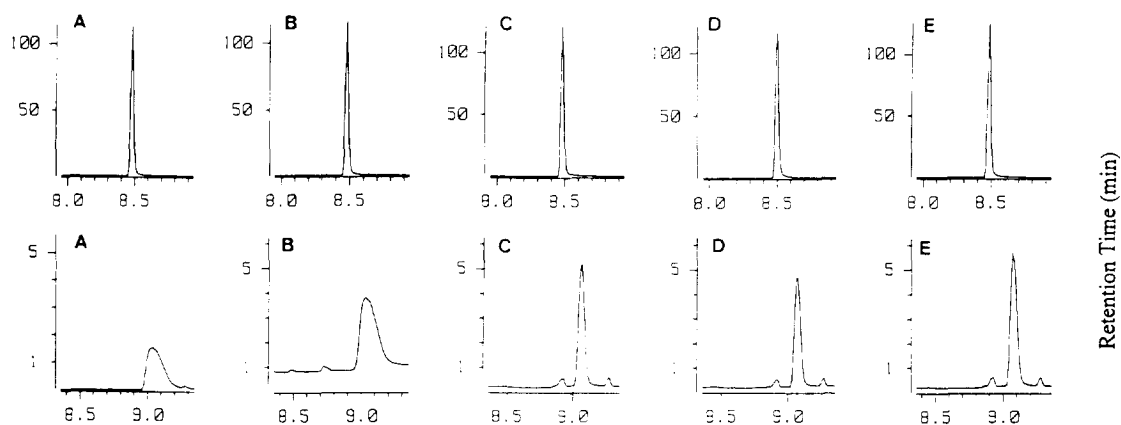


Fig. 3. Effect of polyethylene glycols on peak shapes of pesticides. Concentrations of PEG 200 and 300 are: 0 $\mu\text{g/ml}$ (A); 500 $\mu\text{g/ml}$ (B); 1000 $\mu\text{g/ml}$ (C); 1500 $\mu\text{g/ml}$ (D); and 2000 $\mu\text{g/ml}$ (E): 1st row: fenobucarb; 2nd row: pencycuron.

3. Results and discussion

3.1. GC–MS analytical conditions

Some pesticides, particularly pencycuron and tricyclazole, provide wide tailing peaks in standard solutions. On the other hand, this phenomenon has not been observed for environmental samples. This suggests that compounds present in the environmental samples passivate the active

surfaces in GC or MS. Thus, the quantitative evaluation of these pesticides has been difficult. It has been reported that metolcarb (*m*-tolyl methylcarbamate) and XMC (3,5-xylyl methylcarbamate) in the standard solution gave wide tailing peaks, whereas the two pesticides provided sharp, symmetric peaks with poly(ethylene glycol) (PEG) 200 and PEG 300 [21]. This was caused by the PEGs passivating the activated surface. It was further reported that

Table 2
Efficiencies of pesticides desorption^a (%) from the activated carbon

Pesticide	Solvent				
	Acetone	Hexane	DCM ^b	Toluene	Toluene–EtOH ^c
Buprofezin	23.1	6.6	23.9	43.7	91.4
Edifenphos	14.4	8.4	21.8	76.9	90.3
Ethofenprox	3.1	0.4	49.1	96.8	94.5
Fenitrothion	61.3	7.5	19.8	43.5	90.8
Fenobucarb	65.2	1.5	46.7	58.2	86.2
Fenthion	51.1	8.2	32.0	45.5	91.2
Flutolanil	5.7	2.7	7.1	18.5	90.7
Fthalide	3.2	1.6	0.6	4.3	10.3
Malathion	89.8	5.7	44.7	97.6	98.5
Pencycuron	92.3	53.2	64.1	33.5	69.0
Phenthoate	53.7	17.5	46.7	100	98.7
Pyridaphenthion	41.7	9.1	9.6	8.3	97.4
Tetrachlorvinphos	46.3	9.8	59.9	87.6	92.4
Tricyclazole	9.1	0.4	1.5	10.5	90.5

^a Mean ($n = 2$).

^b Dichloromethane.

^c Toluene–ethanol (4:1, v/v).

the PEGs did not interrupt SIM determinations of most pesticides involving the use of fragment ions of m/z 100 or higher, because they give no fragment ions of in that range [21]. Hence, we elucidated the effect of PEG 200 and PEG 300 on the peak shapes of the 14 standard pesticides.

Fig. 3 shows the chromatograms of fenobucarb and pencycuron. While the peak shape of fenobucarb did not change when the PEGs were added, that of pencycuron sharpened as concentrations increased from 0 to 1000 mg/ml. An improvement in the peak shape of tricyclazole was also achieved in the same manner. The PEGs gave none of the fragment ions selected for SIM determination of the pesticides (Table 1). We therefore used 1000 mg/ml of PEG 200 and 300 (acetone solution) to prepare the pesticide standard solutions for SIM determinations.

All 14 pesticides prepared in this way gave sharp peaks.

3.2. Extraction solvent

Extraction efficiencies for the 14 pesticides from the quartz-fibre wool and the activated carbon were determined by adding 100 ng of the pesticide as an acetone solution to the glass tube packed with 0.5 g of the quartz-fibre wool without the activated carbon (quartz-fibre wool tube) and to the glass tube packed with 5 g of the cleaned activated carbon held by small plugs of the quartz-fibre wool (activated-carbon tube). Purified air was passed through the tube at 0.2 l/min for 30 min in order to evaporate the acetone. The pesticides were then eluted from the tube as described above by using five different solvents. All pesticides were eluted quantita-

Table 3
Recoveries of pesticides from the collection column

Pesticide	Run 1 ^a			R.S.D. ^c (%)	Run 2 ^b		Run 3 ^c	
	Recovery ^d (%)				Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
	QW ^f	AC ^g	Total					
Buprofezin	88.2	5.4	93.6	4.63	90.7	3.67	87.8	5.95
Edifenphos	85.9	6.2	92.1	2.84	84.9	2.42	83.4	3.78
Ethofenprox	84.5	4.7	89.2	3.62	83.7	3.93	92.9	7.42
Fenitrothion	47.0	42.7	89.7	4.17	89.0	1.23	95.5	1.97
Fenobucarb	23.3	66.2	90.5	5.52	88.4	5.54	90.9	3.55
Fenthion	74.2	18.3	92.5	3.65	91.2	6.19	87.8	4.10
Flutolanil	81.7	8.3	90.0	2.99	87.8	3.13	94.6	2.77
Fthalide	90.1	1.1	91.2	2.67	89.1	1.43	90.7	7.37
Malathion	80.1	10.3	90.4	3.95	88.5	4.12	89.4	9.32
Pencycuron	73.7	20.5	94.2	7.39	97.6	3.68	91.2	5.57
Phenthoate	71.7	15.4	87.1	5.78	84.5	4.04	87.6	7.13
Pyridaphenthion	72.2	17.1	89.3	7.25	87.8	3.02	87.2	8.01
Tetrachlorvinphos	66.9	20.2	87.1	0.87	82.4	6.49	86.1	3.94
Tricyclazole	69.5	21.0	90.5	6.72	93.8	4.80	86.6	7.14

^a Mean air temperature = 26.7°C (21.6–34.8°C); mean humidity = 76%.

^b Mean air temperature = 14.9°C (8.1–21.5°C); mean humidity = 68%.

^c Mean air temperature = 20.8°C (10.2–28.7°C); mean humidity = 71%.

^d Mean ($n = 3$).

^e Relative standard deviation.

^f Quartz-fibre wool.

^g Activated carbon.

tively (>92%) from the quartz-fibre wool by each solvent. On the other hand, none of the solvents investigated could elute all the pesticides from the activated carbon, as can be seen from Table 2. Twelve pesticides, with the exception of fthalide and pencycuron, were eluted quantitatively by toluene-ethanol (4:1, v/v). While pencycuron was eluted quantitatively by acetone, fthalide could not be eluted by any solvent investigated. However, the low recovery of fthalide does not appear important, because

this compound can be collected efficiently by the quartz-fibre wool, as described later. Therefore, acetone and toluene-ethanol (4:1) were chosen as the best solvents for elution. No pesticides were observed in the solvent or in the procedure blanks.

3.3. Retention efficiency on filters by air passing

It is difficult to determine collection tube efficiencies for the different pesticides, since it is

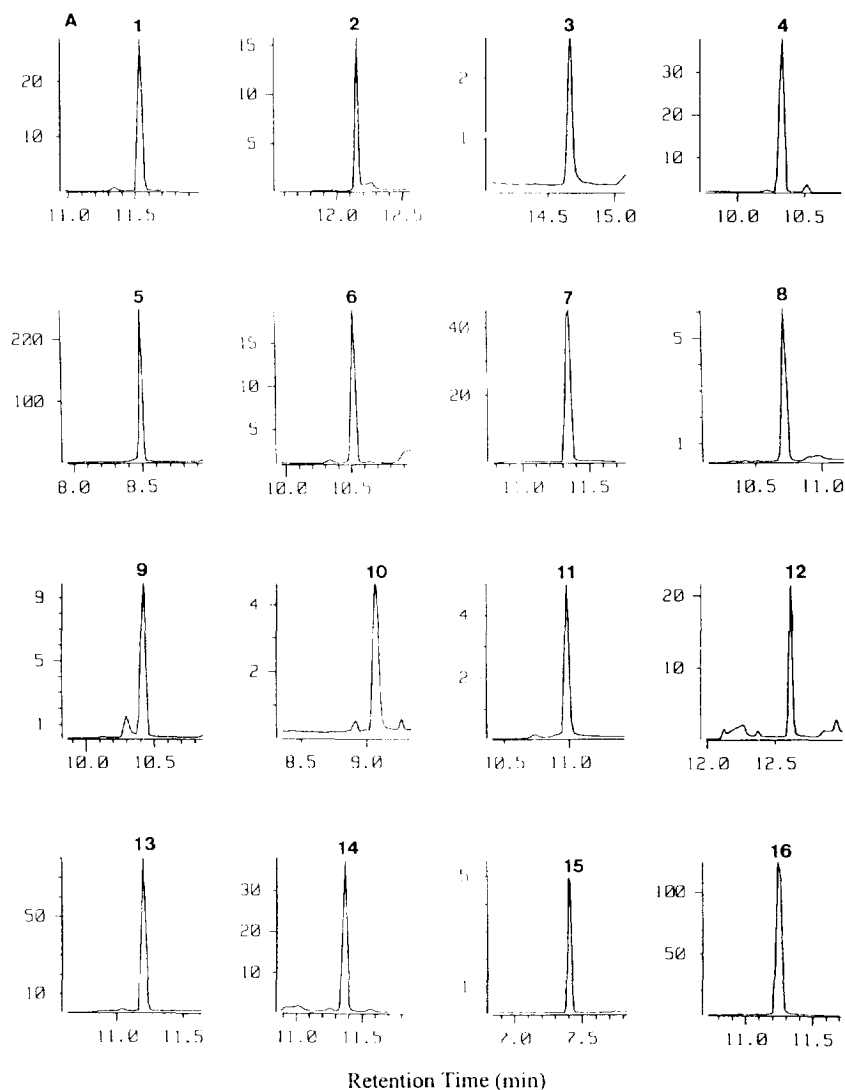


Fig. 4.

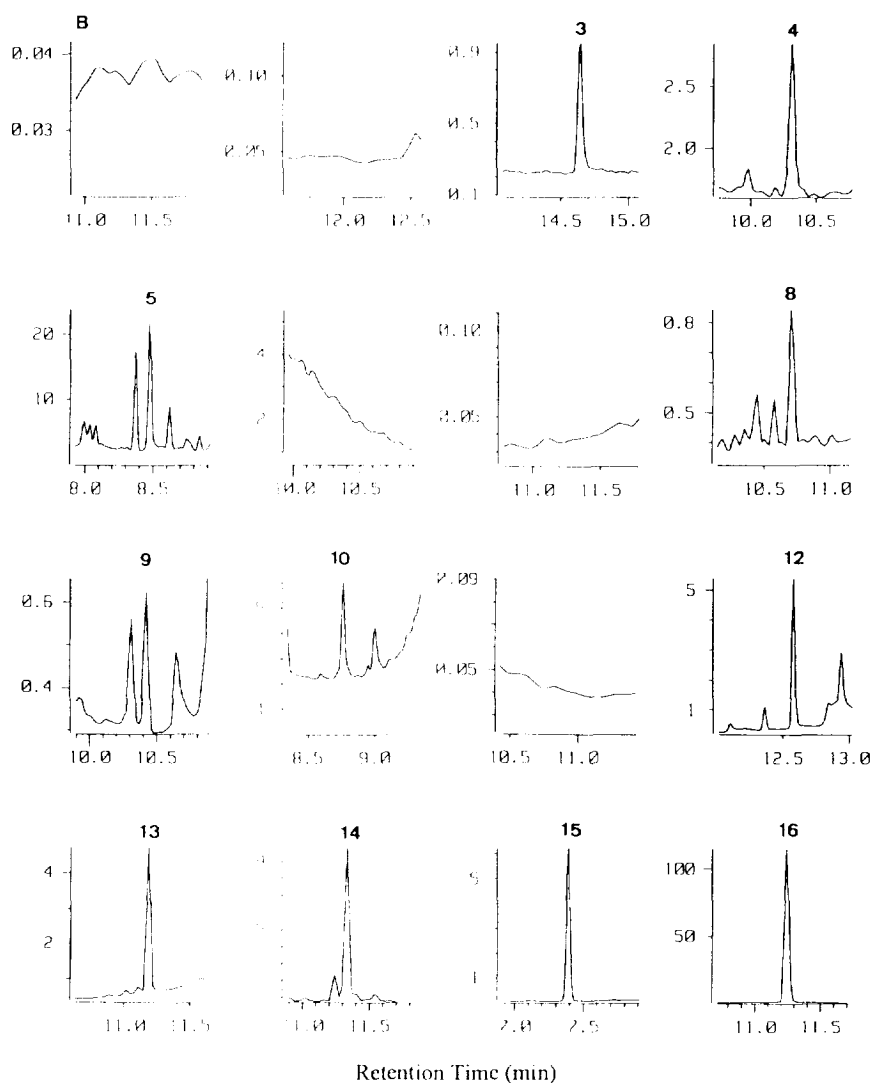


Fig. 4. SIM chromatograms of pesticides. (A) standard; (B) samples. Peaks: 1 = buprofezin; 2 = edifenphos; 3 = ethofenprox; 4 = fenitrothion; 5 = fenobucarb; 6 = fenthion; 7 = flutolanil; 8 = fthalide; 9 = malathion; 10 = pencycuron; 11 = phenthoate; 12 = pyridaphenthion; 13 = tetrachlorvinphos; 14 = tricyclazole; 15 = 1,3-diiodobenzene; 16 = 9-bromoanthracene.

impossible to prepare air samples containing known quantities of specific chemicals. Hence, we elucidated the collection efficiency via the retention efficiency [22,23].

The retention efficiencies of the collection tube with respect to the individual pesticides were determined as follows. A known amount of the pesticide was added to a quartz-fibre wool tube as an acetone solution. Air was passed at

0.2 l/min for 7 days through the tube, connected to two activated-carbon tubes as back-ups. The retention efficiencies of the quartz-fibre wool were very good (>88%) with respect to buprofezin and fthalide, as shown in Table 3, but for the other pesticides a combination with the activated-carbon system would be recommended. No pesticide was detected from the second activated-carbon tube. Therefore, 5 g of

the activated carbon provided sufficient back-up to the quartz-fibre wool. Some experiments for recoveries of spiked pesticides from the collection tube were carried out. The results are shown in Table 3. Recoveries of all pesticides were good (82.4–94.6%).

The minimum detectable concentrations [24] were 0.1 ng/m³ for fenobucarb, fenthion, flutolanil, fthalide, malathion, tetrachlorvinphos and tricyclazole, 0.2 ng/m³ for edifenphos, phenothate and pyridaphenthion, and 1 ng/m³ for buprofezin, ethofenprox, fenitrothion and pencycuron.

3.4. Application to environmental samples

This method was used to monitor pesticides in the air over a rural area near paddy fields from July 5 to August 30, 1993. In all, nine pesticides were detected. The pesticides and concentrations detected were as follows: ethofenprox, 1–110 ng/m³; fenitrothion, 1–13 ng/m³; fenobucarb, 0.1–430 ng/m³; fthalide, 0.1–13 ng/m³; malathion, 0.1–60 ng/m³; pencycuron, 1–69 ng/m³; pyridaphenthion, 0.2–19 ng/m³; tetrachlorvinphos, 0.1–2.7 ng/m³; tricyclazole, 0.1–6.1 ng/m³. Typical SIM chromatograms of standards and samples are shown in Fig. 4. Every pesticide could be determined well without interferences.

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