Bull. Environ. Contam. Toxicol. (1994) 52:419–424

Environmental Contamination and Toxicology

Determination of Fenitrothion and Diazinon in Air

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Received: 19 May 1993/Accepted: 25 July 1993

The effect of atmospheric pesticides on the environment has become of major current interest (Kawata and Yasuhara 1992). A number of studies have been performed on atmospheric variations of aerially-applied pesticides (Chester and Ward 1984; Sundaram 1984; Yule 1971). We have already reported the atmospheric variation of the insecticide, fenitrothion (*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate), after aerial application (Kawata *et al.* 1991). A considerable amount of insecticides are ground-applied in both cropped and non-cropped areas. There are several reports on the atmospheric variations after ground application in cropped areas (Clark *et al.* 1991), but few in non-cropped areas.

Fenitrothion and diazinon (*O,O*-diethyl *O*-2-isopropyl-6-methyl-pyrimidin-4-yl phosphorothioate) are two common insecticides; they are used against household, forest, and various agricultural pests (Matsunaga 1985). Several reports have described the attempts to collect fenitrothion and/or diazinon in air for gas chromatographic or gas chromatography/mass spectrometric (GC/MS) determination; polyurethane foam (Grober *et al.* 1981, Lewis and MacLeod 1982), Porapak C18 (Roper and Wright 1984), Chromosorb 102 (Roper and Wright 1984, Thomas and Nishikawa 1985), Tenax GC (Krzymien 1982), *etc.* These methods, however, have some problems in collection efficiencies, extraction efficiencies, and/or usage. On the other hand, filters have the advantage over other materials in handling and cost. Gudehn and Kolmodin-Hedman (1987) have collected herbicides by glass-fiber filter.

We have discussed sampling efficiencies of insecticides on a quartz-fiber filter and an activated carbon-fiber filter for gas chromatographic determination (Moriyama *et al.* 1990), and have also reported applications of these filters for collections of fungicides (Kawata *et al.* 1990b) and herbicides (Kawata 1992) in air, and deposited insecticides (Kawata *et al.* 1990a). In this paper, we present the determination of fenitrothion and diazinon in air by GC/MS using an automated sequential air sampler with activated carbon-fiber filter for collection and have elucidated variations of the ground-applied insecticides on lawn.

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MATERIALS AND METHODS

An automated sequential air sampler, GS-10D (Tokyo Dylec Co.), was used for sample collection. An ultrasonic apparatus, EN-20S-1A (Shimada Co.), and a centrifugal apparatus, KN70 (Kubota Co.), were used for the extraction procedure. A mass spectrometer, JMS-DX300 (JEOL Ltd.), equipped with a gas chromatograph, HP-5792A (Hewlett Packard Co.) and JMA3500 mass data analysis system (JEOL Ltd.) were used for quantitative analysis. A fused-silica column J&W DB-1301 (1.0 μ m film thickness, 30 m long, 0.53 mm id) was used.

Activated carbon-fiber filter, Toyobo KF Paper P-175, was shaped into a circular form with a diameter of 47 mm for sample collection. Prior to sampling, the collection filter was washed ultrasonically with benzene-95% ethanol (4:1 volume/volume) for 15 min followed by drying at 100℃ for 8 hr at reduced pressure. Standards of the insecticides were purchased from Wako Pure Chemical Co. Other reagents were obtained from Wako Pure Chemical Co. and Kanto Chemical Co.

Air was sampled with two collection filters at 10 L/min for 12 hr using the automated sequential air sampler. Each sampled filter was extracted ultrasonically twice with 3 mL of benzene-ethanol (4:1 volume/volume) for 10 min. The extracts were filtered, and the sample filter was washed with a small amount of benzene-ethanol. The combined extract was concentrated to 1 mL for GC/MS determination. The GC/MS conditions were as follows: injection temperature, 250℃; column temperature, 220℃; injection mode, direction mode; ionizing current, 300 μ A; ionizing voltage, 70 eV; setting mass number, 125 and 109 for fenitrothion and 137 and 152 for diazinon.

Extraction efficiencies for fenitrothion and diazinon from the collection filter were determined by 1) adding 1 μ g of the insecticides to a collection filter as an acetone solution, 2) allowing the filter to stand for 20 min in order to evaporate the acetone, and 3) extracting the insecticides from the filter as described above.

Retention efficiencies (Roper and Wright 1985) for the insecticides on the collection filter by air passing were determined by adding 10 μ g of the insecticides to a collection filter as an acetone solution (Kawata *et al.* 1990; Kawata 1992). Air was passed at 10 L/min for 12 hr through the filter with backup of another collection filter. The insecticides were extracted as described above from the each filter.

Storage stabilities of the insecticides on the collection filter were determined by adding 1 μ g of the insecticides to a collection filter as an acetone solution (Kawata *et al.* 1990; Kawata 1992) and storing at −20℃.

Fenitrothion was applied on 26 sq m of lawn at a rate of 0.5 g/sq m on July, 1990; diazinon was applied on 14 sq m of lawn at 0.4 g/sq m on August, 1990. Air was sampled by the proposed method at a side of the lawn area for a week after the application.

RESULTS AND DISCUSSION

The extraction efficiencies of fenitrothion and diazinon are shown in Table 1. Greater than 90 % extraction efficiency was obtained for the insecticides from the filter with benzene-ethanol (4:1 volume/volume). No fenitrothion and diazinon were observed in the solvent nor procedural blanks.

Table 1. Extraction efficiencies from the collection filter (n=5)

Extraction solvent	Extraction efficiency (%)		Added (μg)
	Fenitrothion	Diazinon	
Acetone	48	89	2.0
Benzene	72	98	2.0
Ethanol	10	23	2.0
Hexane	<2	22	2.0
Xylene	78	96	2.0
Benzene-ethanol	92±4.2	98±5.4	2.0
(4:1 v/v)	95±4.7	95±3.3	0.2

Table 2. Retention efficiencies of the insecticides (n=5) after 12 hr

Retention efficiency (%) [a]		Air temperature (℃)	Relative humidity(%)	Flow rate (L/min)
Fenitrothion	Diazinon			
98±2.6	97±2.8	32	51	10
95±4.1	95±4.7	31	85	10
87±8.1	86±9.4	32	85	15

[a] Retention on fortified filter.

Retention efficiencies of the insecticides are presented in Table 2. It might be possible that the retention efficiencies for the insecticides on filters were effected by air temperature and humidity, but recoveries of the insecticides were quantitative at a flow rate of 10 L/min, and hence the insecticides were collected quantitatively at this flow rate by the collection filter under the conditions listed in

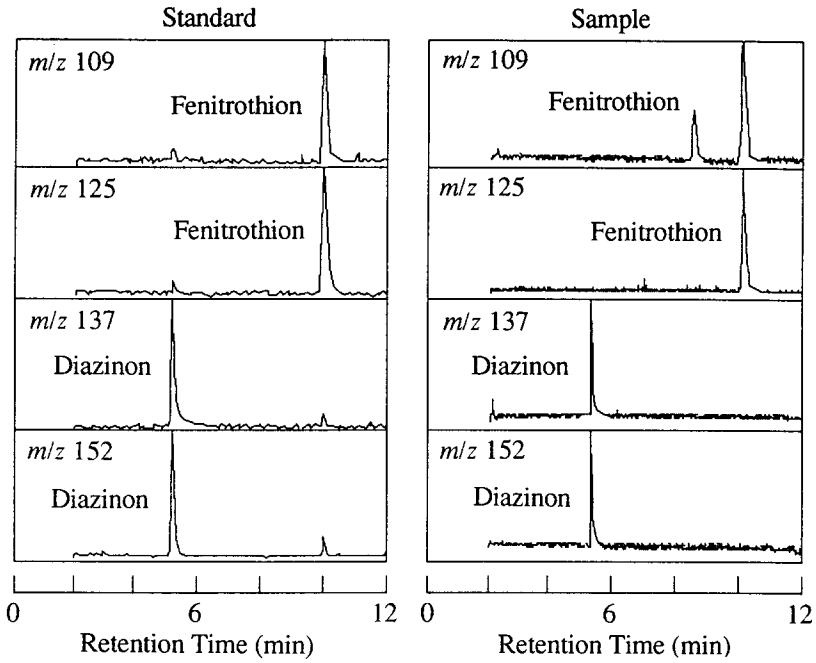

Figure 1. Selected ion chromatograms of insecticides

Table 2. On actual sampling, the two collection filters were extracted and analyzed individually for sampling efficiency.

Storage stabilities of the insecticides on the collection filter were shown in Table 3. This indicated that no significant losses occurred during storage for a week at −20 ±2℃. The minimum detectable concentrations were 1 ng/cu m for fenitrothion and 0.5 ng/cu m for diazinon.

Table 3. Storage stabilities on the collection filters (n=5)

Added	Storage	Recovery on storage (%)	
(μg)	time (d)	Fenitrothion	Diazinon
0.2	0	94±3.9	98±3.3
2.0	0	95±4.6	98±2.4
2.0	2	95±2.4	95±3.1
0.2	7	98±7.9	96±6.2
2.0	7	95±4.5	95±2.7

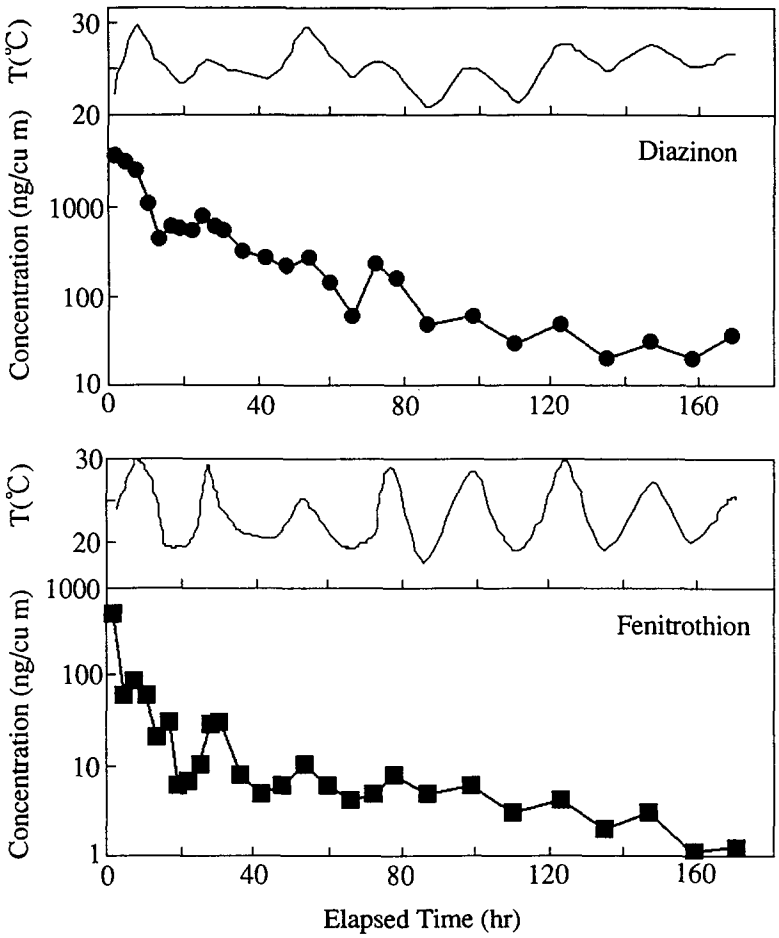

Figure 2. Periodic variation of the insecticide concentrations

Variations in the air concentration of the ground-applied insecticides on lawn were elucidated by using the proposed method. Typical selected ion chromatograms of standards and samples are shown in Figure 1. Each insecticide was determinable without any interferences. Sampling efficiencies of fenitrothion and diazinon were 92 − 100 % and 91 − 100 %, respectively. Concentrations of atmospheric fenitrothion and diazinon are shown in Figure 2. The maximal concentrations, which were detected within 2 hr after application of fenitrothion and diazinon were 470 and 5500 ng/cu m, respectively.

In case of aerial application, concentration of fenitrothion in the applied area was dependent on elapsed time after the application, wind speed, wind direction and air temperature (Kawata *et al.* 1991). In present cases, fenitrothion and diazinon concentrations were mainly depend on elapsed time after the applications and air temperature as shown in Figure 2.

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