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Annual Variation of Insecticides in Precipitation in Rural Japan

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Some parts of applied pesticides are released into the atmosphere during application procedure and due to volatilization after application. Pesticides in the atmosphere decline through decomposition, migration and removal. Precipitation is an important mechanism of pesticide removal from the atmosphere. Therefore, distribution of pesticides in precipitation is important to evaluate their behaviors in the atmosphere as well as aquatic environment. Siebers et al. (1994) reported presence of eleven pesticides in precipitation in northern Germany during March 1990 to March 1992. Dua et al. (1994) reported HCH concentrations in precipitation in India. Uno et al. (1986) reported monthly variation of twelve pesticides in precipitation at an urban site and a mountainous site from June 1984 to July 1985. Haraguchi et al. (1995) detected some kinds of pesticides in urban precipitation in March and June 1992. Although many kinds of pesticides have been used in large amounts in Japan (Kawata et al. 1991; Kawata 1992; Kawata and Yasuhara 1994) there are few investigations upon variations of pesticides in recent precipitation at rural area in Japan.

We have previously reported the atmospheric variations of pesticide concentrations over some rural and suburban areas near paddy field in Niigata Prefecture, Japan, In the prefecture, much pesticide is used during agricultural practice (Kawata et al. 1990; Kawata and Yasuhara 1992; Moriyama and Kawata 1994; Moriyama et al. 1994). The total sale of pesticides in the prefecture was 23,000 - 25,000 t/yr. In this paper, we present annual variation of insecticides in precipitation at a rural area near paddy field in the prefecture. The insecticides investigated were diazinon (*O,O*-diethyl *O*-2-iso-propyl-6-methylpyrimidin-4-yl phosphorothioate; DZN), fenitrothion (*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate; FNT), fenobucarb (2-*sec*-butylphenyl methylcarbamate; FNB), malathion {diethyl (dimethoxyphosphinothioylthio)succinate; MIT}, phenthoate (ethyl 2-dimethoxyphosphinothioylthio(phenyl)acetate; PHN), pyridaphenthion {*O,O*-diethyl-*O*-(3-oxo-2-phenyl-2*H*-pyridaxin-6-yl)phosphrothionate; PYR} and tetrachlorvinphos {(Z)-2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate; TTR}.

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MATERIALS AND METHODS

A gas chromatograph - mass spectrometer, Automass 50 (JEOL Ltd.), equipped with a fused-silica column J&W DB-5, was used for quantitative analysis. Standards of insecticides were purchased from Wako Pure Chemical Co. and GL Science Co. Other reagents were obtained from Wako Pure Chemical Co. and Kanto Chemical Co. An acetone solution containing 100 µg/mL of 1,4-diiodobenzene and 9-bromoanthracene was prepared as an internal standard solution for GC/MS determination. The standard solutions of insecticides were prepared by using an acetone solution of 1000 µg/mL of polyethylene glycol (PEG) 200 and PEG 300 to provide sharp and symmetric peaks of insecticides on chromatogram (Kawata et al. 1995).

The sampling site for precipitation was located at a rural area in Niigata City, Niigata Prefecture. Paddy fields lay 200 m away in both northward and southward directions, 300 m in southwestward direction and 400 m in southeastward direction. Insecticides were sprayed by both aerial and ground application on these paddy fields. Applied amounts of the target insecticides around the site are presented in Table 1 together with their vapor pressures and water solubilities (British Crop Protection Council 1987). Every precipitation during April 1992 through December 1992 and March 1993 was collected in a 20 L glass bottle, that was covered with a black opaque plastic bag, with a 42 cm diameter stainless steel funnel. Snowfalls during January 1993 to February 1993 were collected in a 40 cm diameter stainless steel container.

The collected sample was extracted twice for 10 min with dichloromethane of a tenth volume of the sample. The combined extracts were washed twice with a small amount of pure water and dried over anhydrous sodium sulfate. The dichloromethane solution was concentrated first to about 5 mL in a Kuderna-Danish apparatus and then to 1 mL under a purified nitrogen gas stream. A 10 µL volume of the internal standard solution was added to the solution and the resulting mixture was analyzed by GC/MS in the selected ion monitoring (SIM) mode.

Table 1. Results of recovery test and insecticide concentrations in precipitation

Insecticide	*m/z* for SIM	RI	Recovery [a]	Concentration [b]	vp [c]	ws [d]	wt [e]
DZN	137 and 179	1797	96.4 ± 2.40	0.011 (0.62)	0.097	40	1.1
FNT	260 and 277	1954	93.7 ± 2.90	0.030 (2.4)	18	14	4.0
FNB	122 and 150	1618	96.2 ± 4.58	0.024 (2.0)	48	610	0.74
MLT	158 and 173	1969	96.8 ± 4.57	0.010 (0.44)	5.3	145	0.26
PHN	246 and 274	2079	92.5 ± 3.36	0.014 (1.5)	5.3	11	0.13
PYR	199 and 340	2450	94.0 ± 4.31	0.0081 (1.1)	—	—	2.4
TTR	329 and 331	2125	93.4 ± 2.98	0.016 (1.8)	0.2	11	1.6

[a] Percentile mean ± standard deviation (n = 3). [b] Mean concentration (µg/L). Parenthesis means maximal concentration. [c] Vapor pressure (mPa) at 20℃ except for MLT (30℃) and PHN (40℃). [d] Water solubility (mg/L) at 20℃ except for FNT and FNB (30℃), and PHN (24℃). [e] Applied weight (t) around the investigated site.

GC/MS conditions were as follows: column, DB-5 (0.25 µm film thickness, 30 m length, 0.32 mm id); column temperature programmed from 50°C (held for 1 min) to 200°C at a rate of 20°C/min, then raised to 280°C (held for 2 min) at a rate of 10 °C /min; injector temperature, 250 °C ; injection mode, splitless; ion source temperature, 250 °C ; ionization current, 350 µA; electron energy, 70 eV. The setting ions for SIM quantification of the insecticides are presented in Table 1 together with their temperature programmed retention indices RIs). Setting ions and RIs of internal standards were 330 and 1155 for 1,4-diiodobenzene, and 256 and 2143 for 9-bromoanthracene. RI of compound A, RIA, is given by the following equation:

$$RI_A = 100\,N + 100\,(\log t_A - \log t_N) \,/\, (\log t_{N+1} - \log t_N)$$

where t_A is the retention time of compound A, and t_N and t_{N+1} are the retention times of the normal alkanes bracketing the compound A with carbon number N and N+l (Rohrbaugh and Jurs 1985; Kawata et al.1995).

An overall recovery test was carried out for the seven insecticides. The insecticides (1 µg) were spiked to 3 L rain water (n = 3) collected in March 1992, which included none of the insecticides investigated. The spiked rain water was treated as described above and recoveries of the insecticides were determined. No insecticides were observed in procedural blanks. The results are shown in Table 1. All insecticides were recovered from the rain water quantitatively (92.5 - 96.8 %) with good relative standard deviation (2.40 - 4.58 %).

RESULTS AND DISCUSSION

Maximum and mean concentrations of insecticides in precipitation are summarized in Table 1. Annual mean concentrations were ranged from 0.0081 µg/L for PYR to 0.030 µg/L for FNT. The maximum concentration of an event was 2.4 µg/L for FNT, which was observed in August.

Table 2. Monthly insecticide depositions and precipitation

	Insecticide deposition (µg/sq m/mon)								Precipitation
	DZN	FNT	FNB	MLT	PHN	PYR	TTR	Total	(mm)
Apr	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	127
May	0.32	N.D.	N.D.	N.D.	N.D.	0.46	N.D.	0.78	111
Jun	3.4	N.D.	2.6	10.5	N.D.	1.9	N.D.	18.4	98
Jul	3.3	7.4	4.6	0.74	N.D.	14.0	4.2	25.7	115
Aug	15.5	30.1	25.7	3.6	19.9	2.7	18.4	120	91
Sep	2.6	5.9	1.2	N.D.	N.D.	2.4	0.56	16.4	45
Oct	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.9	148
Nov	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	57
Dec	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	188
Jan	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	145
Feb	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	168
Mar	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	134
Total*	16.3	43.4	34.1	14.8	19.9	11.5	23.2	183	1427

* Insecticide deposition in µg/sq m/yr.

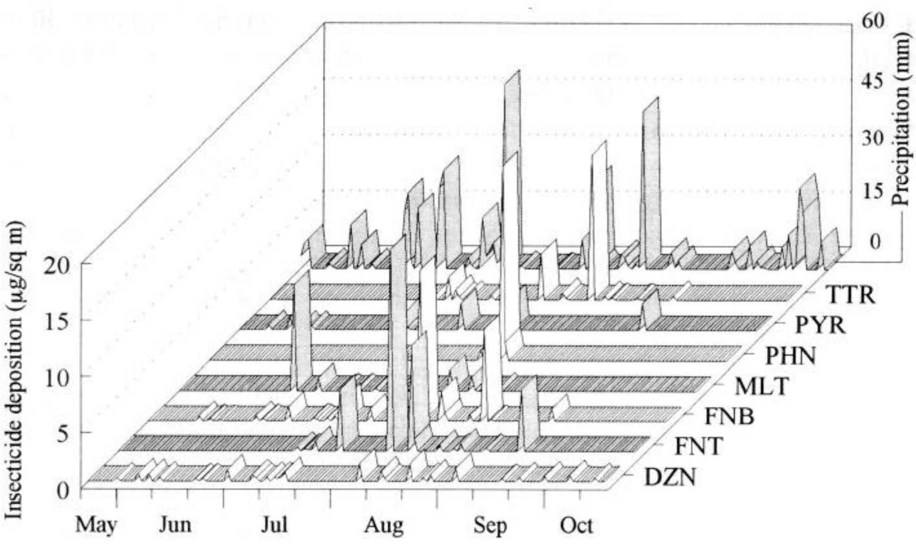

Figure 1. Variation of insecticide depositions during late May through October 1992.

Monthly insecticide depositions are listed in Table 2. The total amounts of insecticide depositions did not correlate with the applied weights of the insecticides (Table 1). Total amount of FNT in precipitation, 43.4 µg/sq m/yr was the largest of the seven insecticides, while that of MLT, 14.8 µg/sq m/yr was the smallest. The total amount of FNT in precipitation was 3 times larger than that of MLT, whereas applied FNT was 15 times greater than that of MLT. This could be caused by their vapor pressures and water solubilities; vapor pressure of FNT is 3.4 times higher than that of MLT, and the water solubility of FNT is a tenth of that of MLT. However insecticides in precipitation could not be predicted by only vapor pressures and water solubilities (Siebers et al. 1994). Schomburg et al. (1990) reported that pesticide concentrations in fog water were higher than those expected from air-water distribution; these enhanced pesticide concentrations might be caused by particles and Colloids in fog water. Further investigation will be needed to predict insecticides in precipitation.

As presented in Table 2, the insecticides were not detected in April and during November through March in precipitation. In contrast, they were detected during May to October. Figure 1 shows variation of the insecticide depositions from May 20 to October 10. The magnitudes of the insecticides were increased through June to September. The insecticides are applied at paddy fields mostly during May through September. We previously reported that pesticides including FNT, FNB and PYR were detected from the atmosphere near paddy fields during May through October, and their concentrations were increased extremely during and just after their applications (Kawata et al. 1990, Kawata and Yasuhara 1992, Moriyama and Kawata 1994; Moriyama et al. 1994). Therefore, the insecticides increased in precipitation during and after the application periods accordingly their increase in the atmosphere. The deposition of the insecticides except for MLT and PRY were the maximum in August (Table 2). This is caused by the fact that the applied amounts of the five insecticides were most elevated in late July through August (Moriyama et al. 1994). On the other hand, MLT and PRY depositions were the highest in June and July, respectively. This is reflected that MLT and PRY were applied mainly in June and July, respectively. Moreover, DZN was detected in precipitation during the most long period of the investigated insecticides, while PHN was detected only in August. These are also caused by the difference in their applied periods.

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