Investigation of Pesticides in Rainwater at Isogo Ward of Yokohama

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Large amounts of various pesticides have been used in farms, rice paddies and gardens. However, few studies on the pesticides in rainwater have been conducted in Japan. Thus, rainwater samples were collected from August 2001 until July 2002 at Isogo Ward of Yokohama, and 51 kinds of pesticides in the 51 samples were investigated. Although sampling point was not located in the agricultural area, dichlorvos (0.33–0.05 μg/l), chlorothalonil (0.27–0.05 μg/l), fenitrothion (0.24–0.05 μg/l), molinate (0.12–0.05 μg/l), diazinon (0.07–0.05 μg/l), and malathion (0.05 μg/l) were detected. Dichlorvos was the most frequently detected (65% of samples) and its highest concentration in rainwater (0.33 μg/l) was found on May 7, 2002. Chlorothalonil was the second most frequently detected (33% of samples) and its highest concentration in rainwater (0.27 μg/l) was found on May 26, 2002.

Key words —— pesticide, rainwater, deposition, dichlorvos, chlorothalonil, precipitation

INTRODUCTION

Persistent pesticides, such as 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), 1,2,3,4,5,6-hexachlorocyclohexane (BHC) and chlordane, which had been used previously, are prohibited to use in Japan at the present time. And large amounts of pesticides, which are degradable in the environment, are used for agricultural and public health purposes. However, some amounts of them are volatilized into air[1] and deposited in unintended areas before degradation if they have relatively high vapor pressures. Thus, pesticides in rainwater and their depositions have been investigated in various regions. Examples of recent reports were as follows: Hamers *et al*. in Holland,[2] Charizopoulos and Papadopoulou-Mourkidou in Axios River Basin,[3] Grynkiewicz *et al*. in northern Poland,[4] Hüskes and Levsen in Lower Saxony,[5] Dubus *et al*. in Europe,[6] Karlsson *et al*. in Southern Africa,[7] Majewski *et al*. in Mississippi River Valley,[8] Hochstedler *et al*. in Iowa,[9] Kawata *et al*. in Niigata[10] and Okuda *et al*. in Mie.[11] However, there have been few investigations of pesticides in rainwater and their depositions over a period of 12 months in Yokohama.

Therefore, samples of rainwater were collected from August 2001 until July 2002 at Isogo Ward of Yokohama. And 51 kinds of pesticides (19 insecticides, 21 herbicides and 11 fungicides) in rainwater were measured using gas chromatography-mass spectrometry (GC-MS) and gas chromatography-flame photometric detector (GC-FPD). In addition, wet-deposition amounts of pesticides were evaluated using rainfall data at Yokohama Local Meteorological Observatory.

MATERIALS AND METHODS

Chemicals —— Acetone was pesticide residue grade purchased from Wako Pure Chemical Industries and Kanto Kagaku Co. (Japan). Pesticides for chromatographic analysis were purchased from Wako Pure Chemical Industries (Japan), Kanto Kagaku Co. and GL Sciences Inc. (Japan).

Sample Collection —— Rainwater samples were collected on the roof of Yokohama Environmental Research Institute located at Isogo Ward of Yokohama, Japan. The ground of this building was 8 m above sea level and the height of the roof was 20 m. There were residential and industrial areas, woods and sea within 5 km of this institute, but few farms or rice paddies. Six glass dishes (240–250 mm i.d., 60–70 mm depth) were set on the roof before raining in order to collect rainwater. If it was stopped raining or glass dishes were filled up by rainwater, samples were poured into the glass bottles and stored in the refrigerator (4°C). If rainfall was less than 5 mm at once, determination of pesticides was not conducted.

Preparation of Samples for GC-FPD and GC-MS Analysis —— Appropriate volume (usually 600 ml to 1000 ml) of rainwater was passed through solid-phase extraction cartridge (Sep-pak PS-2, Waters Co., U.S.A.), and air was passed through it in order to remove moisture. After removing moisture, 3 ml of acetone was passed through it and concentrated

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to about 0.5 ml by a stream of nitrogen.

Determinations of Pesticides by GC-FPD and GC-MS —— Pesticides were determined by GC-FPD (Hewlett-Packard-6890) and GC-MS (Hewlett-Packard-5973). In the case of GC-FPD, separation column was HP-5 (30 m × 0.32 mm i.d.). Injection temperature was 200°C and detector temperature was 240°C. Oven temperature was programmed from 50 to 240°C and helium gas was flowed through the column at 1.8 ml/min as carrier gas. In the case of GC-MS, separation column was HP-5MS (30 m × 0.25 mm i.d.). Injection temperature was 200°C and detector temperature was 240°C. Oven temperature was programmed from 50 to 240°C and helium gas was flowed through the column at 1.0 ml/min as carrier gas. In this experiment, quantitation limit of each pesticide was set at 0.05 μg/l. Measured insecticides were dichlorvos, fenobucarb, α-BHC, γ-BHC, diazinon, disulfoton, fenitrothion, malathion, chlorpyrifos, fenthion, α-endosulfan, isoxathion, β-endosulfan, pyridaphenthion, *O*-ethyl *O*-4-nitrophenyl phenylphosphonothioate (EPN), parathion, methyl-parathion and phenthoate. Measured herbicides were molinate, trifluralin, simazine, swep, atrazine, propyzamide, bromobutide, terbucarb, simetryn, esprocarb, thiobencarb, pendimethalin, methyldymron, butachlor, butamifos, pretilachlor, oxadiazon, nitrofen, chlornitrofen, mefenacet and napropamide. Measured fungicides were chloroneb, pencycuron, pentachloronitrobenzene (PCNB), chlorothalonil, iprobenfos, tolclofos-methyl, fthalide, flutolanil, isoprothiolane, mepronil and *O*-ethyl S S-diphenyl phosphorodithioate (EDDP).

Recovery Test —— Mixture of pesticides was added to 1000 ml of distilled water and the concentration of each pesticide was adjusted to 0.5 μg/l. Then, the concentration of each pesticide in aqueous solution was determined as above method. Recovery test was repeated three times and average recovery of each pesticide was calculated.

Rainfall Data —— Rainfall data from August 2001 until July 2002 were provided by Yokohama Local Meteorological Observatory. It was located 4 km away from Yokohama Environmental Research Institute.

Evaluation of Wet-Deposition Amount —— Wet-deposition amount by rainfall, which was below 5 mm at once, was not counted in this time. Deposition amounts of pesticides were evaluated by concentrations in rainwater and rainfall data.

RESULTS AND DISCUSSION

Average recoveries of all pesticides were more than 75% and coefficients of variation were within 20% in this experiment. Thus, all pesticides could be determined by above method.

Concentrations of 6 pesticides were indicated in Table 1 and others were less than quantitation limit. Although rainfall data at Yokohama Local Meteorological Observatory were above 5 mm on Aug 26, 2001 and on May 8, 2002, determinations of pesticides were not conducted for these two rainwater samples.

Dichlorvos was the most frequently detected pesticide and the frequency of detection in rainwater became 65% in this investigation. The highest concentration in rainwater, 0.33 μg/l was found on May 7, 2002 (sample number 34). This value was higher than previous data in Mie[11] and Kitakyushu,[12] Japan. Occurrence of dichlorvos in rainwater might be related to its vapor pressure (1.6 Pa, 20°C[13]) and used amount (more than 1000 kg per year in Yokohama). However, sampling point was not located in agricultural area and source region of dichlorvos contained in rainwater was not apparent.

Guideline value of dichlorvos in rainwater was not specified in Japan. If determined concentrations of dichlorvos in rainwater were compared with guideline value in river specified by Japan Ministry of the Environment (8 μg/l), all determined concentrations were less than this value. However, *Daphnia magna* (a kind of zooplankton) was affected harmfully by less than 0.33 μg/l of organophosphorous insecticides in previous studies.[14,15] Therefore, monitoring of dichlorvos in rainwater was considered to be valuable for ecological assessment.

Chlorothalonil was the second most frequently detected pesticide. The frequency of detection in rainwater was 33%, although it had never detected in river water in Yokohama.[15,16] It was commonly used fungicide and used amount was considered to be more than 1000 kg per year in Yokohama. On the other hand, its vapor pressure was 7.6×10^{-5} Pa (25°C)[17] and lower than that of dichlorvos. The highest concentration in rainwater, 0.27 μg/l was found on May 26, 2002 (sample number 40) and this value exceeded previous value in Kitakyushu.[12]

Fenitrothion was commonly used insecticide and used amount was considered to be more than 1000 kg per year in Yokohama. It was the third most frequently detected pesticide and frequency of detection was 21%. Its concentration in rainwater (0.24–

Table 1. Concentrations of Pesticides in Rainwater and Rainfall Data

Sample number	Date	Concentrations of pesticides (μg/l)						Rainfall (mm)
		Dichlorvos	Fenitrothion	Diazinon	Malathion	Chlorothalonil	Molinate	
1	8/21/2001	0.05	—[a)]	—	—	—	—	54.5
2	8/22/2001	—	—	—	—	—	—	77.0
3	8/31/2001	0.16	0.08	—	—	—	—	12.5
4	9/3/2001	0.16	0.10	—	—	—	—	14.0
5	9/9–10/2001	—	—	—	—	—	—	86.5
6	9/11/2001	—	—	—	—	—	—	62.5
7	9/21–22/2001	0.05	—	—	—	—	—	19.5
8	9/30–10/1/2001	0.10	0.05	—	—	—	—	101.5
9	10/8/2001	0.20	0.13	0.07	—	0.05	—	9.0
10	10/10/2001	—	—	—	—	—	—	107.0
11	10/17–18/2001	0.08	—	—	—	0.06	—	36.5
12	10/22–23/2001	0.08	—	—	—	—	—	23.5
13	10/28–29/2001	—	—	—	—	—	—	50.5
14	11/3/2001	—	—	—	—	—	—	23.5
15	11/5–6/2001	—	—	—	—	—	—	59.5
16	11/9–10/2001	—	—	—	—	—	—	48.0
17	12/4/2001	0.05	—	—	—	—	—	12.0
18	12/6/2001	0.05	—	—	—	—	—	9.5
19	12/13/2001	—	—	—	—	—	—	16.0
20	1/7–8/2002	0.07	—	—	—	—	—	8.5
21	1/21/2002	—	—	—	—	—	—	53.5
22	1/26–27/2002	—	—	—	—	—	—	41.0
23	2/3/2002	—	—	—	—	—	—	15.0
24	2/5–6/2002	0.06	—	—	—	0.05	—	12.0
25	3/6/2002	0.12	—	—	—	0.05	—	8.0
26	3/15/2002	—	—	—	—	—	—	13.0
27	3/22–23/2002	0.14	—	—	—	—	—	9.0
28	3/27/2002	0.06	—	—	—	—	—	31.0
29	3/29/2002	0.06	—	—	—	—	—	15.5
30	3/30/2002	—	—	—	—	—	—	17.0
31	4/11–12/2002	0.05	—	—	—	0.12	—	17.0
32	4/21–22/2002	0.10	0.05	—	—	0.08	—	38.5
33	4/25/2002	0.17	0.10	—	—	0.22	—	5.0
34	5/7/2002	0.33	0.24	0.05	0.05	0.18	—	5.5
35	5/10/2002	0.15	0.07	—	—	0.17	—	30.0
36	5/11/2002	0.11	—	—	—	—	—	21.0
37	5/13/2002	0.09	—	—	—	0.09	0.12	10.0
38	5/17/2002	0.25	0.13	—	—	0.10	0.05	20.5
39	5/18/2002	0.20	—	—	—	0.10	—	16.0
40	5/26/2002	0.05	—	—	—	0.27	0.06	9.5

a) below quantitation limit.

0.05 μg/l) indicated seasonal trend, and it was not detected in winter.

Molinate was detected only in May at 0.12–0.05 μg/l. It is a selective herbicide used in rice paddies and has relatively high vapor pressure (0.75 Pa, 25°C).[18] However, there were no rice paddies around sampling point within 5 km. Thus, the source of it might be located more than 5 km away.

Although thiobencarb, simetryn and mefenacet had been often detected in river water in Yokohama,[15,16] none of them were detected in rainwater in this investigation.

Next to determinations of pesticides, wet-deposition amounts of them were evaluated by rainfall

Table 1. Continued

Sample number	Date	Concentrations of pesticides (μg/l)						Rainfall (mm)
		Dichlorvos	Fenitrothion	Diazinon	Malathion	Chlorothalonil	Molinate	
41	5/27/2002	0.08	—	—	—	0.12	—	12.0
42	6/12/2002	—	—	—	—	—	—	8.5
43	6/14–15/2002	0.08	—	—	—	—	—	65.0
44	6/18/2002	0.05	—	—	—	—	—	49.5
45	6/20/2002	0.06	—	—	—	0.07	—	22.0
46	6/25–26/2002	0.26	0.07	—	—	0.14	—	16.0
47	6/27/2002	0.24	0.10	—	—	0.08	—	27.0
48	6/29–7/1/2002	—	—	—	—	—	—	49.5
49	7/10–11/2002	—	—	—	—	—	—	77.0
50	7/16/2002	—	—	—	—	—	—	82.0
51	7/25/2002	0.08	—	—	—	—	—	12.5

data provided by Yokohama Local Meteorological Observatory. Annual wet-deposition amount of dichlorvos was considered to be more than 70 μg/m^2 at the sampling point, and this value was the largest in this investigation. In the case of chlorothalonil, annual wet-deposition amount might be more than 30 μg/m^2 at the sampling point. On the other hand, in the cases of herbicides such as molinate, thiobencarb and simetryn, annual wet-deposition amounts were considered to be below 10 μg/m^2.

In conclusion, rainwater at Isogo Ward of Yokohama often contained several kinds of pesticides. However, the source regions and ecological effects of pesticides were not apparent. Thus, further investigations of pesticides in the environment were considered to be important for ecological assessments of them.

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