

# Estimation of Leachability and Persistence of Pesticides at Golf Courses from Point-Source Monitoring and Model To Predict Pesticide Leaching to Groundwater

TOSHINARI SUZUKI,\*† HARUMI KONDO,† KUMIKO YAGUCHI,† TOSHIO MAKI,† AND TETSUYA SUGA‡

Tama Branch Laboratory, Tokyo Metropolitan Research Laboratory of Public Health, 3-16-25, Shibazaki-cho, Tachikawa, Tokyo, 190, Japan, and Department of Clinical Biochemistry, Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

The monitoring of 19 pesticides in drainage and groundwater at a golf course was performed when there was no runoff water. The loading rates of most pesticides via leaching water were lower than 4% of application amount, except for more than 23% for terbutol. The times of pesticides loading into the drainage reducing to 50% of initial [ $t_{1/2}(\text{loading})$ ] were 40.3 months for terbutol, 9.4 months for isoprothiolane, 6.6 months for flutolanil, and within 1 month for the other pesticides. On the basis of several published models for predicting pesticides leaching to groundwater at agricultural land, the pesticides having the GUS score greater than 0.4 or exhibiting  $K_{oc}$  less than  $7000 \text{ cm}^3 \text{ g}^{-1}$ , and  $t_{1/2}(\text{soil})$  greater than 3 days were classified as the pesticides leaching to groundwater at golf courses. The golf course is a high pollution potential area compared with agricultural land. For the persistence of terbutol at golf courses, the concentrations of terbutol in subsoils at the depth greater than 50 cm were higher than the other pesticides after 4 years when terbutol was applied. The half-life [ $t_{1/2}(\text{soil})$ ] of terbutol, isoprothiolane, and flutolanil in the turf grass soils under an aerobic condition was 200, 180, and 360 days, respectively. Organic carbon partition coefficient ( $K_{oc}$ ) and relative mobility in the soil column of terbutol were the same as isoprothiolane and flutolanil. These results suggested that persistence of terbutol was mainly caused by slow degradation rate in the subsoils.

## Introduction

Contamination of drainage and groundwater by pesticides used at golf courses has become of interest since the 1980s in Japan. Most of the golf courses were situated on hilly land or in a village. The drainage from the golf course flows into the river which is utilized as the source of drinking water. Maximum contaminant levels for 30 pesticides in the drainage at the golf courses and in drinking water were set by the

\* To whom correspondence should be addressed. E-mail: tsuzuki@tokyo-eiken.go.jp; fax: +81 425 24 5307.

† Tama Brand Laboratory.

‡ Tokyo College of Pharmacology.

Environmental Agency and Ministry of Health and Welfare in Japan, respectively, until 1997.

For the risk assessment of water pollution by the pesticides used at golf courses, it is necessary to predict the extent to which pesticides would leach to drainage or groundwater through the soil. This has led to the models based on the screening of pesticides which were established by Gustafson (1), Jury et al. (2), and Cohen et al. (3) and computer simulation models such as PRZM2 (4), GIS (5), and GLEAMS (6). The field studies on the loading time of the pesticides in the drainage or groundwater are also important for the point of view of pesticide amounts loaded into the environmental water. The experiments with lysimeter (7, 8) and soil column (9, 10) under laboratory conditions provide useful data for runoff, loading amounts, and leaching of pesticides in the fields.

Monitoring of pesticides in the drainage at golf courses in Japan have been reported by many researchers (11-14). A few studies have been reported on runoff property of pesticides applied at golf courses during rainfall (7, 8, 14), although study on pesticides loading via leaching water has been scarcely published. The criteria to predict pesticide leaching to drainage or groundwater has not been reported. The previous monitoring reports showed that fungicides (isoplothiolane and flutolanil), insecticides (diazinon and fenitrothion), and herbicides (asulam, simazine, triclopyr, MCPP, and terbutol) were detected at high frequency in the drainage at concentrations from nanograms per liter to micrograms per liter levels (11-14). Environmental fate of terbutol (2,6-di-*tert*-butyl-4-methylphenyl-*N*-methylcarbamate) differs from the other pesticides detected in the drainage at the golf courses. Terbutol is a herbicide belonging to phenylcarbamate herbicides. In Japan, it has been mainly applied at the golf courses for controlling crab- and goosegrass at fairway and rough. Terbutol and its metabolites were detected in the drainage and groundwater at the golf courses more than 2 years after when terbutol was applied (15). The cause of terbutol persistence has not been elucidated. Terbutol is regarded as a model compound for screening pesticide persistence at the golf courses. Elucidation of the cause of terbutol persistence and then development of the screening method in the laboratory or the criteria for predicting pesticides persistence are useful to prevent application of another persistent pesticide to the golf courses.

Therefore, the objectives of this research are (1) to estimate the loading amount and time of the pesticides into the drainage via leaching water in the field; (2) to predict pesticides leaching to drainage through the soil by the screening level models previously established; (3) to investigate the cause of terbutol persistence at the golf courses by search for vertical distribution of the pesticides in the soils in the field, degradation, and leaching study in the laboratory.

## Materials and Methods

**Sampling Points and Sample Collection.** Sampling sites at a golf course investigated in this study are shown in Figure 1. The flow rates of drainage I, II, plus III (depth of drain from soil surface, 2 m), and the exit of pond water from 1994 to 1996 were  $35 \pm 20$ ,  $39 \pm 20$ , and  $(125 \pm 62) \times 10^4 \text{ L month}^{-1}$ , respectively. The flow rates at the exit of pond from 1994 to 1996 are shown in Figure 2A. Leaching water, which did not pass the drainage pipes, flowed into the pond shown in Figure 1. Rainfall around this golf course from 1994 to 1996 was  $1140 \pm 150 \text{ mm year}^{-1}$ , rainfall in every month from 1994 to 1996 is shown in Figure 2A. The drainage samples were collected by stainless steel basket and stored in an amber

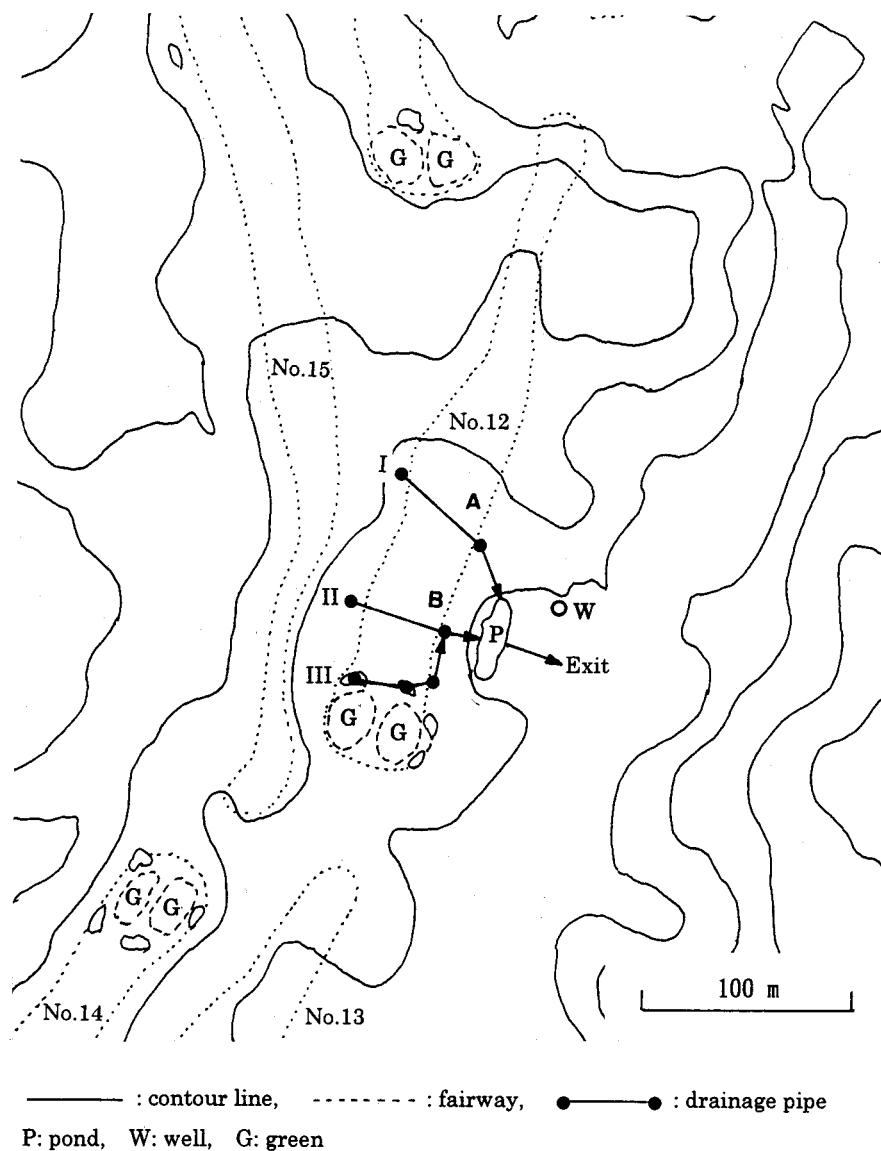


FIGURE 1. Geographical features and sampling points of drainage and groundwater at a golf course. The interval of contour line is 10 m. The drainage flows in the direction of the arrow. A and B are sampling points of soil samples on fairway of the course no. 12. The area of runoff and leaching water flowing into the pond is approximately 12 000 m<sup>2</sup>.

glassware. The groundwater shown in Figure 1 was pumped up the well (well depth, 5.2 m; depth to groundwater, 2.6 m; diameter, 90 cm; covered with concrete plate; distance from pesticides scattered area, 30 m) after 5 min of pump running and stored in an amber glassware. The drainage and groundwater were collected once a month when there was no rainfall and inflow of runoff water. The pesticides in the water samples were extracted within 3 h after sampling as described below. The extracted pesticides were stored in the refrigerator at 4 °C and measured within 1 week after extraction. The soil samples at the sampling points A and B on the fairway in Figure 1 were fractionated with hand auger at a distance of 10 cm in May, 1993, and May, 1995. The soil samples were collected in a plastic container and stored in the refrigerator at -25 °C. The pesticides in the soil samples were extracted within 1 month after sampling as described below, and the extracts were stored in the refrigerator at 4 °C. The pesticides in the extracts were measured within 1 week after pesticides extraction.

**Application of Pesticides.** The application amount and rate of each pesticides around the sampling area, course no. 12, from 1994 to 1996, were listed in Table 4. Fungicides were used mainly on the greens and fairways from April to

October. Insecticides were applied mainly on the greens, fairways, and rough from April to September. Herbicides were scattered mainly on the fairways and rough from April to May and from October to November. The diluent of the pesticides is water, and the amount of sprinkling water per application of fungicides, pesticides, and herbicides was 1.0, 1.1, and 0.4 L m<sup>-2</sup>, respectively.

**Determination of Pesticides in Water and Soil Samples and Soil Property.** The extraction of pesticides in water was performed according to the previous methods (15, 16). A 1000 mL water sample added with 50 g of sodium chloride (NaCl) was extracted twice with 100 mL of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) by vigorously shaking for 5 min. The CH<sub>2</sub>Cl<sub>2</sub> was dehydrated with sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to about 10 mL with a rotary evaporator at 40 °C. *n*-Hexane was added to the CH<sub>2</sub>Cl<sub>2</sub> extract and reconcentrated to 1 mL with a rotary evaporator and then a stream of nitrogen. The final solution was analyzed by GC-MS after addition of the internal standard. For asulam, MCPP, MCPA, triclopyr, and terbutol metabolites containing the carboxyl group, a 1000 mL water sample acidified with hydrochloric acid (HCl) to pH 2 was extracted twice with 100 mL of CH<sub>2</sub>Cl<sub>2</sub> by vigorously shaking for 5 min. The CH<sub>2</sub>Cl<sub>2</sub> was dehydrated with Na<sub>2</sub>SO<sub>4</sub>

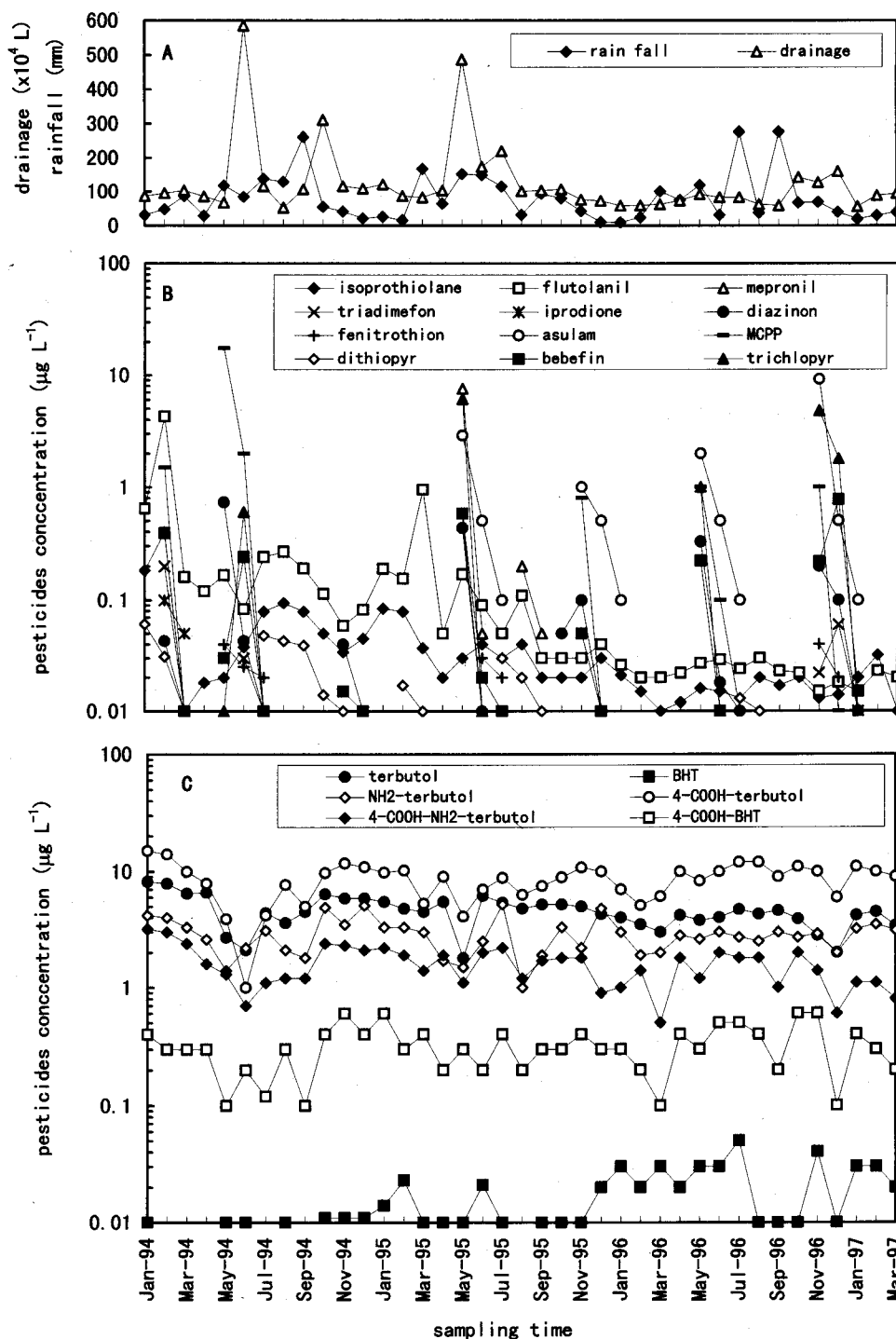


FIGURE 2. Changes in rainfall, drainage rate, and pesticides concentration in the drainage at the golf course. Sampling point of the drainage is the exit of the pond in Figure 1.

and concentrated with a rotary evaporator at 40 °C and evaporated to dryness under a stream of nitrogen. The residue was subjected to methylation with a diazomethane and then analyzed with GC-MS after addition of the internal standard. The recovery and detection limit of each pesticide in the water sample are listed in Table 1.

A soil sample (10 g dry weight) was transferred to a 60 mL centrifugation tube and extracted three times with 20 mL of acetone by vigorously shaking for 5 min, sonicating for 5 min, and centrifuging at 3000 rpm for 10 min, respectively. The acetone solution was filtered, and the filtrate was concentrated to about 10 mL with a rotary evaporator at 40 °C. The concentrated acetone solution was added to 100 mL

of 5% NaCl and extracted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution extract was dehydrated with Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under a stream of nitrogen. The residue was dissolved in acetone-*n*-hexane (25:75) and then analyzed by GC-MS after addition of the internal standard. For asulam, MCPP, MCPA, toriclopyr, and terbutol metabolites containing the carboxyl group, the concentrated acetone solution was added to 100 mL of 0.1 N HCl and extracted twice with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution was dehydrated with Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under stream of nitrogen. The residue was subjected to methylation with a diazomethane and then analyzed with GC-MS after addition of the internal standard. The detection limit of each pesticide

**TABLE 1. Retention Time, Monitor Ions, Detection Limit on GC-MS Analysis, and Maximum Contaminant Levels of Pesticides**

no.	pesticides	CAS no <sup>a</sup>	retention time <sup>b</sup> (min)	monitor ions <sup>c</sup> (m/z)	detection limit <sup>d</sup> ( $\mu\text{g L}^{-1}$ )	recovery <sup>e</sup> (%)	MCL <sup>f</sup> (mg L <sup>-1</sup> )
<b>Fungicides</b>							
1	isoprothiolane	50512-31-1	19:07	118 162	0.01	98 ± 6	0.40
2	flutolanil	66332-96-5	18:58	173 145	0.01	97 ± 8	2.00
3	iprodione	36734-19-7	24:24	314 187	0.05	90 ± 6	3.00
4	triadimefon	43121-43-3	15:54	57 208	0.01	90 ± 4	
5	mepronil	55814-41-0	21:37	119 91	0.05	87 ± 3	1.00
<b>Insecticides</b>							
6	isoxathion	18854-01-8	20:09	105 177	0.05	88 ± 4	0.08
7	diazinon	333-41-5	12:38	137 304	0.01	91 ± 7	0.05
8	dichlorvos	62-73-7	7:00	109 185	0.05	89 ± 5	
9	fenitrothion	122-14-5	15:03	125 277	0.02	90 ± 4	0.03
<b>Herbicides</b>							
10	asulam	3337-71-1	19:20	92 156	0.10	80 ± 10	2.00
11	atrazine	1912-24-9	11:55	200 215	0.05	89 ± 5	
12	simazine	122-34-9	11:47	201 203	0.05	86 ± 6	0.03
13	triclopyr	553355-06-3	10:90	210 269	0.01	101 ± 5	0.06
14	terbutol	1918-11-2	14:04	205 220	0.01	91 ± 5	0.20
15	MCPP	7805-19-0	9:06	142 228	0.01	102 ± 6	0.05
16	MCPA	94-74-6	9:69	141 214	0.01	99 ± 8	
17	dithiopyr	97886-45-8	14:53	286 354	0.01	86 ± 5	0.08
18	pyributicarb	88678-67-5	24:16	108 165	0.01	89 ± 8	0.20
19	benefin	1861-40-1	10:57	292 264	0.01	87 ± 5	0.80
<b>Terbutol Metabolites</b>							
	4-COOH-terbutol	—	19:65	249 264	0.01	104 ± 6	
	NH <sub>2</sub> -terbutol	—	14:29	205 220	0.01	90 ± 5	
	4-COOH-NH <sub>2</sub> -terbutol	—	20:45	249 264	0.05	110 ± 5	
	BHT	128-37-0	9:12	205 220	0.01	99 ± 5	
	4-COOH-BHT	1421-49-4	13:15	249 264	0.01	103 ± 8	
<b>Internal Standard</b>							
	fluoranthene- <i>d</i> <sub>10</sub>	206-44-0	17:16	212			

<sup>a</sup> CAS no., Chemical Abstract Registry Number; —, no CAS no. <sup>b</sup> Typical retention time on GC-MS. <sup>c</sup> Left column is a base peak of the compounds. <sup>d</sup> Detection limit of pesticides in water samples. <sup>e</sup> Values are mean ± SD (*n* = 3) obtained from water sample spiked pesticides at 1  $\mu\text{g L}^{-1}$ . <sup>f</sup> MCL, maximum contaminant levels of pesticides for drainage in Japan; —, no MCL.

**TABLE 2. Physicochemical Properties of Turf Grass Soil on Fairway at Golf Course in May 1995<sup>a</sup>**

soil depth <sup>b</sup> (cm)	pH	water content (%)	organic matter (%)	organic carbon (%)	CEC (mequiv 100 g <sup>-1</sup> )
0–10	6.8	30.1	8.4	4.7	9.9
10–20	7.0	22.5	6.2	1.6	12.1
20–30	6.1	19.5	4.8	0.4	11.6
30–40	6.0	20.5	5.0	0.3	10.1
40–50	6.2	21.0	5.1	0.7	12.1
50–60	6.4	23.0	5.7	0.4	12.4
60–70	6.5	23.0	5.5	0.4	11.3
70–80	6.6	24.1	5.7	0.4	12.2
80–90	6.5	25.8	6.1	0.5	12.2
90–100	6.5	25.2	5.5	0.3	10.6
100–110	6.6	24.6	5.8	0.5	12.1
110–120	6.5	26.9	6.0	0.6	13.0
120–130	6.6	26.7	6.4	0.8	12.0
130–140	6.6	27.4	6.2	0.8	13.2
140–150	6.7	28.6	9.4	1.0	12.9
150–160	6.7	28.3	6.0	0.9	10.0
160–170	6.8	30.1	6.3	0.8	12.0
170–180	6.9	34.1	7.3	1.4	14.5
180–190	7.0	37.4	11.0	2.4	19.4
190–200	7.0	36.1	9.7	2.2	16.6

<sup>a</sup> Values are means from two experiments with the soils collected at sampling points A and B in Figure 1. CEC, cation exchange capacity. <sup>b</sup> Turf grass soil, soil depth of 0–10 cm; subsoils, soil depth greater than 10 cm.

in the soil sample was a 10-fold concentration in relation to the water sample.

The organic carbon partition coefficient (*K*<sub>oc</sub>) of each pesticide between the soil and water was determined by

**TABLE 3. Point Source Monitoring of Pesticides in Drainage at 24 Golf Courses in Tokyo from 1994 to 1996<sup>a</sup>**

no. <sup>b</sup>	pesticides	drainage sample no.	detection	
			no.	max concn (mg/L) <sup>c</sup>
<b>Fungicides</b>				
1	isoprothiolane	123	13	0.014
2	flutolanil	123	36	0.037
3	iprodione	61	1	0.001
4	mepronil	123	3	0.003
<b>Insecticides</b>				
6	isoxathione	126	0	ND
7	diazinon	126	6	0.005
9	fenitrothion	126	3	0.002
<b>Herbicides</b>				
10	asulam	82	18	0.021
12	simazine	123	3	0.013
13	toriclopyr	48	6	0.015
14	terbutol	123	15	0.010
15	MCPP	78	11	0.035
19	benefin	123	1	0.002

<sup>a</sup> This list does not include all pesticides. <sup>b</sup> Numbers refer to Table 1. <sup>c</sup> max concn, maximum concentration of pesticide in drainage; ND, less than 0.001 mg L<sup>-1</sup>.

measuring the pesticide in the solution centrifuged after vigorously shaking for 4 h at 25 °C with turf grass soils (10 g dry weight) and 100 mL of distilled water, as described previously by McCall et al. (17). Organic matter content in the soil was determined by loss on ignition at 375 °C for 16 h after heating at 105 °C for 12 h. Organic carbon content

TABLE 4. Application Amount and Loading Amount and Time of the Pesticides Detected in the Drainage from 1994 to 1996

no. <sup>a</sup>	pesticides	application <sup>b</sup>			loading period <sup>c</sup>			t <sub>1/2</sub> (loading) (month)
		rate (g/m <sup>2</sup> )	times	amount/application (g)	times	amount/period (g)	(%)	
Fungicides								
1	isoprothiolane	0.40	1	2100	1	2.1	0.100	9.4
2	flutolanil	0.50	1	2300	1	9.2	0.400	6.6
3	iprodione	0.30	6	200–2800	1	0.9	0.150	0.1
4	triadimefon	0.04	5	100–400	3	0.1–0.2	0.001–0.003	0.3–0.7
5	mepronil	0.40	5	200–3600	2	0.3–37.1	0.001–0.490	0.2–0.4
Insecticides								
6	isoxathion	0.50	2	200–4300	0	ND	0.000	–
7	diazinon	0.40	7	100–2200	7	0.1–0.3	0.004–0.080	0.1–1.3
8	dichlorvos	0.01	7	30–400	0	ND	0.000	–
9	fenitrothion	0.05	7	100–1300	3	0.1–0.7	0.010–0.040	0.3–1.0
Herbicides								
10	asulam	0.26	6	1300–2400	4	0.8–14.1	0.030–1.088	0.1–0.2
13	tricypyr	0.22	5	500–700	4	0.9–29.8	0.100–4.300	0.1–0.2
14	terbutol <sup>d</sup>	0.32	1	2100	1	203.7	23.1	40.3 (52.9)
15	MCPP	0.25	6	800–1400	6	0.6–3.0	0.040–0.168	0.1–0.3
17	dithiopyr	0.06	5	200–300	5	0.1–0.2	0.030–0.100	0.3–3.2
18	pyributicarb	0.40	7	100–400	0	ND	0.000	–
19	benefin	0.38	7	100–2400	7	0.1–2.6	0.007–0.107	0.2–2.3
Terbutol metabolites								
	4-COOH-terbutol	–	0	–	1	370.6	–	63.6 (28.5)
	NH <sub>2</sub> -terbutol	–	0	–	1	137.5	–	47.1 (26.7)
	4-COOH-NH <sub>2</sub> -terbutol	–	0	–	1	74.4	–	29.4 (19.3)
	BHT	–	0	–	1	0.6	–	42.0 (19.3)
	4-COOH-BHT	–	0	–	1	15.2	–	25.0 (25.0)

<sup>a</sup> Numbers refer to Table 1. <sup>b</sup> –, unknown or no application. <sup>c</sup> Values are statistically calculated based on the results in Figure 2. –, no calculation. The t<sub>1/2</sub> (loading) were calculated by following first-order kinetics:  $C = C_0 e^{-\lambda t}$ ; t, month; C, pesticide concentration in drainage; C<sub>0</sub>, initial pesticide concentration in drainage, t<sub>1/2</sub> (loading) =  $\ln 2 \lambda^{-1}$ . t<sub>1/2</sub> (loading) in well water in Figure 2 in the parenthesis. <sup>d</sup> Last application of terbutol is in May 1991.

in soil was determined by colorimetric assay, treating the soil with sodium dichromate dihydrate and sulfuric acid, using sucrose as the standard, as described previously by Metson (18). Soil pH was measured with pH meter after addition of 5 mL of distilled water to the soil sample (2 g dry weight). Cation exchange capacity (CEC) was determined by ammonium acetate method previously published by Schollenberger and Simon (19). The physiochemical properties of the soil (Kanto loam) samples at this golf course are listed in Table 2. Bulk density of turf grass soil corresponding to the soil at depth of 0–10 cm was 1100 kg m<sup>-3</sup>.

The degradation of pesticide in soils under aerobic conditions was examined with the turf grass soil on the fairway according to our previous work (16). The soil (10 g dry weight) removed turf grass and thatch by the sieve of 2 mm mesh was adjusted moisture content to 60% of field capacity. After preincubation in the dark at 25 °C for 2 weeks, 50 μL of 0.6 mg L<sup>-1</sup> of pesticide in dimethyl sulfoxide was added to the soil. The sample was incubated for 25 °C in the dark, and sterilized water with membrane filter (pore size, 0.22 μm) was added in every week to maintain the moisture conditions. The pesticide was extracted initially, and 15, 30, 60, 90, and 180 days after pesticide addition and determined by GC-MS by the methods mentioned above. The time for the dissipation of 50% of the initial amount of each pesticide [half-life, t<sub>1/2</sub>(soil)] was estimated by first-order kinetics from duplicate samples.

**Leaching Study of Pesticides with Soil Column.** The leaching of pesticides was examined with soil column in which turf grass soil or subsoils (10 g dry weight) at the sampling points of A and B on the fairway shown in Figure 1 was packed into a polypropylene tube (10 × 40 mm), and a polyethylene filter (pore size, 20 μm) was placed in the top and bottom of the soil. Pesticides (100 μL of 0.1 mg mL<sup>-1</sup> in acetone) were loaded on the top of the soil column, and acetone was evaporated under a stream of nitrogen. The

pesticides were eluted with 300 mL of distilled water at a flow rate of 1 mL min<sup>-1</sup> at 25 °C by an HPLC pump of which pressure was less than 1 kg m<sup>-2</sup>. Every 100 mL of the leaching water from the soil column was fractionated, and the pesticides in each fraction were extracted by a 1/20 scale as mentioned above.

**Apparatus and Conditions.** GC-MS analysis of the pesticides was performed with an HP-5890 Series II (Hewlett-Packard) and a Trio-1000 mass spectrometer (VG MassLab) as the following conditions: GC, injector temperature, 200 °C; column head pressure, 80 kPa; carrier gas, helium; auto sampler, HP-7673 (Hewlett-Packard); sample size, 2 μL; analytical column, DB-5, 0.25 mm i.d. × 30 m, film thickness 0.25 μm (J&W Scientific); MS, an ionization potential, 70 eV; an ionization current, 150 μA; ion source temperature, 200 °C; temperature of transfer line between GC and MS, 250 °C. The GC oven temperature was programmed as follows: held at 50 °C for 1 min, increased from 50 to 180 °C at 20 °C min<sup>-1</sup> and from 180 to 270 °C at 4 °C min<sup>-1</sup>. The sample was introduced into the GC by splitless injection for 1 min, and pesticides were determined with fluoranthene-d<sub>10</sub> as an internal standard by single ion monitoring using the two ion peaks per each pesticide as shown in Table 1.

**Materials.** All of the pesticides, organic solvents, and other chemicals for pesticides analysis were purchased from Wako Pure Chemical Industries, Tokyo. Terbutol metabolites, 2,6-di-*tert*-butyl-4-methylphenyl carbamate (NH<sub>2</sub>-terbutol), 2,6-di-*tert*-butyl-4-carboxyphenyl *N*-methylcarbamate (4-COOH-terbutol), and 2,6-di-*tert*-butyl-4-carboxyphenyl carbamate (4-COOH-NH<sub>2</sub>-terbutol) were prepared by the previous methods (15). 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was obtained from Tokyo Chemical Industry. 2,6-Di-*tert*-butyl-4-carboxyphenol (4-COOH-BHT) was provided by Aldrich Chemical, Milwaukee, WI. Fluoranthene-d<sub>10</sub> was obtained from Hayashi Pure Chemical, Osaka.

## Results and Discussion

### Estimation of Loading Amount and Period of Pesticides in the Drainage at Golf Courses by Point-Source Monitoring.

Monitoring results of the pesticides in the drainage collected at the exit of pond water in Figure 1 are presented in Figure 2, panels B and C. All of the fungicides applied around the sampling point were detected in the drainage after their application. Isoprothiolane and flutolanil appeared in the drainage in every sampling time, although there was no application after May 1994. For the pesticides, diazinon and fenitrothion were appeared in the drainage although isoxathion and diclorvos were not detected in the drainage. For the herbicides, asulam, MCPP, dithiopyr, benefin, triclopyr, and terbutol were detected in the drainage. Atrazine, simazine, and MCPA have not been applied from 1994 to 1996. Isoxathion was not detected in the drainage on point-source monitoring researched by Tokyo Metropolitan Government for 24 golf courses as shown in Table 3. The degradation products of terbutol previously described (15),  $\text{NH}_2^-$ , 4-COOH $^-$ , and 4-COOH-NH $_2^-$ -terbutol, BHT, and 4-COOH-BHT, were detected continuously in the drainage as shown in Figure 2C. When the flow rates of the drainage were relatively high in June 1994 and May 1995, the concentrations of terbutol and its metabolites, except for BHT and 4-COOH-BHT, decreased whereas the concentrations of MCPP, mepronil, asulam, benefin, and diazinon in the drainage increased.

For the groundwater located at the distance of 30 m from pesticides scattered area shown in Figure 1, terbutol and its metabolites were only detected, and the concentrations of these compounds, except for BHT and 4-COOH-BHT, were about 3 times of drainage concentration in every sampling times. These compounds were also detected at  $0.01 \mu\text{g L}^{-1}$  in two wells' waters, whose depth is greater than 80 m but the depth and number of strainer of the well were unknown, at the other site on this golf course. Terbutol was also high frequently detected in the groundwater at the golf courses in Fukuoka Prefecture in Japan (9).

Loading amount and period of the pesticides into the drainage are statistically estimated and listed in Table 3. Loading amount and  $t_{1/2}$ (loading) of terbutol from 1994 to 1996 was 23% of its application amount and 40.3 months, respectively. For the terbutol metabolites,  $t_{1/2}$ (loading) of 4-COOH $^-$  and 4-COOH-NH $_2^-$ -terbutol were greater than the parent compound. Terbutol has appeared in the drainage from 1991 after last application in May 1991 at 2100 g on the fairway and rough, course no 12, shown in Figure 1. The flow rate of the drainage was not measured from 1991 to 1993. Loading amount contained terbutol and its metabolites into the drainage from 1991 to 1996 was estimated more than 70% of application amount by calculating with the mean drainage rate from 1994 to 1996. It seems that  $\text{NH}_2^-$ , 4-COOH $^-$ , and 4-COOH-NH $_2^-$ -terbutol slowly undergo further degradation to low molecular compound such as carbon dioxide or water soluble compounds. To the loading period to the well water,  $t_{1/2}$ (loading) of terbutol in the well was greater than that for the drainage, and  $t_{1/2}$ (loading) of the other metabolites were lower than that of terbutol. Loading amount of the other pesticides in the drainage were from 0.001 to 4.3% of application amount. Loading period of isoprothiolane and flutolanil were longer following terbutol and its metabolites. The relationship between the application amount and loading amount was not found as to the pesticide detected in the drainage. This phenomenon may be reflected in the difference in localization of the drainage pipes, the pesticide treated area, or rainfall after pesticides application. In the previous report (8), the proportion of rainfall flowing into the drainage via runoff was from 30 to 49% in the case within 33 mm rainfall, and simazine and iprodione applied on the golf course were drained less than 1% of application

amount into the drainage via runoff water during rainfall. To assess water pollution by the pesticides used at golf courses, it is necessary to consider sufficiently loading the amount of the pesticides in the drainage through the soil at golf courses in addition to loading via runoff water.

### Prediction of Pesticides Leaching to the Groundwater.

Several screening-level models based on a statistical analysis of groundwater occurrence data to predict groundwater pollution of the pesticides have been established (1-3). The drainage collected in this study is the same quality as the groundwater, because the sampling of the drainage was performed without rainfall and inflow of peripheral water, and the drainage pipes were buried at about 2 m under the turf grass soil. The published models were applied to predict pesticides leaching to the drainage through the soil on golf courses.

Gustafson (1) has published an empirical model as follows:

$$\text{GUS} = (4 - \log K_{oc}) \log[t_{1/2}(\text{soil})]$$

$K_{oc}$ , organic carbon partition coefficient ( $\text{cm}^3 \text{g}^{-1}$ );  $t_{1/2}(\text{soil})$ , half-life in the soil (days).

The pesticides leaching to groundwater are classified as having scores greater than 2.8. The pesticides having the scores lower than 1.8 are improbable to contaminate groundwater. The pesticides having the scores from 1.8 to 2.8 were transitional.

Jury et al. (2) have conducted a particular model simulation in order to derive a screening method. The pesticides conforming to the following inequality considers to be groundwater contamination risk in the field.

$$K_{oc} < a[t_{1/2}(\text{soil})] - b$$

where  $a = 0.253J_w[0.693(L + r^{-1})B_d f_{oc}]^{-1}$  and  $b = \theta(B_d f_{oc})^{-1}$ ;  $K_{oc}$ ,  $\text{m}^3 \text{kg}^{-1}$ ;  $t_{1/2}(\text{soil})$ , days;  $J_w$ , drainage rate ( $\text{m year}^{-1}$ );  $L$ , surface zone (m);  $r$ , depth constant ( $\text{m}^{-1}$ );  $B_d$ , soil bulk density ( $\text{kg m}^{-3}$ );  $f_{oc}$ , organic carbon fraction;  $\theta$ , water content. At high pollution potential,  $J_w$ ,  $1.0 \text{ m year}^{-1}$ ;  $L$ ,  $0.5 \text{ m}$ ;  $r$ ,  $3 \text{ m}^{-1}$ ;  $B_d$ ,  $1500 \text{ kg m}^{-3}$ ;  $f_{oc}$ ,  $0.005$ ;  $\theta$ ,  $0.2$ , in consequence  $a = 0.0058$ ,  $b = 0.027$ .

Cohen et al. (3) have been reported that the pesticide characteristics and field conditions leaching to groundwater were as follows:  $K_{oc}$ , less than  $300-500 \text{ cm}^3 \text{g}^{-1}$ ;  $t_{1/2}(\text{soil})$  greater than 2-3 weeks; specification, negatively charged at ambient pH; total precipitation and irrigation recharge, greater than about  $25 \text{ cm year}^{-1}$ , soil with a pH providing high stability to the pesticide. It appeared that when all chemical characteristics and field conditions appear in combination, the potential for groundwater contamination is high.

$K_{oc}$  and  $t_{1/2}(\text{soil})$  are key parameters in the three models mentioned above to predict groundwater contamination risk.  $K_{oc}$  and  $t_{1/2}(\text{soil})$  of the pesticides with the turf grass soils sampled at A and B in Figure 1 and previously published data were presented in Table 4. Isoxathion exhibited  $K_{oc}$  greater than  $10\,000 \text{ cm}^3 \text{g}^{-1}$ . The  $K_{oc}$  of mepronil, dichlorvos, fenitrothion, dithiopyr, and benefin were greater than  $1000 \text{ cm}^3 \text{g}^{-1}$ . The  $K_{oc}$  of asulam, phenoxy acid herbicides, and s-triazine herbicides were less than  $50 \text{ cm}^3 \text{g}^{-1}$ . These weakly acidic and s-triazine herbicides exhibit low  $K_{oc}$  in any soil types shown in Table 4. The  $K_{oc}$  of terbutol was the same as that of isoprothiolane, and flutolanil.

The  $t_{1/2}(\text{soil})$  of isoprothiolane, terbutol, flutolanil, and dithiopyr were estimated to be greater than 160 days. Simazine, atrazine, pyributicarb, and benefin were from 30 to 60 days. The  $t_{1/2}(\text{soil})$  of the other pesticides was lower than 2 weeks. Isoprothiolane and dithiopyr were persistent in the turf grass soil in comparison to already published data (refs 20 and 21, respectively).

**TABLE 5. Half-life [ $t_{1/2}$  (soil)], Soil Organic Carbon Coefficient ( $K_{oc}$ ), and the Values Obtained from Published Modeling of Pesticides**

no.	pesticides	$t_{1/2}$ (soil) (day)		$K_{oc}$ ( $\text{cm}^3 \text{g}^{-1}$ )		GUS score <sup>c</sup>	Jury's inequality <sup>d</sup> ( $\text{cm}^3 \text{g}^{-1}$ )
		turf grass soil <sup>a</sup>	other soil <sup>b</sup>	turf grass soil <sup>a</sup>	other soil <sup>b</sup>		
<b>Fungicides</b>							
1	isoprothiolane	160	50 (8), 30 (20)	528	—	2.8	4275
2	flutolanil	300	160–300 (21)	418	—	3.4	8020
3	iprodione	7	4–30 (22)	134	—	1.6	181
4	triadimefon	15	15 (23)	150	300 (33)	2.1	396
5	mepronil	10	46–50.5 (24)	408	—	1.4	262
<b>Insecticides</b>							
6	isoxathion	5	15–40 (25)	14 568	—	–0.1	128
7	diazinon	8	32 (2), 28–36 (26)	640	85 (2)	1.1	208
8	dichlorvos	8	16 (26)	1048	—	0.9	208
9	fenitrothion	4	22 (2), 18–28 (27)	1717	—	0.5	101
<b>Herbicides</b>							
10	asulam	5	7 (28)	10	—	2.1	128
11	atrazine	60	64 (2), 60 (29)	30	140 (2), 130 (29)	4.5	1599
12	simazine	30	75 (2), 60 (29)	30	160 (2), 100 (29)	3.7	797
13	triclopyr	10	10 (30)	36	59 (33)	2.4	262
14	terbutol	200	180 (16)	350	—	3.4	5345
15	MCPD	6	7–9 (31)	10	12–15 (33)	2.3	155
16	MCPA	3	5–7 (31)	17	—	1.3	74
17	dithiopyr	350	35 (32)	1858	1920 (32)	1.9	9358
18	pyributicarb	30	13–18 (33)	5500	1885 (33)	0.4	797
19	benefin	60	40 (29)	6000	9000 (29)	0.4	1599

<sup>a</sup> Data obtained with the turf grass soils at the depth from 0 to 10 cm shown in Table 2. <sup>b</sup> Data from previously published literatures; references in the parenthesis; —, no data. <sup>c</sup> GUS score =  $(4 - \log K_{oc}) \log t_{1/2}$  (soil), the values of  $K_{oc}$  and  $t_{1/2}$  (soil) from turf grass soil. <sup>d</sup> Values derived from the following formula:  $0.0268 t_{1/2}$  (soil) – 0.0058, each constant determined by the golf course as described in the text.

The values from the models of Gustafson and Jury et al. based on  $t_{1/2}$ (soil) and  $K_{oc}$  obtained from turf grass soil at this golf course are presented in Table 5. Criteria by the three models mentioned above are also presented in Figure 3. On the basis of Gustafson's criteria, iprodione, triadimefon, diazinon, fenitrothion, and benefin were judged as improbable pesticides leaching to groundwater; however, they were detected in the drainage in the field as shown in Figure 2 and Tables 3 and 4. Simazine was not detected in the drainage in this study, although it was detected in the drainage at the other golf courses in Japan (8) or in Tokyo presented in Table 3. The fungicide chlorothalonil and insecticide chlorpyrifos, which have  $K_{oc}$  of 1400 and 6000  $\text{cm}^3 \text{g}^{-1}$  and  $t_{1/2}$ (soil) of 70 and 63 days, respectively, were detected in the groundwater at the golf courses in Massachusetts (34). In the case of the golf courses, the pesticides having GUS score more than 0.4 are possible to leach to groundwater as shown in Figure 3.

For Jury's model, iprodione, mepronil, diazinon, fenitrothion, and benefin, which were detected in the drainage at golf course, were classified as no contamination risk based on the parameter values at high pollution potential as shown in Figure 3. At the golf course examined in this study, asulam, phenoxy acid herbicides, and triclopyr, which were scarcely adsorbed in the soil, were detected in the drainage within 2 weeks after their application. Therefore, The drainage rate ( $J_w$ ) at this golf course was estimated to be greater than 24  $\text{m year}^{-1}$ . The values for the other parameters in the inequality were as follows:  $L$ , 0.3 m;  $r$ , 3  $\text{m}^{-1}$ ;  $B_d$ , 1100  $\text{kg m}^{-3}$ ;  $f_{oc}$ , 0.047;  $\theta$ , 0.3, in consequence  $a = 0.0268$ ,  $b = 0.0058$ . Even if these parameter values for this golf courses were introduced, mepronil, diazinon, fenitrothion, and benefin were judged as no contamination risk as shown in Table 4 and Figure 3.

For Cohen's criteria, the pesticide having  $K_{oc}$  less than 500  $\text{cm}^3 \text{g}^{-1}$  and  $t_{1/2}$ (soil) greater than 2 weeks has groundwater pollution potential. The pesticides exhibiting the  $K_{oc}$  more than 500  $\text{cm}^3 \text{g}^{-1}$  and  $t_{1/2}$ (soil) less than 2 weeks such as iprodione, mepronil, diazinon, fenitrothion, and benefin as shown in Figure 3 were detected in the drainage. According to his manner, the pesticides of which  $K_{oc}$  less than 7000  $\text{cm}^3$

$\text{g}^{-1}$  and  $t_{1/2}$ (soil) greater than 3 days have contamination risk of groundwater at the golf courses as shown in Figure 3.

The three models mentioned above were developed in order to predict the pesticide leaching to groundwater at agricultural land on the basis of pesticides monitoring results in the groundwater. The golf course is a high pollution potential area compared with agricultural land. The criteria of Gustafson and Cohen established to predict leaching to groundwater at the golf course is restricted at the depth of a few meters because the pesticides, except for terbutol and its metabolites, detected in the drainage were not detected in the well water located at the distance of 30 m from pesticides application area as shown in Figure 1.  $K_{oc}$  and  $t_{1/2}$ (soil) of the pesticides varied in different to soil type (35) and microbial species or density in soils (36). It is necessary to examine  $K_{oc}$  and  $t_{1/2}$ (soil) with the turf grass soil at golf courses before pesticide application.

**Persistence of the Pesticides at the Golf Courses.** The concentrations of pesticides in turf grass- and subsoils sampled in May 1995 are shown in Figure 4. Terbutol and its metabolites were distributed in the turf grass- and subsoils as shown in Figure 4A. Terbutol has not been applied after May 1991 in this golf course. The concentration of terbutol decreased logarithmically at the depth from 0 to 30 cm and increased at a depth from 30 to 100 cm. The concentrations of terbutol metabolites,  $\text{NH}_2$ -terbutol, 4-COOH-terbutol, and  $\text{NH}_2$ -4-COOH-terbutol, in subsoils were the same as for terbutol. The distribution patterns of terbutol and its metabolites were similar to those in May, 1993, and their concentration in each soil fraction was about 2-fold of May 1995. On the other hand, as shown in Figure 4B, the other pesticides detected in the drainage distributed at the highest concentration in turf grass soil. Isoprothiolan, flutolanil, diazinon, MCPD, asulam, and benefin have been applied in every year before May 1995, although they were not accumulated in subsoils at the depth greater than 30 cm.

The study with the soil column in the laboratory provide useful data to predict downward movement of pesticides in the fields. The pesticide contents in leaching water from the

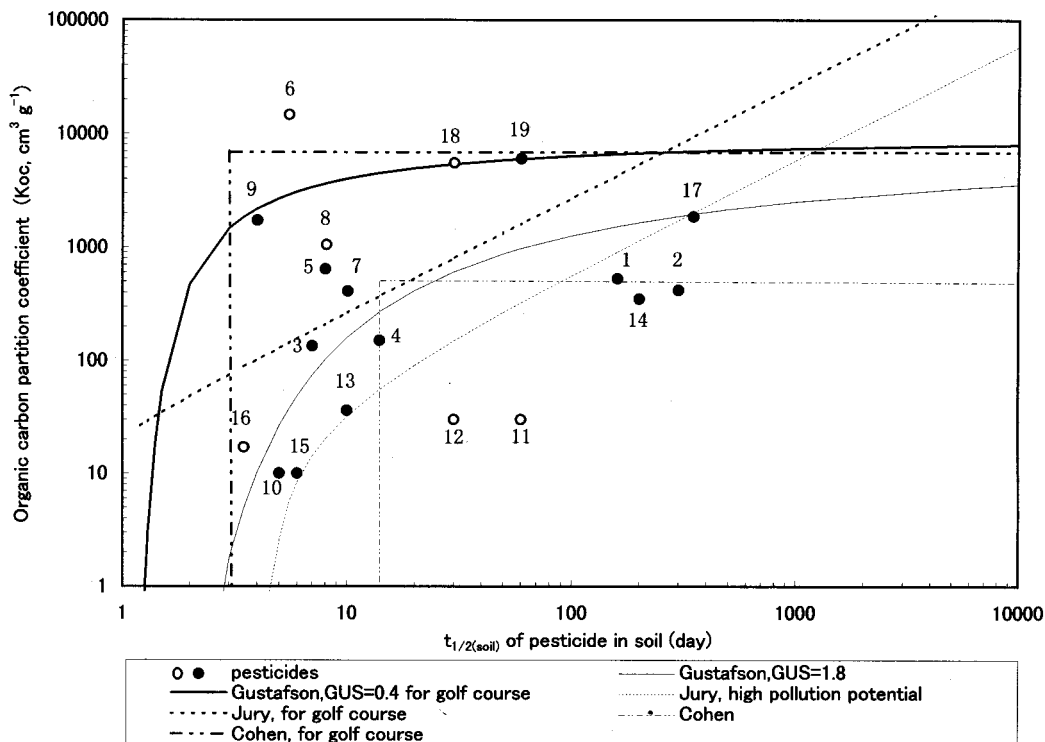


FIGURE 3. Persistence and mobility properties of several pesticides under laboratory conditions together with the criteria for evaluation of the pesticide leaching to groundwater.  $K_{oc}$  and  $t_{1/2}(\text{soil})$  of each pesticide for the turf grass soil in Table 4 are plotted. Pesticides are numbered according to the number in Table 1. Open and closed circles refer to not-detected and detectable pesticides in the drainage in this study, respectively. Pesticides to the right of each line based on the criteria are considered to be a contamination risk to groundwater. Gustafson (1), criteria corresponding to the GUS score reported in the text; Jury (2), criteria corresponding to the inequality in high pollution potential area and in the golf course reported in the text. Cohen (3), criteria corresponding to  $K_{oc}$  of 500  $\text{cm}^3 \text{g}^{-1}$  and  $t_{1/2}(\text{soil})$  of 14 days for agricultural land and  $K_{oc}$  of 7000  $\text{cm}^3 \text{g}^{-1}$  and  $t_{1/2}(\text{soil})$  of 3 days for the golf course.

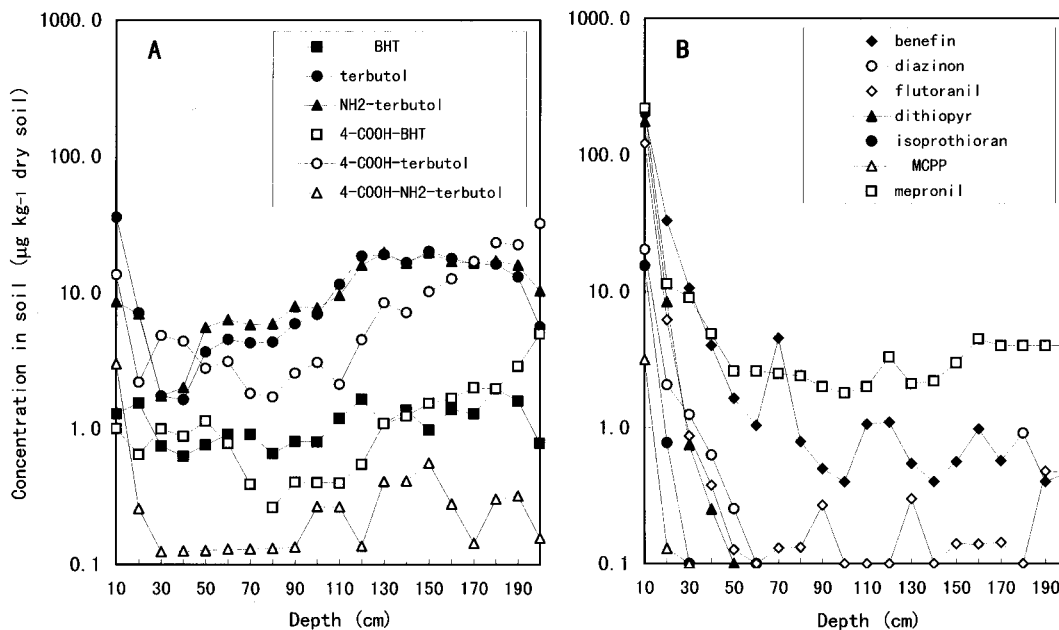


FIGURE 4. Distribution of pesticides in the turf grass- and subsoil on the fairway at golf course in May 1995. The soils are collected at A and B in Figure 1 at a distance of 10 cm from the surface of the turf grass soil. The mean value of pesticides concentration in soils A and B are presented in each soil depth.

soil column are listed in Table 6. For the soil column packed with the turf grass soil, almost all of the acidic herbicides and about 90% of s-triazine herbicides applied onto the column were eluted in the first 100 mL. The amounts in leaching water of the first 100 mL were about 50% for terbutol and from 16 to 40% for all five fungicides, diazinon, and dichlorvos.

Isoxathion, dithiopyr, pyributicarb, and benefin were scarcely detected in the leaching water even when the 300 mL volume of water passed through the soil column. In the case of the subsoil at a depth from 50 to 60 cm, the content of each pesticide in the first fraction was increased in comparison with turf grass soil. The amount of pesticides in the first



TABLE 6. Leaching Pattern of Pesticides from Soil Column with Turf Grass Soil and Subsoils<sup>a</sup>

no.	pesticides	pesticide content in fractionated leaching water (%) <sup>b</sup>								
		turf grass soil (0–10 cm)			subsoil (50–60 cm)			subsoil (140–150 cm)		
		0–100 mL	100–200 mL	200–300 mL	0–100 mL	100–200 mL	200–300 mL	0–100 mL	100–200 mL	200–300 mL
Fungicides										
1	isoprothiolane	30.0	12.0	4.6	48.4	2.2	1.0	25.6	1.0	0.4
2	flutolanil	28.8	16.6	7.6	75.2	4.2	1.4	53.2	2.4	1.0
3	iprodione	23.8	10.0	5.4	61.2	2.8	0.8	46.6	1.6	0.4
4	triadimefon	39.5	15.6	6.4	64.0	4.4	1.8	40.6	3.2	1.6
5	mepronil	33.0	17.0	8.4	58.0	3.0	1.0	38.0	1.6	0.6
Insecticides										
6	isoxathion	ND	0.2	0.2	16.0	10.8	4.0	0.6	0.2	0.4
7	diazinon	22.4	11.8	7.2	36.6	1.6	0.8	29.6	2.6	0.8
8	dichlorvos	16.2	0.2	ND	95.0	1.8	0.6	82.0	1.4	0.6
9	fenitrothion	5.6	8.0	6.0	28.6	2.4	0.8	15.8	3.6	1.0
Herbicides										
10	asulam	99.0	ND	ND	99.0	ND	ND	99.0	ND	ND
11	atrazine	93.0	3.2	0.8	94.0	3.2	1.2	94.0	2.0	1.0
12	simazine	89.8	2.4	0.6	96.0	2.0	0.6	95.4	1.6	0.6
13	triclopyr	98.8	0.8	ND	99.0	ND	ND	99.0	ND	ND
14	terbutol	50.4	16.8	6.0	55.6	4.0	2.0	53.6	2.4	1.4
15	MCPP	95.0	0.4	ND	99.0	ND	ND	99.0	ND	ND
16	MCPA	95.4	0.4	ND	99.0	ND	ND	99.0	ND	ND
17	dithiopyr	1.8	1.6	2.0	15.4	6.6	3.0	2.2	4.0	5.4
18	pyributicarb	0.8	ND	ND	4.4	6.6	3.6	0.4	0.2	0.2
19	benefin	0.8	ND	ND	0.8	2.8	2.6	0.1	ND	ND

<sup>a</sup> Each soil (10 g dry weight) collected at sampling points A and B in Figure 1 is packed into the column (10 mm i.d. × 40 mm). Pesticides mixture (10 µg of each pesticide) is loaded on the top of the soil column and eluted with 300 mL of distilled water at 1 mL min<sup>-1</sup>, and leaching water is fractionated. <sup>b</sup> Values in each fractionated leaching water are means from two experiments. ND, less than 0.1% of loading pesticide amount.

fraction with the soil at a depth from 140 to 150 cm was similar to that with the turf grass soil. The difference of pesticide leaching in the soil depth explains the organic carbon contents in soils shown in Table 2. In every soil, the mobility of weakly acidic compounds such as asulam and phenoxy acidic and s-triazine herbicides also exhibited high mobility. The relative mobility of the pesticides containing a nitro group at the benzene ring and phosphorothioate linkage in the side chain of the benzene ring was small. The relative mobility of MCPA, simazine, and atrazine in the soil is in good agreement with the data obtained from soil thin-layer chromatography reported by Helling (37).

For the cause of terbutol persistence at the golf courses,  $t_{1/2}(\text{soil})$  of terbutol in the soil under the laboratory conditions, which were modeled on the conditions in the turf grass soil on golf courses, was similar to that of isoprothioalme or shorter than that of dithiopyr and flutotanol as shown in Table 5. As for the leachability of the pesticides in the soil,  $K_{oc}$  obtained with turf grass soil and the elution pattern of terbutol from the soil columns was similar to that of flutolanil and isoprothiolane. In the previous report for the degradation of terbutol in soils under laboratory conditions, terbutol was degraded oxidatively by microbial in the soil, and its degradation rate decreased extensively by the reduction of the oxygen supplement (16). From these results, the slow degradation rate of terbutol in the subsoil at depth more than 50 cm seems to be the reason for terbutol persistence at the golf courses. The  $t_{1/2}(\text{soil})$  of the pesticides in the turf grass soil under aerobic conditions alone was insufficient to evaluate the persistence of the pesticides at the golf courses. A degradation system modeled on the conditions in the subsoil seems to offer useful data for persistence of the pesticides at the golf courses.

### Conclusion

The loading amount of the pesticides per one application via leaching water was more than 23% of application amounts

for terbutol and lower than 4% for the other pesticides. These loading rates were equal to or greater than that via runoff water. To assess water pollution by the pesticides used at golf courses, it is necessary to consider sufficiently not only loading of pesticides into the drainage via runoff water occurred during rainfall but also loading of the pesticides into the drainage via leaching water.

By predicting pesticides leaching to groundwater with the previous screening-level models for agricultural land, the pesticides having a GUS score greater than 0.4 or exhibiting  $K_{oc}$  less than 7000 cm<sup>3</sup> g<sup>-1</sup> and  $t_{1/2}(\text{soil})$  greater than 3 days were classified as the pesticides leaching to groundwater through the soil at golf courses. The golf courses were high pollution potential area compared with agricultural land.

The cause of detecting terbutol in the drainage and groundwater for a long period after its application was investigated. Terbutol concentrations in the subsoils at the depth more than 50 cm were higher than the other pesticides in the field. Relative mobility of terbutol in the soil column was the same as isoprothiolane and flutoranil, and  $t_{1/2}(\text{soil})$  of terbutol in turf grass soil were shorter than flutoranil and dithiopyr. The slow-degradation rate of terbutol in the subsoils seems to be the reason for terbutol persistence.

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