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Variation of 4,5,6,7-Tetrachlorophthalide in Water After Aerial Application to Rice Cultivation Area

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Abstract Variation in the fungicide, 4,5,6,7-phthalide, in water was investigated in order to evaluate the runoff of the fungicide after aerial application to paddy fields by a radio-controlled helicopter. The survey was conducted for 4 months after the application. The average and maximum concentrations of phthalide were 3.7–4.4 μg/L and 30.5–33.8 μg/L in the paddy fields, 0.37–0.64 μg/L and 2.7–7.5 μg/L in the drainage channels, and 0.18 and 0.83 μg/L in a river, respectively. The runoff ratios of the aerially applied phthalide from the paddy fields into the drainage channels were calculated to be 1.7–2.4%.

Keywords Pesticide · Runoff · Water · Drainage

Paddy rice farming has been playing an important role in food production around the world. A large number of pesticides are applied to paddy fields with the consequence that pesticide runoff from the paddy fields impacts the water environment (Wang et al. 2007; Watanabe et al. 2007). In Japan, paddy fields covered a total area of 2.54 million ha, and accounted for 54.46% of the total cultivated area (4.67 million ha) in 2006. More than 100 kinds of pesticides are applied to paddy fields, and some of the applied pesticides flow from the paddy fields into rivers and lakes through drainage channels (Inao et al. 2003; Kawata et al. 2005; Nakano et al. 2004; Tanabe et al. 2001). Some pesticides have been aerially applied to paddy fields in Japan. Among them, 4,5,6,7-tetrachlorophthalide (phthalide) is a common fungicide in Japan. Phthalide is mainly applied to paddy fields in May to August against the rice blast, which is one of the most destructive diseases of rice. The water solubility and the logarithm of the octanol–water partition coefficient (log P_{OW}) are reported to be 2.5 mg/L and 3.01 (British Crop Protection Council 2000), respectively.

We have previously reported the runoff ratios of phthalide aerially applied by helicopters (Mitobe et al. 1999). Although radio-controlled helicopters have recently been used for pesticide spraying instead of manned helicopters, few reports have been published on the behavior and runoff ratios of pesticides applied by these radio-controlled helicopters. Therefore, we have previously investigated variations in the concentrations of phthalide in paddy field waters, drainage channel waters and river waters after application by a radio-controlled helicopter in August 2005, and evaluated the runoff ratios of phthalide (Shiota et al. 2006). The investigation in 2005 was conducted for 9 days after the application, because the concentrations in the water samples significantly decreased over this the period. However, phthalide could be detected at 0.01 μg/L levels from river waters in September (Mitobe et al. 1999; Tanabe et al. 2001). Therefore, we investigated the variations in the concentrations of phthalide aerially applied in August 2006 to evaluate a longer runoff period of the fungicide. In this paper, we describe the runoff of phthalide from the paddy fields to the river through the drainage channels during August to December.

Materials and Methods

The investigated area and the sampling sites were the same as the investigation on August 2005. Phthalide was aerially

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sprayed by a radio-controlled helicopter at 18 mg/m^2 on a rice cultivation area in Agano City, Niigata, Japan, on August 4–6, 2006. The locations of the sampling sites were previously reported (Shiota et al. 2006). Water samples were collected from paddy fields 1 and 2 (sites A and B) with areas of 1,470 and 1,200 m^2, respectively. Phthalide was applied to the paddy fields on August 4. Samples were also collected from drainage channels 1 and 2 at sites C and D, respectively, as well as the Anno River at site E. The drainage areas flowing to sites C and D were 168,000 and 1,082,000 m^2, respectively. The drainage from paddy fields 1 and 2 flowed to drainage channel 1 and then drainage channel 2. The drainage from drainage channel 2 then flowed into the Anno River. The sampling sites C, D and E were located on the downstream side of the investigated paddy fields.

The sample collection and the determination of phthalide were performed using a previously published method (Shiota et al. 2006). Briefly, the sample water (50–500 mL) was passed through a Waters Sep-Pak Plus C18 cartridge at 10 mL/min. After the cartridge was washed with 10 mL of purified water, it was dried by passing air over it for 5 min at 2.7 kPa using an aspirator. Phthalide collected on the cartridge was eluted with 6 mL of acetone at 1 mL/min. The obtained eluate was concentrated to 1 mL under a pure nitrogen gas stream. A 0.5 μg of 9-bromoanthracene was added to the concentrated solution as an internal standard. All the samples were stored at −20°C until the GC/MS analysis. A 1-μL aliquot of the resulting solution was analyzed by GC/MS (Shimadzu GCMS-QP5050A, Kyoto, Japan), equipped with a 30 m × 0.25 mm id (0.25-μm film thickness) fused-silica SGE BPX-5 column (Victoria, Australia). The GC/MS conditions were as follows: column temperature, programmed from 100°C (held for 1 min) to 280°C (held for 3 min) at a rate of 20°C/min; injector temperature, 250°C; injection mode, splitless; helium carrier gas flowrate, 1.0 mL/min; MS transfer temperature, 290°C; ion source temperature, 250°C; ionization mode, electron impact; ionization energy, 70 eV. The quantitation ions for phthalide and 9-bromoanthracene were 243 and 256, respectively.

Results and Discussion

The phthalide concentrations in paddy waters are summarized in Table 1. Since the investigated period in 2006 was different from that (4 days after the application) in the 2005 investigation, the results during the same period with the investigation in 2005 are also shown in the table. The average and the maximum concentrations were 1.4–2.3 times and 1.3–3.0 times those in 2005, respectively. The variations in the phthalide concentrations in the paddy waters at sites A and B are shown in Fig. 1. The maximum concentrations (1 h after application) were 33.8 μg/L at paddy field 1 and 30.5 μg/L at paddy field 2. The phthalide concentrations in paddy fields 1 and 2 decreased to 2.3–4.3 and 0.83–1.0 μg/L after 24–28 h, and 0.04 and <0.01 μg/L after 4 days, respectively.

Table 1 Phthalide in waters from paddy fields

Year	Paddy field	Concentration (μg/L)			Amount (g)		
		Average	Max	Min	Average	Max	Min
2006[a]	1 (site A)	4.4	33.8	<0.01	0.092	0.46	0.0024
	2 (site B)	3.7	30.5	<0.01	0.037	0.37	<0.00002
2006[b]	1	6.4	33.8	1.8	0.13	0.46	0.04
	2	5.6	30.5	<0.01	0.056	0.37	<0.00002
2005[b,c]	1	4.6	25.4	<0.01	0.28	2.6	<0.00002
	2	2.4	10.2	<0.01	0.15	1.2	<0.00002

[a] Results during 14 days after the application

[b] Results during 4 days after the application

[c] Shiota et al. (2006)

The variations in the phthalide amounts in the paddy fields are given in Fig. 2. The applied phthalide amounts to paddy fields 1 and 2 were calculated to be 26.5 and 21.6 g, respectively. The phthalide amounts in the waters of paddy fields 1 and 2 were 0.46 and 0.37 g 1 h after the application, respectively (Table 1). These values were 1.7% of the phthalide amounts applied to the paddy fields. The ratios were a third to a sixth of the ratios in 2005 (Shiota et al. 2006). This was caused by the smaller volumes of paddy waters in 2006 compared to the volumes in 2005. This implied that the larger amounts of phthalide transferred to the paddy soils in 2006 compared to those in 2005. The phthalide amounts in the paddy waters varied from the maximum values to 0.0024 g in paddy field 1 and less than 0.0001 g in paddy field 2 after 14 days of the application.

The phthalide concentrations in the water from the drainage channels (sites C and D) and the Anno River (site E)

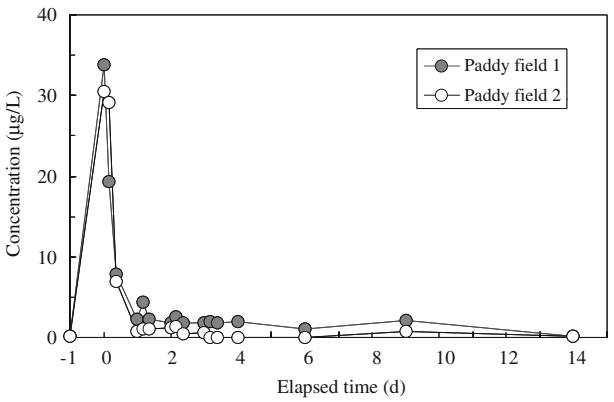

Fig. 1 Variations in phthalide concentrations in paddy waters

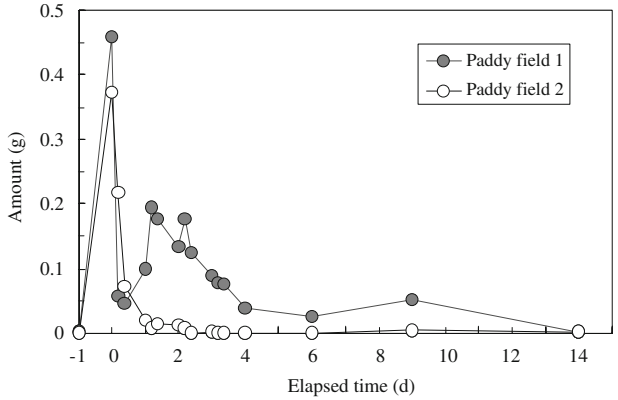

Fig. 2 Variations in phthalide amounts in paddy waters

Table 2 Phthalide in waters from drainage channels and the Anno River

Year	Site	Concentration (μg/L)			Load (g/h)		
		Average	Max	Min	Average	Max	Min
2006[a]	Drainage 1	0.62	7.5	<0.03	0.11	1.2	<0.0001
	Drainage 2	0.36	2.7	<0.03	0.50	3.0	<0.0003
	Anno River	0.17	0.86	<0.03	5.5	31	<0.1
2006[b]	Drainage 1	1.0	7.5	0.15	0.19	1.2	0.028
	Drainage 2	0.59	2.7	0.15	0.85	3.0	0.27
	Anno River	0.26	0.86	0.13	8.6	31	2.9
2005[b,c]	Drainage 1	0.97	6.4	0.15	0.12	0.62	0.012
	Drainage 2	0.59	2.0	0.14	1.1	4.6	0.044
	Anno River	0.26	0.68	0.07	13	55	2.2

[a] Results during 137 days after the application

[b] Results during 9 days after the application

[c] Shiota et al. (2006)

are summarized in Table 2. The average and maximum concentrations at the investigated sites were almost comparable to those in the 2005 investigation. The variations in the phthalide concentrations in the drainage channels and the river are given in Fig. 3. The maximum concentration in drainage channel 1 was observed within 1 h after the application on August 4 in the area including paddy fields 1 and 2, and then decreased to 0.32 μg/L within 1 day after the application. On the other hand, the concentration in drainage channel 2 increased to 1.7 μg/L after the application on August 4, the maximum concentration (2.7 μg/L) after the application on August 5, and 0.64 μg/L after the application

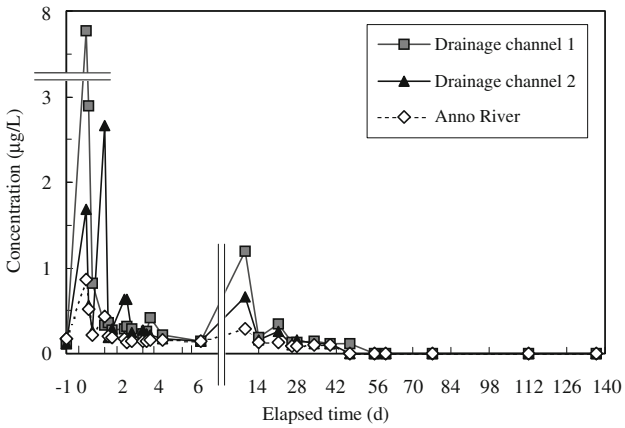

Fig. 3 Variations in phthalide concentrations in waters from drainage channels and the Anno River

on August 6. This reflects the fact that the drainage waters from the applied areas on the 3 days flowed into drainage channel 2. The concentration in the Anno River increased to the highest value on August 4 and to 0.43 μg/L on August 5. On August 13 (9 days after the application on August 4), remarkable increases in the concentrations were observed at sites C–E. These increases were caused by the rainfall (35 mm) of August 12 as will be mentioned later. The concentrations decreased to below the minimum detection limit at 56 days after the application (September 29) in drainage channel 1 and at 47 days after the application (September 20) in drainage channel 2 and the Anno River. These results are consistent with those previously reported that phthalide was predominantly detected in July to August from the rivers in Niigata Prefecture, while it decreased to below the detection limit in the middle of September (Mitobe et al. 1999; Tanabe et al. 2001).

Figure 4 shows the variations in the runoff loads of phthalide in the drainage channel waters. A significant runoff event occurred in drainage channels 1 (1.2 g/h) and 2 (2.2 g/h) as well as the Anno River (31 g/h) immediately after the application on August 4. A significant runoff event the occurred in drainage channel 2 (3.0 g/h) and the Anno River (13 g/h) after the application on August 5; a distinct runoff event was observed in drainage channel 2 (0.96 g/h) after the application on August 6. These events appeared to be caused by the drainage of the paddy water in the drainage area flowing into the channel as well as the drifts of the applied phthalide in air to the channel. The runoff load of phthalide in the drainage channels and the Anno River are also summarized in Table 2. Although the variations at the investigated sites in this study were different from those from the 2005 investigation (Shiota et al. 2006), the average and maximum loads at the investigated sites were almost comparable to those in 2005.

Furthermore, an additional distinct runoff event occurred 9 days after the application (August 13) in drainage

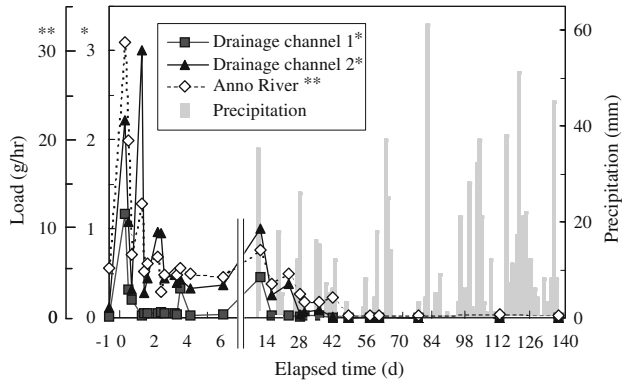

Fig. 4 Variations in phthalide loads in waters from drainage channels and the Anno River

Table 3 Phthalide runoff from paddy fields

Site	Applied amount (g)	Runoff amount (g)			Runoff ratio (%)		
		2006[a]	2006[b]	2005[b,c]	2006[a]	2006[b]	2005[b,c]
Drainage 1	3024	74	60	47	2.4	2.0	1.6
Drainage 2	19400	321	219	320	1.7	1.1	1.7
Anno River	–	4700	1380	4350	–	–	–

[a] Runoff during 137 days after the application

[b] Runoff during 9 days after the application

[c] Shiota et al. (2006)

channels 1 (0.46 g/h) and 2 (1.0 g/h) as well as the Anno River (7.7 g/h). These runoffs were caused by the rainfall (35 mm) of August 12. Transport of the pesticides by surface runoff during the rainfall events is a major process contributing to the pesticide contamination in the rivers (Fox et al. 2007; Guo et al. 2004). The runoffs into drainage channels 1, 2 and the Anno River on August 13 were estimated to be 29, 75 and 690 g, which were 40%, 23% and 15% of the total runoff amounts during the 137 days investigation (Table 3), respectively. In 2005, major runoffs occurred during 5–7 days after the application owing to an 87 mm total precipitation (Shiota et al. 2006). The runoffs into drainage channels 1, 2 and the Anno River over the 3 days were estimated to be 21, 170 and 2780 g, which were 44%, 52% and 64% of the total runoff amounts in the 2005 investigation (Table 3).

The runoff ratio of phthalide was evaluated using the runoff load of phthalide in a drainage channel. RR was calculated using the following Eq. 1:

$$R_R = 100(A_R/A_A) \quad (1)$$

where R_R is the runoff ratio, A_R is the runoff amount, and A_A is the applied amount. The runoff ratios were calculated for sites C and D. The calculated runoff ratios are listed in Table 3 together with the results of the 2005 investigation (Shiota et al. 2006). The runoff ratios of phthalide during 9 days after the application were calculated to be 2.0% at site C and 1.1% at site D. These values were almost comparable to those in 2005. The ratios during the 10–137 days after the application were only 0.4% at site C and 0.6% at site D. Therefore, 65–83% of the total runoffs occurred during the 9 days after the application. Consequently, the runoff ratios of the aerially applied phthalide from paddy fields were 1.6–2.4% in the 2005 and 2006 investigations, depending the volume of the paddy water as well as the overflow and drained volumes from the paddy water.

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