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Decrease of 4,5,6,7-Tetrachlorophthalide in Paddy Field Soil After Aerial Application

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Abstract Variation in the fungicide, 4,5,6,7-tetrachlorophthalide (phthalide), in paddy field soil was investigated in order to evaluate its decrease after aerial application by a radio-controlled helicopter. The maximum concentrations of phthalide were 309–320 μg/kg dry, which were 83%–96% of the applied phthalide. The organic carbon normalized soil sorption coefficient (K_{oc}) was calculated to be 94–96 mL/g at 1 h after the application. The calculated K_{oc} values increased to 620–1,300 mL/g from 1 through 9 days after the application and then 4,700–7,200 mL/g 14 days after the application. The half-life of the phthalide was calculated to be 20–31 days.

Keywords Pesticide · Soil · Sorption coefficient · Half-life

Paddy rice farming has been playing an important role in food production in a large number of countries. In Japan, rice is the major agricultural product, and the paddy field for rice farming covers more than 50% of the total cultivated area. Several hundred kinds of pesticides have been applied to paddy fields in Japan; some pesticides are aerially applied to the paddy fields. Among them, 4,5,6,7-tetrachlorophthalide (phthalide) is a common fungicide in Japan. 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. Phthalide is mainly applied to paddy fields in May through August against the rice blast, which is one of the most destructive diseases of rice.

We have previously investigated variations in the concentrations of phthalide in paddy field water, drainage channel water and river water after application by a radio-controlled helicopter, and evaluated the runoff ratios of phthalide from the paddy fields (Shiota et al. 2006; Maeda et al. 2008). The runoff ratios of the applied phthalide from the paddy fields were 1.6%–2.4%. Moreover, the maximum phthalide amounts in the waters of the investigated paddy fields were 1.7%–9.9% of the phthalide amounts applied to the paddy fields. Therefore, it appears that adsorption into the paddy soil could be the main route of residual phthalide. There are several reports about the behavior of pesticides in soil, e.g. herbicides (Amano et al. 2001; Ishii et al. 2004; Dorado et al. 2005), nematicide (Qin et al. 2004) and insecticides (Shegunova et al. 2007). However, few reports have been published on the behavior of phthalide in paddy soil after the application by radio-controlled helicopters. In this paper, we describe the variations in the phthalide concentrations in paddy field soils after application by a radio-controlled helicopter, and evaluate the decreasing rates of phthalide in the paddy fields as well as the partitions of phthalide between the paddy soil and water.

Materials and Methods

A gas chromatograph-mass spectrometer (GC/MS) model, Shimadzu GCMS-QP5050A, Kyoto, Japan, was used for the quantitative analyses. A 30 m × 0.25 mm i.d. (0.25 μm film thickness) fused-silica BPX-5 column (SGE,

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Ringwood, Victoria, Australia) was used for the gas chromatographic separation.

Acetone, hexane, anhydrous sodium sulfate (pesticide grade) and phthalide (>99%) were purchased from Kanto Kagaku (Tokyo, Japan). 9-Bromoanthracene purchased from Aldrich (Milwaukee, WI, USA) was used as the internal standard. Standard solutions of phthalide and an internal standard solution (50 μg/mL) were prepared in acetone. The purified water was from a Milli-Q system (Millipore, Bedford, MA, USA).

The experiments were carried out at two paddy fields (paddy fields 1 and 2) located in Agano City, Niigata, Japan (Shiota et al. 2006). Paddy fields 1 and 2 had areas of 1,470 and 1,200 sq m, respectively. Phthalide was aerially sprayed at 18 mg/sq m by a radio-controlled helicopter on August 4, 2006. The paddy waters in paddy fields 1 and 2 were 9.2 and 10.2 mm in depth during application of the phthalide, respectively. Soils were collected from the 0–4 cm surface layer at four locations in a paddy field, and the equal weights of these soils were combined and mixed well as samples. Twenty samples were collected from each the paddy field during August 3 to December 19, 2006. Paddy waters were also sampled from the paddy fields during August 3–18. The results of the water samples were previously reported (Maeda et al. 2008). The water contents of paddy soils 1 and 2 were 26.5 ± 1.3% and 23.3 ± 3.2%, respectively; the soil densities were 1.30 ± 0.13 g/cu cm (paddy soil 1) and 1.33 ± 0.13 g/cu cm (paddy soil 2). The organic content was estimated as the loss on ignition (550°C, 15 h) and calculated as percent dry weight (Emilsson and Rolf 2005; Kawata et al. 2005). The organic contents of paddy soils 1 and 2 were 9.7% ± 2.4% and 11.0% ± 3.4%, respectively. All samples were stored at 5°C in the dark, and were extracted within 24 h after collection.

The extraction of phthalide from the soil samples was carried out according to a previously published method (Kawata et al. 2005) without the purification procedures. The procedure is as follows. A 10 mL portion of acetone was added to a 10 g soil sample. The mixture was ultrasonicated for 15 min and then shaken at 2,500 strokes/min for 15 min. The slurry was centrifuged at 3,000 rpm (1,700 × *g*) for 10 min. The supernatant solvent phases were filtered through the glass-fiber filter. The extraction procedure was repeated twice. The extracts were combined and evaporated to 5 mL at 30°C. The solution was added to 10 mL hexane, and the resulting solution was washed four times with 2 mL purified water.

After the hexane layer was dried over anhydrous sodium sulfate, the combined eluates were concentrated to ca 1 mL under a stream of purified nitrogen, and the solution was concentrated to 1 mL under a stream of pure nitrogen gas. A 10 μL aliquot of the internal standard solution was added to the concentrated solution. 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. 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-bromanthracene were 243 and 256, respectively. Phthalide was determined using the internal standard method. The phthalide concentrations were calculated as a dray basis. The phthalide amounts in the paddy surface layer (0–4 cm) were calculated from the concentrations (μg/kg dry) on the basis of the surface area and the soil densities of the paddy fields.

The correlation coefficient (*r*) of the calibration curve was 0.999. The linear range of the standard curve was from 0.02 to 0.5 ng. The minimum detection limit was 4 μg/kg. The overall recovery of phthalide from the paddy soil sampled from paddy field 1 on August 3 was investigated by adding 0.1 μg of phthalide to 10 g of the soil. Phthalide was not detected in the blank sample. The mean of the overall recoveries and relative standard deviation (n = 3) were 78% and 1.9%, respectively.

Results and Discussion

Phthalide was not detected in paddy soils 1 and 2 on August 3. The phthalide concentrations in the paddy soils after the aerial application on August 4 are summarized in Table 1. The maximum concentrations were observed 1 h after the application to both paddy fields. Phthalide was detected from August 4 through November 24 (112 d after the application), while not detected on December 19 (137 days after the application) in both paddy fields.

The phthalide amounts in the surface soils after the application are also summarized in Table 1. The applied phthalide amounts to paddy fields 1 and 2 were calculated to be 26.5 and 21.6 g, respectively. Therefore, the maximum amounts (21.9 and 20.7 g) were 83% and 96% of the applied phthalide in paddy fields 1 and 2, respectively. At that time, 1.7% of the applied phthalide amounts existed in

Table 1 Phthalide in soils from paddy fields

Paddy field soil	Concentration (μg/kg dry)			Amount (g)		
	Average	Max	Min	Average	Max	Min
1	114	309	<4	8.6	21.9	<0.3
2	86	320	<4	5.6	20.7	<0.3

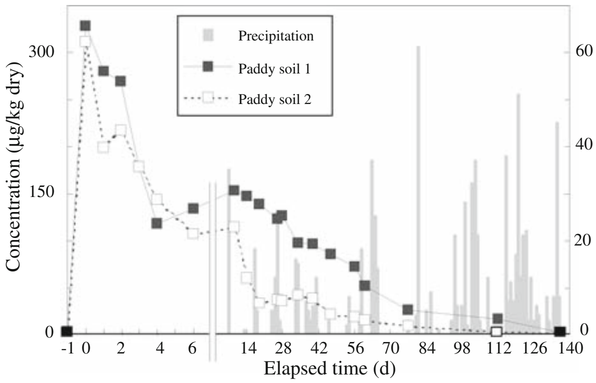

Fig. 1 Variations in phthalide concentrations in paddy soils

the paddy waters (Maeda et al. 2008). The variations in the phthalide concentrations in the paddy soils are given in Figure 1 along with the precipitation. The phthalide amounts in paddy soils 1 and 2 decreased to 18.7 g (70% of the applied amount) and 13.3 g (62%) on August 5, and to 8.9 g (34%) and 7.2 g (33%) on August 10 (6 days after the application), respectively. Amano et al. (2001) reported the behavior of thiobencarb and mefenacet when applied to a paddy field. The amounts of the herbicides in the paddy soil were maximized (about 20% of the applied amounts) 3–4 days after their applications, while about 15% of the applied herbicides existed in the paddy water (60–120 mm in depth). The behavior of phthalide in this study was different from the reported results. This could be predominantly caused by the differences in the paddy water depth as well as the properties of the pesticides.

In the investigated paddy fields, paddy waters were present from August 3 through August 18 except for August 8 and 10 in paddy field 2. Therefore, phthalide was distributed among the soil and the water in the paddy fields during this period. Figure 2 shows the phthalide amounts in the paddy soils together with those in the paddy waters (Maeda et al. 2008) during this period. The phthalide amounts in paddy waters 1 and 2 accounted for 2.1% and 1.8% of the total phthalide residues in the paddy fields 1 h after the application. The ratios in paddy waters 1 and 2 decreased to 0.53% and 0.14% on August 5 (1 day after the application), then to 0.024% and 0.025% on August 18 (14 days after the application), respectively.

The organic carbon normalized soil sorption coefficient (K_{oc}) was calculated using the following Eq. 1:

$$K_{oc} = (C_s/C_w) \times (100/C_{oc}) \quad (1)$$

where C_s and C_w are the phthalide concentrations in the paddy soil (μg/kg) and the paddy water (μg/L), respectively, and C_{oc} is the concentration of the organic carbon (%). The variations in the calculated K_{oc} values (mL/g) are given in Fig. 3. The K_{oc} value of phthalide, reported as 738 (Kanazawa 1996), is also given in the figure. The calculated K_{oc} values, 94 and 96 mL/g, in paddy fields 1 and 2, respectively, 1 h after the application were one-eighth of the reported value, indicating that the applied phthalide was not distributed between the soil and water in the ratio at equilibrium, existing more in the paddy water than under the equilibration conditions. The calculated K_{oc} values during days 1 through 9 after the application increased to 620–1,300 mL/g (990 ± 270 mL/g in average) and 1,600–2,700 mL/g (2,200 ± 520 mL/g in average) in paddy fields 1 and 2, respectively. The average values were 1.3 and 2.9 times of the reported value. The calculated values increased to 7,200 and 4,700 mL/g (9.7 and 6.3 times of the reported value) 14 days after the application.

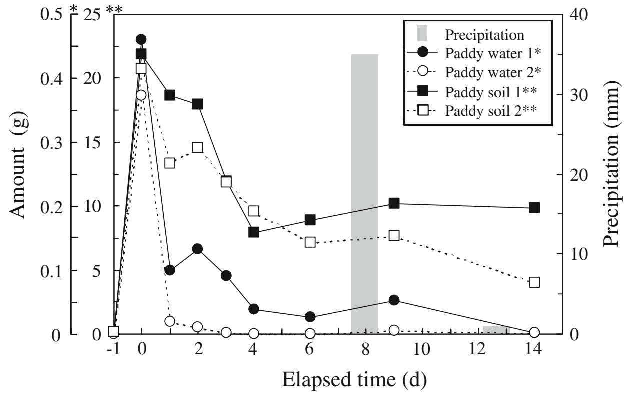

Fig. 2 Variations in phthalide amounts in paddy waters and soils. Data of paddy waters are cited from Maeda et al. (2008)

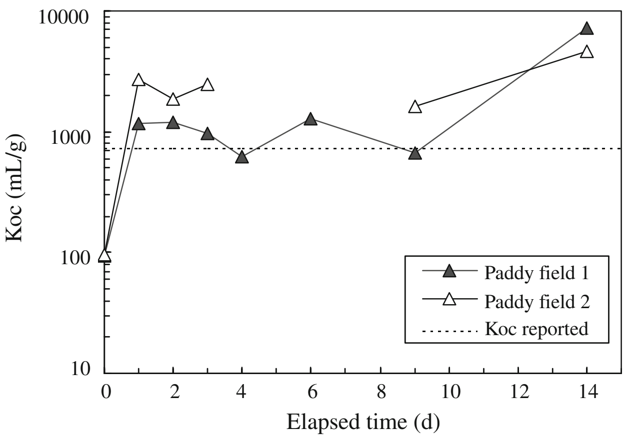

Fig. 3 Variations in calculated K_{oc} values in paddy fields

The decrease of phthalide in the soil could be interpreted using first-order reaction kinetics (Qin et al. 2004) in the following equation:

$$\text{In}\ A = kt + C \quad (2)$$

where A is the amount of phthalide in the paddy soil (g), k is the decreasing rate (/day), t is the elapsed time after the

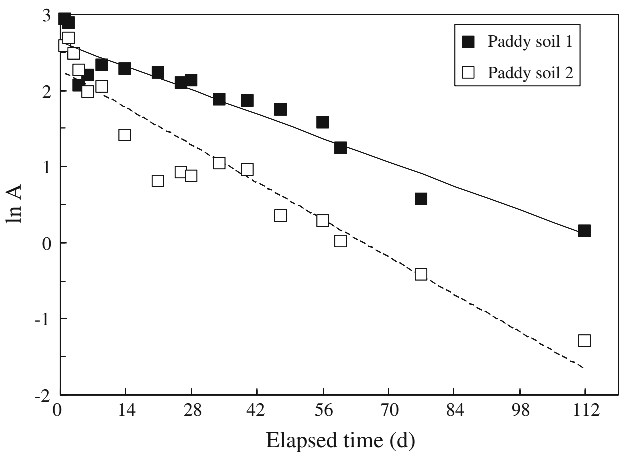

Fig. 4 Natural logarithm of phthalide amount in paddy soil versus elapsed time with regression lines by the least-squares method

Table 2 DT_{50} values of phthalide in paddy field soils

	k (/day)	C	n	r^2	p	DT_{50} (days)
Paddy soil 1	−0.0224	2.631	18	0.911	<0.01	31
Paddy soil 2	−0.0349	2.220	18	0.915	<0.01	20

aerial application (days) and C is a constant. Figure 4 shows the ln A values versus elapsed time with the regression lines using the least-squares method. The decreasing plots of paddy field soils 1 and 2 were well fitted to the first order reaction given by Eq. 2. The calculated k values and the determination coefficients (r^2) are given in Table 2. The natural logarithm of the phthalide amount in the paddy soil concentration significantly correlated ($p < 0.01$) with the elapsed time.

To evaluate the decreasing rate of phthalide in the soil, the half-life (DT_{50}) was estimated using the established relation (Table 2). The DT_{50} value in paddy soil 1, estimated to be 31 days, was 1.5 times that in paddy soil 2 (20 days). The half-life of phthalide in the soil was reported to be 70 days (Kanazawa 1996). The obtained DT_{50} values were 0.44 and 0.28 of the reported half-life value for paddy soils 1 and 2, respectively. The decreasing rate could depend on the matrix of the soil including the organic matter content and the clay content. Qin et al. (2004) reported that the degradation rate of a nematicide, fosthiazate, correlated inversely with the organic matter content or clay content. The organic content of paddy soil 1, 9.7% ± 2.4%, was smaller than that of paddy soil 2, 11.0% ± 3.4%, while the decreasing rate in paddy soil 1 was slower than that in paddy soil 2. This result did not agree with that of fosthiazate. García-Valcárcel and Tadeo (1999) reported that the degradation rates of two herbicides, hexazinone and simazine, increased with the soil moisture content. However, the decreasing rate in paddy soil 1 with the water content of 26.5% ± 1.3% was lower than the rate in paddy soil 2 with the content of 23.3% ± 3.2%. These different tendencies between the decreasing rate and the organic matter or moisture content could be attributed to the properties of the investigated pesticides as well as those of the investigated soils. Moreover, we dealt with the phthalide decrease in the surface soil in this study. Therefore, the obtained results reflected not only the degradation of phthalide, but also the potential migration of phthalide into the deeper layer of the paddy soil (López-Pérez et al. 2006).

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