Bull. Environ. Contam. Toxicol. (2006) 77:508–515

DOI: 10.1007/s00128-006-1093-9

Bulletin of Environmental Contamination and Toxicology

Runoff of Aerially Applied Phthalide from Paddy Fields

N. Shiota, T. Hori, K. Nissato, T. Asada, K. Oikawa, K. Kawata

Faculty of Applied Life Sciences, Niigata University of Pharmacy and Applied Life Sciences, 265-1 Higashijima, Niigata, Niigata 956-8603, Japan

Received: 15 June 2006/Accepted: 15 August 2006

Several hundred different pesticides are applied worldwide to agricultural crops. The movement of pesticides from cultivated areas into the environment has been an ecological and human health concern. Pesticide runoff from agricultural lands impacts the water environment. Commonly used pesticides have been detected in river waters (Lerch and Blanchard 2003, Mitobe et al. 1999, Shipitalo and Owens 2003, Southwick et al. 2003, Tanabe et al. 2001). Spray drift and runoff are important routes of pesticides to surface water (Schulz 2001). The runoff ratios of the applied herbicides from cultivated areas to drainage channels or rivers were reported for the insecticides endosulfan (Schulz 2001), diazinon and fenitrothion (Sudo et al. 2002, Mitobe et al. 1999), the herbicides atrazine, metolachlor (Southwick et al. 2003), mefenacet (Inao et al. 2003), clomeprop and oxaziclomefone (Kawata et al. 2005), and the fungicides isoprothiolane (Sudo et al. 2002), phthalide and tricyclazole (Mitobe et al. 1999).

Paddy rice farming plays an important role in the food production in Japan. In 2004, paddy fields had a total area of 2.57 million ha, and accounted for 54.6 % of the total cultivated area (4.71 million ha) in Japan. A large number of pesticides have been aerially applied to paddy fields using helicopters. We have previously reported runoff ratios of pesticides aerially applied by helicopters (Mitobe et al. 1999). Recently, radio-controlled helicopters have been used for pesticide spray instead of manned helicopters. However, few reports have been published on the behavior and runoff ratios of pesticides applied by radio-controlled helicopters. In this paper, we describe the variations in the phthalide concentrations in paddy field waters, drainage channel waters and river waters after application by a radio-controlled helicopter, and evaluate the runoff ratios of phthalide.

Phthalide (4,5,6,7-tetrachlorophthalide) is a common fungicide in Japan. The water solubility and the logarithm of the octanol–water partition coefficient (log P_{ow}) are reported as 2.5 mg/L and 3.85 (Kanazawa 1996), 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. Phthalide has been detected in Japan from river waters (Mitobe et al. 1999; Tanabe et al. 2001), the atmosphere (Kawata et al. 1995) and rainwaters (Suzuki et al. 2003).

Correspondence to: K. Kawata

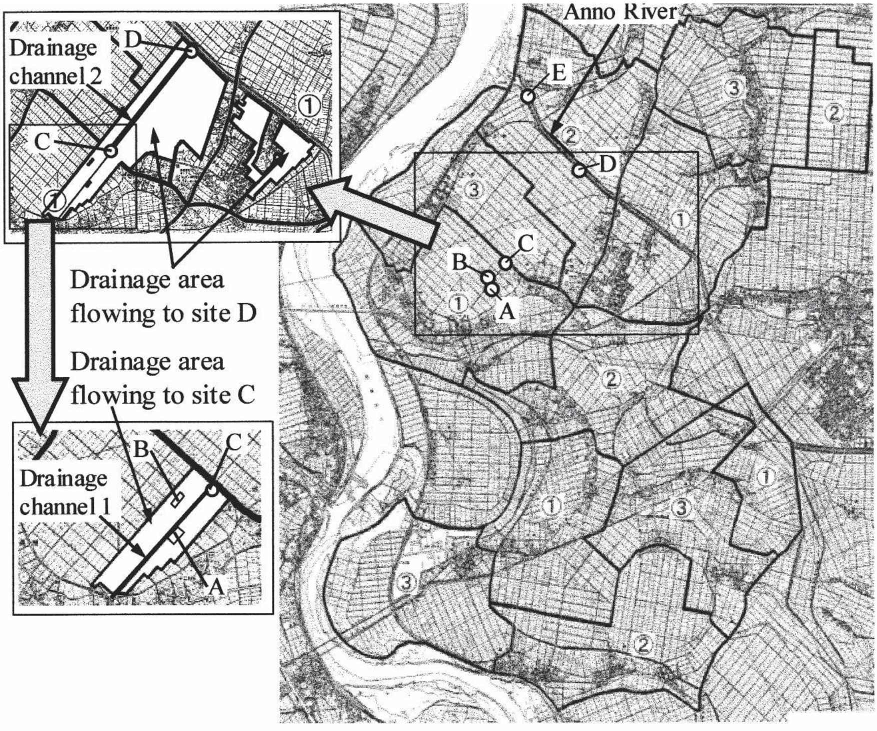

Figure 1. Investigated area and sampling points. A, paddy field 1; B, paddy field 2; C, drainage channel 1; D, drainage channel 2; E, Anno River.

MATERIALS AND METHODS

Phthalide was aerially sprayed by a radio-controlled helicopter AYH3 (Yanmer, Osaka, Japan) to a rice cultivation area in Agano City, Niigata, Japan on August 5 - 7, 2005. Figure 1 shows the applied area and the sampling points. Phthalide was applied at 18 mg/sq m to the areas indicated as ①, ② and ③ on August 5, 6 and 7, respectively. Water samples were collected from two paddy fields (1 and 2) in the area (sites A and B, respectively). The paddy waters were sampled at 4 points in a paddy field, and the equal volumes of these water samples were combined. Paddy fields 1 and 2 were 1470 and 1200 sq m in area, respectively. Phthalide was applied to the paddy fields on August 5. Samples were also collected from two drainage channels (1 and 2) at sites C and D, respectively, and the Anno River at site E. The drainage from paddy fields 1 and 2 flowed to drainage channel 1 and then drainage channel 2. The sampling sites C and D were located on the downstream side of the paddy fields. The drainage areas flowing to sites C and D were 168,000 and 1,082,000 sq m, respectively. The drainage from drainage channel 2 flowed into the Anno River. All samples were stored at 5 °C in the dark, and were analyzed within 24 hours after collection.

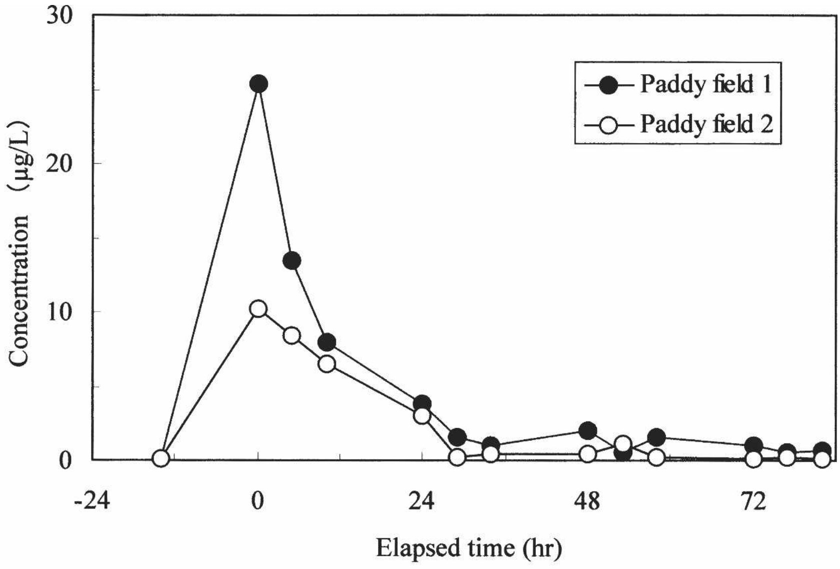

Figure 2. Variation in phthalide concentration in paddy waters.

A Waters Sep-Pak Concentrator was used for the solid phase extraction. A gas chromatograph–mass spectrometer (GC/MS) model, Finnigan POLARIS Q, equipped with a Combi Pal auto injection system (CTC Analytics, Zwingen, Switzerland) 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, Ringwood, Victoria, Australia) was used for the gas chromatographic separation.

Acetone (pesticide grade) and phthalide (>99 %) were both purchased from Kanto Kagaku (Tokyo, Japan). 9-Bromoanthracene purchased from Aldrich (Milwaukee, WI, USA) was used as the internal standard. Standard solutions of phthalide (1000 and 50 μg/mL) 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 Waters Sep-Pak Plus C_{18} cartridges were washed with 5 mL of acetone, followed by 10 mL of the purified water prior to use.

The determination of phthalide was performed using a previously published method (Tanabe et al. 2000). A C_{18} cartridge was used instead of a styrene-divinylbenzene copolymer cartridge. Briefly, the sample water (50 – 500 mL) was passed through a C_{18} 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 10 μL aliquot of the internal standard solution was added to the concentrated solution. The eluates from the paddy waters sampled

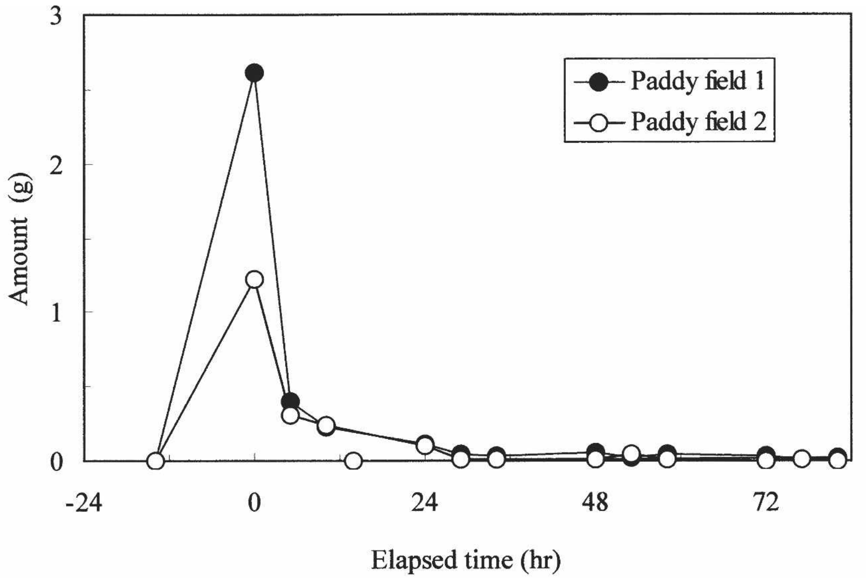

Figure 3. Variation in phthalide amount in paddy waters.

within 24 hours after the application were diluted 10 fold with acetone. To a 1 mL aliquot of the solution, 10 μL of the internal standard solution was added. 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; mass scan range, m/z 50–350. The quantitation ions for phthalide and 9-bromanthracene were 243 and 256, respectively.

The correlation coefficient (*r*) of each calibration curve was 0.999. The linear range of the standard curve was from 0.01 to 1 ng. The minimum detection limit was 0.01 μg/L. The overall recoveries of the target herbicides from 500 mL of the drainage channel water were investigated by adding 0.2 μg of phthalide to the water. A drainage channel water sample (500 mL) was used as the blank sample. No target herbicides were detected in the blank sample. The mean of overall recoveries and relative standard deviation (n = 3) were 87 and 9.2 %, respectively.

RESULTS AND DISCUSSION

The variations in the phthalide concentrations in the paddy waters at sites A and

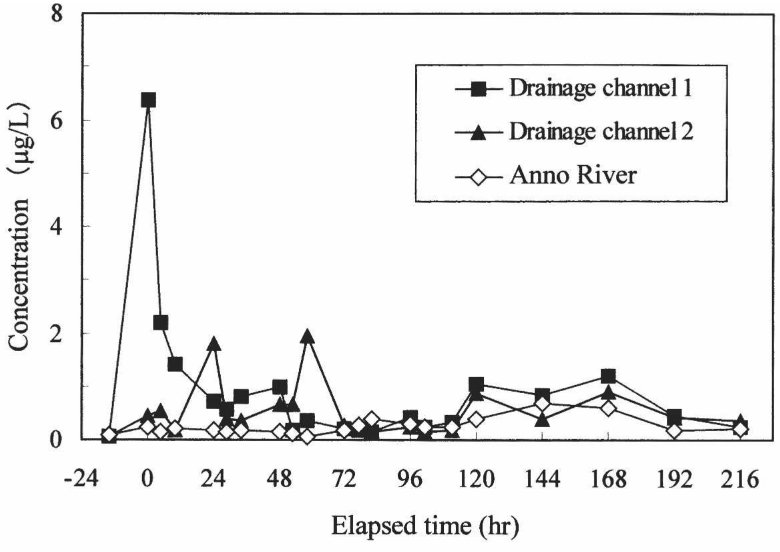

Figure 4. Variation in phthalide concentration in waters from drainage channels and the Anno River.

B are shown in Figure 2. The maximum concentrations (one hour after application) were 25.4 μg/L at paddy field 1 and 10.2 μg/L at paddy field 2. The phthalide concentrations at the paddy fields 1 and 2 decreased to 3.8 and 3.0 μg/L after 24 hours, and 2.0 and 0.40 μg/L after 48 hours, respectively. These values at paddy fields 1 and 2 were 15 and 29 % of the maximum concentrations, respectively, within 24 hours, and 7.8 and 3.9 % within 48 hours.

The variations in the phthalide amounts in the paddy fields are given in Figure 3. The applied phthalide amounts to paddy fields 1 and 2 were calculated to be 26.5 and 21.6 g. The phthalide amounts in the waters of paddy fields 1 and 2 were 2.62 and 1.23 g one hour after the application, respectively. These values were 9.9 and 5.7 % (mean, 7.8 %) of the phthalide amounts applied to paddy fields 1 and 2, respectively. The ratios of the amounts in the paddy waters to the applied amounts decreased to 0.42 and 0.50 % (mean, 0.46 %) after 24 hours, and 0.22 and 0.066 % (mean, 0.14 %) after 48 hours, respectively. The ratio in each the paddy had decreased to <0.04 % after 96 hours.

Figure 4 shows the variations in the phthalide concentrations in waters from the drainage channels (sites C and D) and the Anno River (site E). The concentrations ranged from 0.05 to 6.4 μg/L at drainage channel 1, 0.06 to 1.9 μg/L at drainage channel 2, and 0.07 to 0.68 μg/L at the Anno River. The maximum concentration at drainage channel 1 was observed within one hour after application at area ① including paddy fields 1 and 2. On the other hand, the concentration at drainage channel 2 varied and increased immediately after the application at area ② and within 10 hours after the application at area ③. This

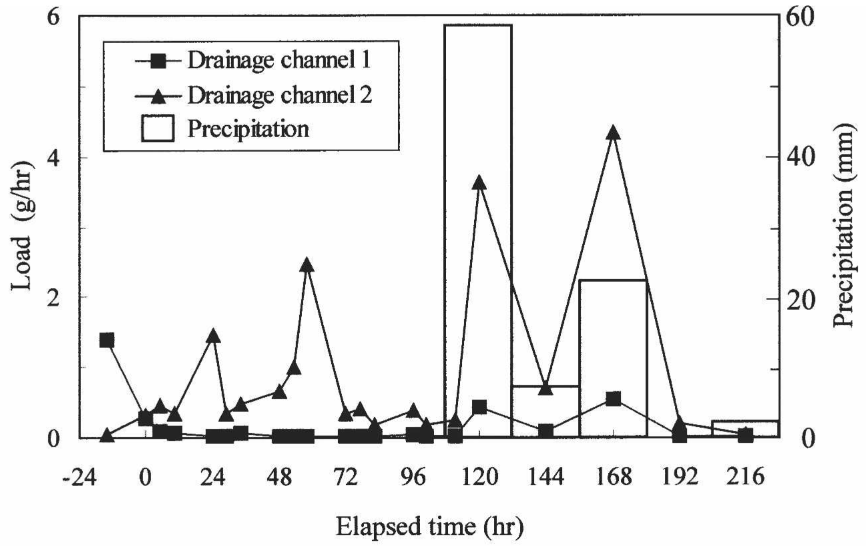

Figure 5. Variation in phthalide load in drainage channel waters.

suggests that the water in drainage channel 2 was mainly from the paddy fields located in areas ② and ③. The concentration in the Anno River was the highest six days after the application in area ①. However, it appears that the variation at the river was affected by the phthalide applied to the investigated area as well as the fungicide applied to the upstream areas.

The variations in the runoff loads of phthalide in the drainage channel waters are given in Figure 5. There were no significant runoff events (0.017 - 0.28 g/hr) in drainage channel 1 within 96 hours after the application at the investigated paddy fields. In contrast, significant runoff events (0.33 - 2.47 g/hr) occurred in drainage channel 2 from five to 96 hours after the application. In particular, distinct runoff events (1.47 and 2.47 g/hr) occurred in the channel after 24 and 58 hours, respectively, after the application. 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. On the other hand, significantly distinct runoff events (0.1 - 0.54 g/hr and 0.72 - 4.33 g/hr) occurred in drainage channels 1 and 2, respectively, 120 - 168 hours after the application. These events were caused by rainfall, because the precipitation amounts increased to 7 - 58 mm/d during this period (Figure 5).

Figure 6 shows the variation in the runoff load of phthalide in the Anno River. The runoff loads of phthalide in the river increased to 2.2 - 11.4 g/hr within 101 hours after the application in the investigated paddy fields; the significantly distinct runoff events (30.9 - 55.3 g/hr) occurred 120 - 168 hours after the application. These loads were caused by the drainage from the aerially applied areas ① - ③ through the drainage channels in the areas. The rainfalls of 7 - 58

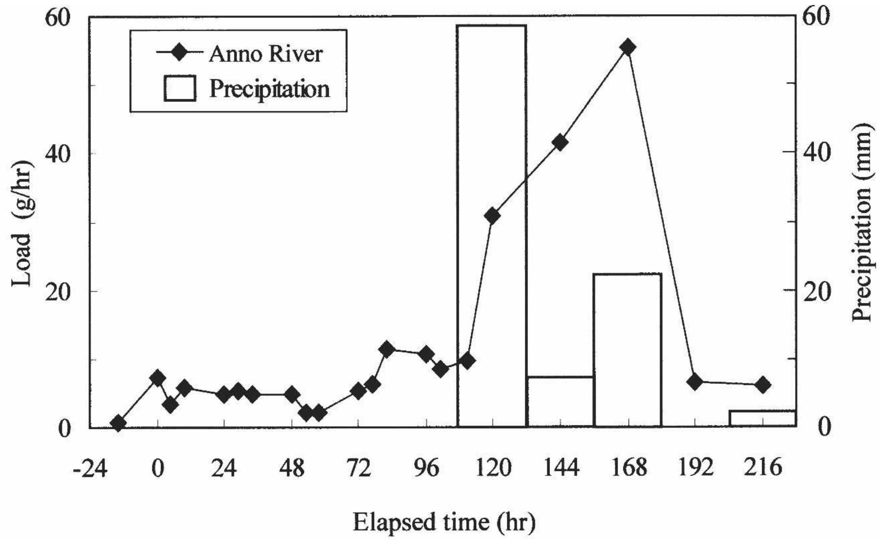

Figure 6. Variation in phthalide load in the Anno River waters.

mm/d (Figure 5) caused the runoff events during the 120 - 168 hours after the application.

The runoff ratio of phthalide was evaluated using the runoff load of phthalide in a drainage channel. R_R was calculated by the following equation [1]:

$$R_R = 100\ (A_R / A_A) \qquad [1]$$

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 at sites C and D. The calculated runoff ratios are listed in Table 1. The runoff ratios of phthalide applied by helicopters to the paddy fields from 1995 to 1997 in Niigata, Japan, were reported to be 1.6 - 3.1 % (Mitobe et al. 1999). Although the runoff ratios depended on the application conditions as well as the precipitation amounts, the runoff ratios in this study were almost comparable to the reported values.

As described above, the average ratios of the phthalide amounts in the paddy waters to the applied amounts were 7.8 % one hour after the application, 0.46 % after 24 hours, 0.14 % after 48 hours and <0.04 % after 96 hours. Since the runoff ratio was calculated as 1.6 % by equation [1], the margin of 6.2 % of the

Table 1. Phthalide runoff from paddy fields.

Drainage channel	Applied amount (g)	Runoff amount (g)	Runoff ratio (%)
1 (site C)	3,020	47	1.6
2 (site D)	19,400	320	1.7

phthalide in the paddy water appears to remain in the paddy fields or evaporate into the air. Adsorption into the paddy soil could be the main route of residual phthalide.

REFERENCES

Inao K, Ishii Y, Kobayashi Y, Kitamura Y (2003) Landscape-scale simulation of pesticide behavior in river basin due to runoff from paddy fields using pesticide paddy field model (PADDY). J Pesticide Sci 28: 24-32

Kanazawa J (1996), Environmental character and toxicity data of pesticides. Godo-shuppan, Tokyo

Kawata K, Asada T, Tanabe A, Oikawa K (2005) Runoff of clomeprop and oxaziclomefone from a paddy field. Bull Environ Contam Toxicol 75: 922 - 928

Kawata K, Mukai H, Yasuhara A (1995) Monitoring of pesticides in air by gas chromatography/mass spectrometry and the use of quartz-fiber wool and activated carbon for sampling. J Chromatog A 710: 243-250

Lerch RN, Blanchard PE (2003) Watershed vulnerability to herbicide transport in northern Missouri and southern Iowa streams. Environ Sci Technol 37: 5518-5527

Mitobe H, Ibaraki T, Tanabe A, Kawata K, Sakai M, Kifune I (1999) Variation of pesticides in a river flowing through paddy fields area. J Environ Chem 9: 311-320

Schulz R (2001) Comparison of spray drift- and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa. Chemosphere 45: 543-551

Shipitalo MJ, Owens LB (2003) Atrazine, deethylatrazine, and deisopropylatrazine in surface runoff from conservation tilled watersheds. Environ Sci Technol 37: 944-950

Southwick LM, Grigg BC, Fouss JL, Kornecki TS (2003) Atrazine and metolachlor in surface runoff under typical rainfall conditions in southern Louisiana. J Agr Food Chem 51: 5355-5361

Sudo M, Kunimatsu T, Okubo T (2002) Concentration and loading of pesticide residues in Lake Biwa basin (Japan). Water Res 36: 315-29

Suzuki S, Otani T, Iwasaki S, Ito K, Omura H, Tanaka Y (2003) Monitoring of 15 Pesticides in Rainwater in Utsunomiya, Eastern Japan, 1999-2000. J Pest Sci 28: 1-7

Tanabe A, Mitobe H, Kawata K, Sakai M, Yasuhara A (2000) A new monitoring system for 90 pesticides and related compounds in river water by solid-phase extraction with gas chromatography/mass spectrometry. J AOAC Int 83: 61-77

Tanabe A, Mitobe H, Kawata K, Yasuhara A, Shibamoto T (2001) Seasonal and spatial studies on pesticide residues in surface waters of the Shinano River in Japan. J Agr Food Chem 49: 3847-2852