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Runoff of Clomeprop and Oxaziclomefone from a Paddy Field

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Herbicide transfer from cultivated areas to the environment is an ecological and human health concern. Commonly used herbicides, such as atrazine, mefenacet, metolachlor, simazine and thiobencarb, have been detected in the river waters of Japan (Mitobe et al. 1999; Nakano et al. 2004; Tanabe et al. 2001) as well as in the USA (Clark and Goolsby 1999; Lerch and Blanchard 2003; Shipitalo and Owens 2003; Southwick et al. 2003). The runoff ratios of the applied herbicides from cultivated areas to drainage channels or rivers were reported to be 5.2 - 10.8% for atrazine (Southwick et al. 2003), 4.2 - 11.1 % for mefenacet (Amano et al. 2001; Inano et al. 2003) and 3.7 - 8.0% for metolachlor (Southwick et al. 2003). These relatively high ratios were caused by the relatively high water solubility (Nakano et al. 2004; Tanabe et al. 1998) and by the logarithm of the octanol–water partition coefficient (log P_{ow}) of less than 5 for these herbicides. For example, the water solubilities of atrazine, mefenacet, metolachlor, simazine and thiobencarb are 30, 4, 530, 6.2 and 30 mg/L, respectively, and the log P_{ow} are 2.34, 3.23, 2.90, 3.43 and 3.42, respectively.

Paddy rice farming has been playing an important role in the food production of the world. 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 herbicides are applied to paddy fields, and a part of the applied herbicides flow from the paddy fields into rivers and lakes through drainage channels (Amano et al. 2001; Inano et al. 2003; Nakano et al. 2004).

Recently, clomeprop and oxaziclomefone (Table 1) have been used for reducing herbicide loads on the water environment in Japan, because their water solubilities are very low. Moreover, their log P_{ow} values (greater than 5) indicate that these herbicides are strongly fat-soluble substances (Hamilton et al. 2003). These herbicides are applied to paddy fields before planting rice in April through May to control the growth of spring weeds. However, few reports have been published on their behavior in paddy fields or on their ratios of runoff from the paddy fields to the environment. In this paper, we describe the variation in the clomeprop and oxaziclomefone concentrations in paddy field water as well as drainage water, and evaluate the runoff ratios of the herbicides from a paddy field.

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MATERIALS AND METHODS

Water samples were collected from a paddy field with an area of 100 sq m in Kameda, Niigata, Japan. Thirty-five grams of clomeprop and 6 g of oxaziclomefone were applied to the paddy field on May 15, 2003. The applied concentrations in the paddy water were calculated as 7000 μg/L for clomeprop and 1200 μg/L for oxaziclomefone. Samples were also collected from the drainage channel the water from which the investigated paddy had drained into. The sampling point was located on the downstream side of the paddy field. Drainage from 500 sq m of paddy fields including the investigated paddy flowed to the sampling point. All samples were analyzed within 24 hours after collection.

A Waters Sep-Pak Concentrator and a J&W SPE Manifold were used for the SPE and elution, respectively. A liquid chromatograph–mass spectrometer model, Shimadzu LCMS 2010A equipped with a Develosil C30-UG-5 (5 μm C_{30}-bonded silica, 2.0 mm id, 150 mm long; Nomura Chemicals, Aichi, Japan) was used for the quantitative analyses.

Acetonitrile (pesticide grade), methanol (HPLC grade) and hydrochloric acid (trace metal grade) were purchased from Kanto Kagaku (Tokyo, Japan). Clomeprop and oxaziclomefone were purchased from Hayashi Pure Chemical Industries (Osaka, Japan) and Kanto Kagaku, respectively. [$^2H_{10}$]Simazine (simazine-d_{10}) purchased from Kanto Kagaku was used as the internal standard. Mixed standard solutions of the target herbicides (100 and 10 μg/mL) and an internal standard solution (10 μg/mL) were prepared in methanol. Ultrapure water purchased from Kanto Kagaku was used as the purified water. Waters Sep-Pak Plus C_{18} cartridges were washed with 5 mL of acetonitrile, followed by 5 mL of the purified water prior to use.

To extract clomeprop, the sample water (10 – 500 mL), whose pH had decreased to 3 with the addition of 1 M hydrochloric acid, was passed through the C_{18} cartridge at 10 mL/min. After the cartridge was washed with 10 mL of purified water, followed by 8 mL of water-acetonitrile (70:30 v/v), it was dried by passing air over it for 5 min at 2.7 kPa using an aspirator. Clomeprop collected on the cartridge was eluted with 10 mL of acetonitrile at 1 mL/min. For oxaziclomefone, the sample water (10 - 100 mL) was passed through a C_{18}

Table 1. Properties of target herbicides

	IUPAC name	Sw [a] (μg/L)	Log Pow
Clomeprop	(R,S)-2-(2,4-dichloro-m-tolyloxy)propionanilide	32	5.26
Oxaziclomefone	3-[1-(3,5-dichlorophenyl)-1-methylethyl]-3,4-dihydro-6-methyl-5-phenyl-2H-1,3-oxazin-4-one	180	5.46

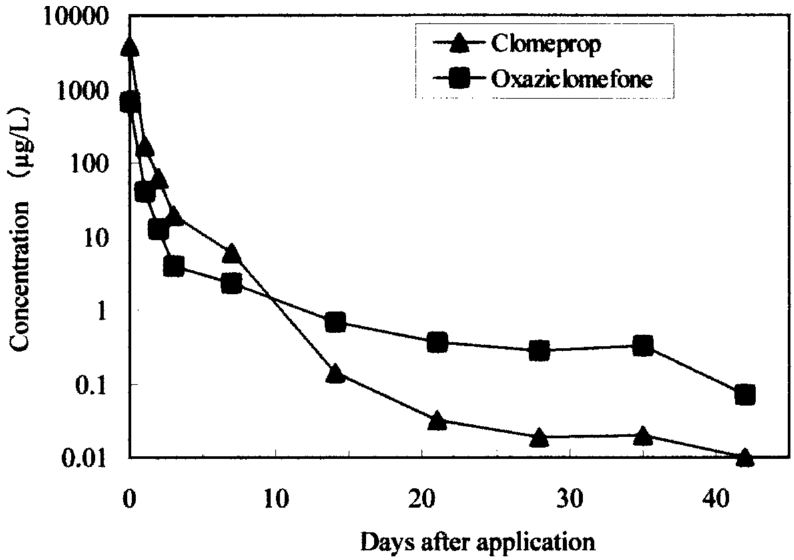

Figure 1. Changes in herbicide concentrations in paddy water.

cartridge at 10 mL/min. After the cartridge was washed with 10 mL of purified water, followed by 10 mL of water-acetonitrile (60:40 v/v), it was treated using the same procedure described above. The obtained eluate was added to the eluate containing clomeprop. The combined eluates were evaporated to about 5 mL followed by concentration to 1 mL under a pure nitrogen gas stream. A 10 μL aliquot of the internal standard solution was added to the concentrated solution. Regarding the combined eluates from the paddy waters sampled within 24 hours after the application were diluted 10 – 100 fold with acetonitrile. 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 LC/MS analysis.

A 10-μL aliquot of the resulting solution was analyzed by LC/MS. The operating conditions of the LC/MS were as follows: column temperature, 40 °C; mobile phase, water-methanol (30:70 v/v) at 0.2 mL/min; ionization mode, positive ion electrospray; probe voltage, 4.5 kV; nebulizing gas flow, 4.5 L/min; curved desolution line temperature, 250 °C. Ions used for the analysis were *m/z* 346 and 348 for clomeprop, *m/z* 398 and 400 for oxaziclomefone, and *m/z* 212 for simazine-d_{10}. The ratios of the peak areas of the ions to that of the internal standard were used for quantification of the herbicides.

The correlation coefficient (*r*) of each calibration curve was greater than 0.999. The linear range of the standard curve was from 0.1 to 10 ng. The minimum detection limit for each the target herbicide was 0.01 μg/L. The overall recoveries of the target herbicides from 500 mL of the drainage channel water were investigated by adding 0.1 μg of each standard herbicide to the water. A drainage channel water sample (500 mL) was used as the blank sample. No

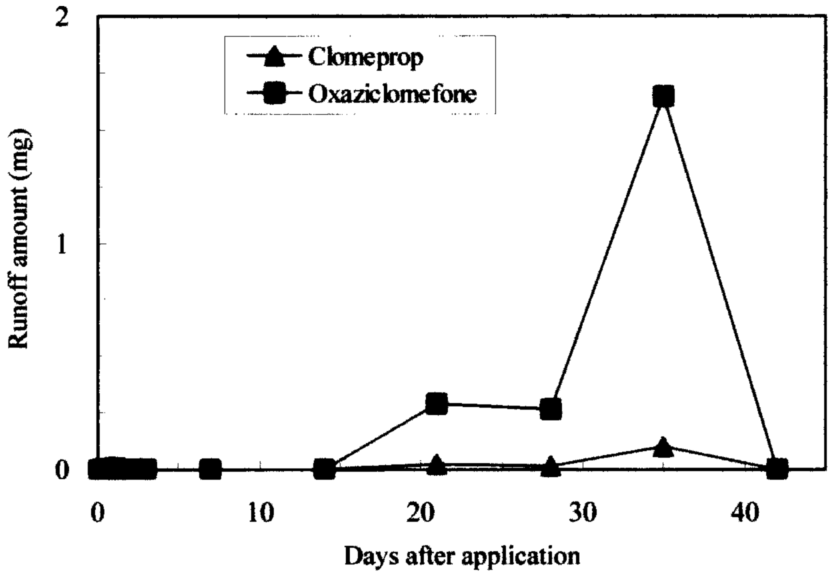

Figure 2. Changes in herbicide runoff from a paddy field.

target herbicides were detected from the blank sample. The overall recoveries and relative standard deviation (*n* = 5) were 92 and 4.1 % for clomeprop, and 88 and 3.5 % for oxaziclomefone, respectively.

RESULTS AND DISCUSSION

Variations in the clomeprop and oxaziclomefone concentrations in the paddy water are given in Figure 1. The maximum concentrations (one hour after application) were 3760 μg/L for clomeprop and 680 μg/L for oxaziclomefone. These values were nearly 54 % (clomeprop) and 57 % (oxaziclomefone) of the calculated concentrations. The concentrations of clomeprop decreased to 170 μg/L after 24 hours and 61μg/L after 48 h. Since the water solubility of clomeprop is 32μg/L, the major part of clomeprop dispersed in the paddy waters after the application through 48 h. Furthermore, the major part of oxaziclomefone also dispersed in the paddy waters within a few hours after the application, because the oxaziclomefone concentration exceeded its water solubility by 500μg/L. The concentrations of clomeprop and oxaziclomefone decreased to 4.5 and 6.2 %, respectively, of the maximum concentrations within 24 hours, and 13 and 1.9 % within 48 hours. In addition, no water was poured

Table 2. Herbicide runoff from paddy field

	Applied amount (mg/sq m)	Runoff amount (μg/sq m)	Runoff ratio (%)
Clomeprop	350	1.4	0.00040
Oxaziclomefone	60	22	0.037

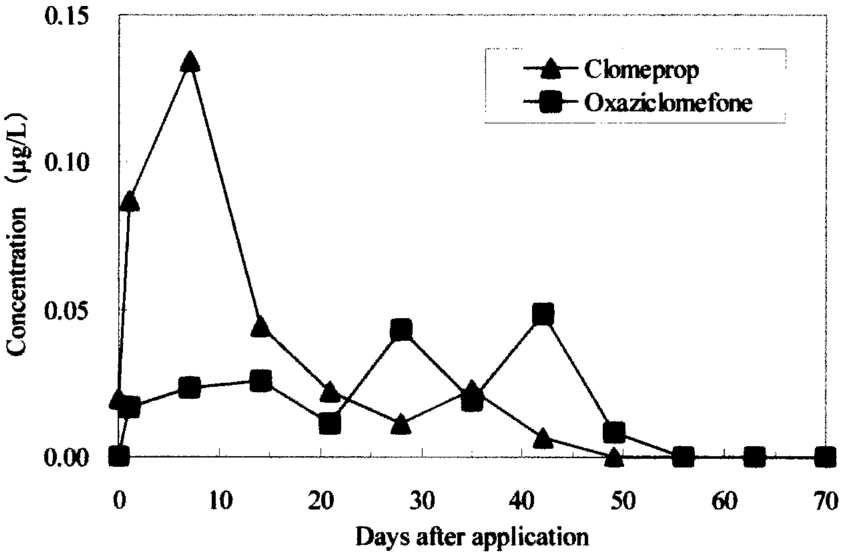

Figure 3. Changes in herbicide concentrations in drainage channel.

into the paddy field, and no paddy water had drained from the paddy during the period. Therefore, the major amounts of the deposited herbicides were adsorbed by the paddy soil immediately after the application due to their low water solubility and high log P_{ow}.

The clomeprop and oxaziclomefone concentrations decreased to 6.1 μg/L and 2.3 μg/L within a week after application, respectively. These values were 0.16 % and 0.33 % of the maximum concentrations. Amano et al. (2001) reported that two typical herbicides, thiobencarb and mefenacet, in paddy water were 4.05 g/a and 0.47 g/a within 6 hours after application, and decreased to 1.50 g/a and 0.35 g/a within 7 days after application, respectively. The concentrations of clomeprop and oxaziclomefone in the paddy water rapidly decreased compared to those of the reported thiobencarb and mefenacet. This could be predominantly caused by their low water solubility and high log P_{ow}.

Changes in the runoff amounts of clomeprop and oxaziclomefone from the paddy field are given in Figure 2. The first and second runoff events on days 21 and 28 after the application occurred as the overflows of the paddy water. These events were caused by rainfall. On the other hand, the last event on day 35 occurred with the drainage of all the paddy water. The runoff amounts of the clomeprop and oxaziclomefone for the last event were 70 % and 75 % of the total runoff amounts (Table 2), respectively.

A runoff ratio (R_R) was calculated by the following equation:

$$R_R = 100\,(A_R / A_A)$$

where A_R is the runoff amount and A_A is the applied amount. The calculated R_R

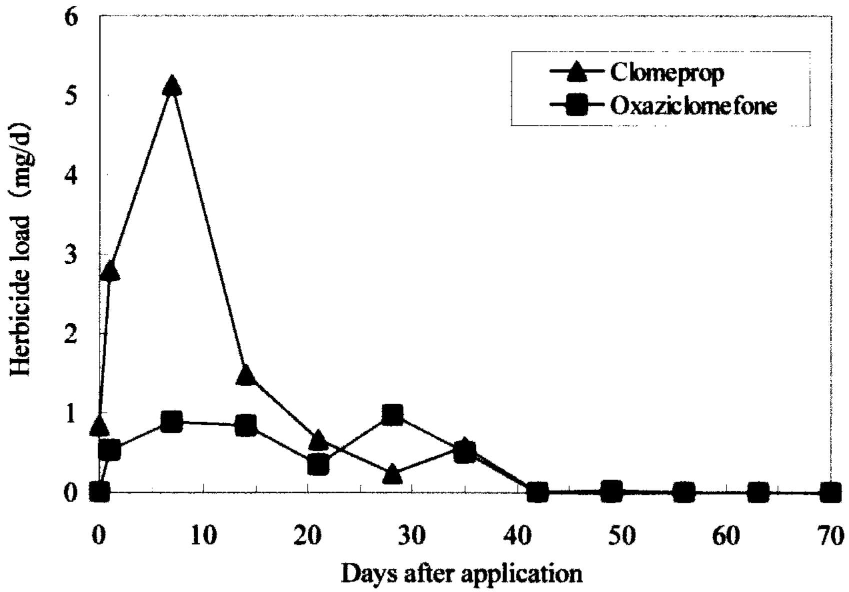

Figure 4. Changes in herbicide loads in drainage channel.

values are listed in Table 2. The runoff ratios from the paddy fields were reported to be 36 % for thiobencarb (Amano et al. 2001), and 4.2 - 6.9 % 11.1 % (Inano et al. 2003) and 11.1 % (Amano et al. 2001) for mefenacet. The runoff ratios of clomeprop and oxaziclomefone in this study were extremely low compared to the reported values. These results were caused by the low water solubility and high log P_{ow} (more than 5) of the investigated herbicides. Moreover, the extremely low ratios were attributed to the rather small amount of precipitation (78 mm) during the investigated period and the fact that no paddy water had drained into the drainage channel during the three weeks after the application.

Figure 3 shows the concentration changes in the clomeprop and oxaziclomefone in the water from the drainage channel. The concentrations ranged from <0.01 to 0.13 μg/L for clomeprop and <0.01 to 0.05 μg/L for oxaziclomefone. The concentration of clomeprop was the highest after seven days of the application, and decreased except for day 35 when the paddy water was drained from the investigated paddy. On the other hand, the concentration of oxaziclomefone moderately varied and increased on days 28 and 42 after the application. These results suggest that the behaviors of the herbicides were affected by the differences in their applied amounts and time of the herbicides in the paddy fields as well as the time when the paddy waters were drained into the channel.

Loading variations of the herbicides in the drainage channel are shown in Figure 4. The total loads of the herbicides during the investigated period were calculated to be 68 mg and 27 mg for clomeprop and oxaziclomefone, respectively.

Therefore, the runoff amounts from the investigated paddy (Table 2) were estimated to be 0.21 % for clomeprop and 8.1 % for oxaziclomefone of the loads in the drainage channel. Since the herbicides were drained from the investigated paddy field from day 21 through day 35 after the application, the loads of the herbicides before day 21 were attributed to the runoff from the other paddy fields. The mean runoff amounts from the paddy fields except for the investigated one were calculated to be 170 μg/sq m for clomeprop and 63 μg/sq m for oxaziclomefone. Although the herbicide amounts applied to each paddy field from which drainage water flowed at the sampling point could differ from each other, most of the clomeprop load was on days 1 - 14 after the application. This suggests that a small amount of paddy water containing clomeprop at an extremely high concentration could have drained from any of the paddy fields except for the investigated one.

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