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Measuring of some selected herbicides in paddy surface water in the Saijo Basin, Western Japan

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Abstract – An analysis of the dissipation of herbicides was done in paddy water and in drainage channels of farm paddies as well as in experimental plots. A field study was conducted in three selected paddy farms of Higashi Hiroshima and an experiment was carried out in the Hiroshima Prefecture Agriculture Research Center in the paddy season of the year 2002. The herbicides were mefenacet, thiobencarb, pyributicarb and cyhalofop –butyl. The sample water was analyzed by using gas chromatography after solid phase extraction. The maximum concentration of all herbicides was detected within 1 to 3 days after herbicide application and became trace level after 21 to 28 days. The highest amount of herbicide detected was 338 µg/L mefenacet in Farm B. No cyhalofop-butyl was detected in the experiment but was found in farm paddies until 7 days. Thiobencarb was detected until 21 and 28 days, respectively, in farm paddies and in the experiment. Pyributicarb was detected until 28 days in farm paddies and in the experiment. We found that the concentration of all herbicides in drainage channels was comparable with the paddy field at 1 day and 3 days and thiobencarb at 1 day.

herbicides / paddy surface water / drainage / dissipation / Saijo basin

1. INTRODUCTION

Currently, great emphasis is being given to the environmental fate of agricultural pesticides. Herbicides, being important agricultural chemicals, are one of the targets of environmental concern. To be more effective, many herbicides need to kill more weed species, for which most of the herbicides should stay in the soil and water for a longer period of time. However, excessive persistence of herbicides in soil and water may pose a great threat to the environment.

The environmental burden of herbicides applied in paddy fields is heaviest in water. Rice herbicides are applied directly to surface water on the paddy fields; the paddy field system is extremely susceptible to herbicide runoff upon significant rainfall events or inappropriate water management. Irrigation drainage and runoff flow sequentially from the paddy fields to irrigation channels, small rivers and large rivers, whereby they are dispersed widely throughout the water systems, and carry herbicides used in rice fields [9]. In Japan, the runoff rate into water systems is higher than 1 % of herbicides applied to upland fields [20]. In the case of paddy fields, continuous irrigation and drainage management practices may have significant runoff losses of up to 38% of applied herbicide [21]. Herbicides used in paddy fields are often detected in river water from May to July after the pesticide application. The highest herbicide con-

centration in paddy water appears between the time immediately following application and the following day, and the greater the herbicide water solubility, the higher the concentration in the paddy water tends to be. The half-life of herbicides in paddy water is 2–5 days for nearly all herbicides used in Japan.

The drainage from paddy field areas in Japan was monitored for a 5-year period and 12 herbicides, 5 insecticides and 5 fungicides were detected [14]. The concentration ranged from 1 to 1000 ppb; the low concentration was associated with long exposure (1–3 months) and high concentration with short exposure (one week). The runoff rates differed depending upon herbicide properties and environmental conditions, such as rainfall and temperature, as well as amounts used per unit area and paddy water management methods. High rainfall immediately after herbicide application, as well as flow irrigation, will increase the runoff rate into water systems. Recently, concern has arisen that runoff of pesticides applied to agricultural land may cause contamination of surface water sources and have adverse effects on aquatic ecosystems. In Japan, more than half of all agricultural lands are paddy fields, where applied pesticides can easily flow out through paddy field water to public water areas. Considering this situation, Japanese regulatory agencies have established water quality regulations and standards for pesticides [11].

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Figure 1. Location of the study area. The dotted areas represent the paddy fields.

A study of Itagaki et al. [10] detected 18 pesticides in the Minaga River and Minaga Reservoir of Higashi Hiroshima City of Hiroshima Prefecture during July–October 1997 and September–November 1998. All of the pesticides had been used in paddy fields. Another study revealed that the surveyed farmers used 10 out of those 18 pesticides in their fields in the 2000 paddy season [16]. A study by Hayase et al. [7] detected some pesticides in paddy fields of Higashi Hiroshima where no pesticides had been applied, indicating contamination by pesticides from surrounding paddy fields. Most studies have reported the presence of the herbicides mefenacet, pyributicarb and thiobencarb in rivers, ponds or reservoirs [15, 18, 19]. Dissipation rates of herbicides after application provide important information for the assessment of the behavior of their residue [1]. Therefore, it is important to conduct studies on the dissipation of herbicides in farm paddy water, as well as in drainage water, and relate this to the environmental consequences. This study will analyze pesticide dissipation in the paddy water under farmers' management conditions and compare with the experiment by using standard management practices.

2. MATERIALS AND METHODS

2.1. Study area

The study was conducted in three selected farm paddies of Higashi Hiroshima City of Hiroshima prefecture, Japan (Fig. 1).

Only 3.2% of the city's populations are engaged in farming activities and only 0.5% of the farming populations are full-time farmers. The city area is 288.25 km², of which about 12% is agricultural land, and about 95% of that agricultural land is under paddy cultivation. The altitude is approximately 200 m above sea level and the city is located in the Saijo basin under the Kurose watershed, which is surrounded by mountains of about 500 m above sea level. The mean annual rainfall of this area was 1071 mm in 2002, and the corresponding mean annual temperature ranged from 3.3 °C in January to 26.4 °C in July. The soil type of the basin is sandy loam with 15.5% clay content and 1.89% humus. The cation exchange capacity (CEC) varies from 8.6 to 11.0 meq/100 g soil. The water pH of the study paddy fields were acidic at the early stage and acidic to neutral at the later stage, varying from 6.2 to 7.5. The minimum temperature of paddy water was 18.2 °C in early May and rose to 32.5 °C in early June. The study area can be regarded as a typical paddy cultivating area in Japan.

2.2. Herbicide application and water management

The herbicides selected are widely used by the farmers of Hiroshima prefecture. Mefenacet was common in all three herbicides used by the farmers, and this is contained in about 50% of the commercial herbicides used in Hiroshima prefecture, as per use statistics for 2001. On the basis of herbicide use, three commercial and full-time farmers were selected from the study

area, keeping the homogeneity of soil conditions, micro-climatic conditions and sources of irrigation water the same as the Hiroshima Prefecture Agriculture Research Center. The selected farms were designated as Farm A, Farm B and Farm C. The commercial herbicides were: Ulfues 1 kg granule 51 (Kumiai) containing mefenacet 3.0%, thiobencarb 15% and bensulfuron methyl 0.51%; Longet flowable (Takeda) containing mefenacet 8%, pyributicarb 10%, dymron 18% and imazosulfuron 1.5%, and Inegreen (Hokko) containing mefenacet 7.5%, cyhalofopbutyl 1.5%, dymron 4.5% and bensulfuron methyl 0.51%. Farm A, Farm B and Farm C used Ulfues, Longet flowable and Inegreen, respectively. Along with mefenacet as the common compound, thiobencarb for Ulfues, pyributicarb for Longet flowable and cyhalofop-butyl for Inegreen were analyzed on the basis of the method used in this study. Among these herbicides, mefenacet was the second most widely used in paddy fields all over Japan and in our study area. Bensulfuron methyl is the most common compound found in any formulation. Thiobencarb and pyributicarb are also widely used paddy herbicides. Cyhalofop-butyl (Clincher) is also a special herbicide, which is usually used by the farmers for spot control of paddy weeds.

The paddy fields of the farms studied were those having direct inlets and outlets with irrigation and drainage channels, and it was not possible for drainage water from other paddy fields to enter. In Japan, drainage water from paddy fields is used repeatedly in other paddy fields downstream and the movement of herbicide residues from other fields occurs. At least two paddy fields of 1000 m² (10 a) were studied for each of the farms. In addition, an experiment was conducted using the same herbicide under standard management practices to measure the rate of herbicide dissipation in the paddy field as compared with farm paddies under farmers' management condition. All the operations (from land preparation to herbicide application and water management) of the studied farm paddies were conducted by the farmers. Water samples were collected from the selected paddies for analysis and other relevant information also gathered from them. On the other hand, in the experimental plots all operations were done by our research team and strictly maintained recommended practice for water management (such as controlled drainage until 10 days after application) and herbicide application.

All experiments were conducted at the experimental station of Hiroshima Prefecture Agriculture Research Center in Higashi Hiroshima from May to July 2002. During the experiment, the plots (3 m × 6 m) with 2 replications and 1 control for each of the herbicides were planted with rice (*Oryza sativa* L. Koshihikari). Commercial granular formulation of Ulfues and Inegreen 1 kg / 1000 m² and Emulsifiable Concentrate of Longet Flowable 500 mL / 1000 m² were used. The herbicides were applied within one week after transplanting by sprayer.

The paddy farms of the study area usually use pond irrigation where rainwater is retained and connected to the paddy fields. The water from the pond runs through the irrigation channel to the paddy field and all the paddy fields are again connected to the drainage channel and ultimately to the river. Not all farm paddies are artificially constructed and strictly maintained. It is recommended that for at least 10 days after herbicide application draining be restricted. But due to field conditions and rainfall, the farmers seldom maintain this. Therefore, overflow

Table I. Water conditions of the study paddy fields.

	Farm A	Farm B	Farm C
Area (m ²)	1000	1000	1000
Average depth of water (cm)	3.5	3.6	4.5
Field water volume (m ³)	35	36	45
Outflow rate of water (m ³ /day)	7.7	6.7	5.6
Penetration rate of water (m ³ /day)	0.95	0.76	0.7
Evaporation rates of water (cm/day)	0.14	0.01	0.89
p ^H of the water			
Minimum	6.2	6.3	6.3
Maximum	7.5	7.5	7.4
Water temperature			
Minimum	18.2	16.8	19.2
Maximum	32	28.2	32.5

and draining of paddy water are common even immediately after herbicide application.

During the study period, the inflow and outflow rates of water, water depth and evaporation rate of water were measured at each sampling time. The water conditions of each paddy field are shown in Table I.

2.3. Samplings

The sampling was done at or around 1, 3, 7, 14, 21, 28 and 35 days after herbicide application. Two samples were taken from random spots in each of the paddy fields (4 for 2 paddy fields) and the experiment plots (4 for 2 replications). From each of the fields and plots 1000 mL samples were collected during the whole study period. In the same way, water from the drainage channel was also collected. The water samples were brought to the laboratory immediately and analyzed using gas chromatography after solid phase extraction. The method used for the residue analysis was developed at the Pesticide Analysis Laboratory of Hiroshima Prefecture Agriculture Experimental Center. The samples from all the fields and plots were analyzed before application of herbicides to check the residue from the previous year or irrigation water.

2.4. Analysis of the samples

A Sep-Pak Cartridge Rack (Nippon Millipore Co.) was used for solid phase extraction and elution. Herbicides and other reagents were purchased from Kanto Chemicals (Japan). All solvents used were of pesticide residue-grade. Water samples were filtered through No. 7 filter paper of 4 µm pore size with Hyflo-Super-Cel (Kiryama, Japan) to remove the particles. Sep Pak-PS2 (C18) cartridges (Waters, Ireland), 2 per sample, were preconditioned by washing with 10 mL acetonitrile and 30 mL distilled water and dried with a water aspirator. A 200 mL volume of filtered water with 2 repetitions of each sample was passed through the cartridge at a flow rate of 10 mL/min. The herbicides trapped on the cartridge were eluted with 10 mL of acetonitrile. The elutes were passed through Sodium Sulfate by phase separators silicone-treated filter paper (15.0 cm diameter, Whatman) to remove water. Then the elutes were concentrated to 1 mL by using a rotary evaporator, followed by nitrogen gas concentration until dried. The extracts were then

redissolved in 1 mL acetone and the resulting solution was analyzed by using a gas chromatograph.

A Shimadzu GC – 14A gas chromatograph with FTD – 8 (Flame Thermionic Detector) was used for the analysis. The glass column was a chromosorb (w) HP (i.d. 3 mm and length 1.0 m) with 1.5% silicone OV-17 and 1.95% silicone DC QF-1. The column temperature was 190 °C for 4 minutes, with an increase of 30 °C/min and the final temperature was 230 °C for 11 minutes, with an injection temperature of 250 °C, and a detector temperature of 280 °C. The GC was equipped with an automatic sampler with the injection volume set to 2 µL. The temperature program was the same for all the herbicides. The recovery for thiobencarb was 96.5% (S.D. = 3.6, n = 4), 93.1% for mefenacet (S.D. = 4.3, n = 4), 91% for pyributicarb ((S.D. = 3.3, n = 4) and 95% for cyhalofop-butyl (S.D. = 3.8, n = 4). The determination curve for thiobencarb was $y = 46594x + 348.72$ ($R^2 = 0.9907$); for pyributicarb, $y = 31602x + 1275.2$ ($R^2 = 0.993$); for cyhalofop-butyl, $y = 11689x + 4607.8$ ($R^2 = 0.9987$), and $y = 27263x + 25830$ ($R^2 = 0.9943$) for mefenacet.

2.5. Data analysis

Dissipation rates were calculated using simple first-order kinetics (SFOK). The equation $C = C_0 e^{-kt}$ was used for the first order kinetics, where C is the amount of herbicide (mg/L water) at time t ; C_0 is the amount of herbicide (mg/L water) at time 0; k is the rate constant (day^{-1}) and t is the time (day). Initial concentrations of herbicide (C_0) were calculated on the basis of the total amount of water (in liters) in the paddy field at the time of application and the total amount of herbicide active ingredient (gm) applied, assuming that 100% of active ingredient had been dissolved in the water. The dissipation rate constant (k) was calculated by linear regression from the transformed first-order rate equation, $\ln C = \ln C_0 - kt$. Half-life (DT_{50}) was calculated using the equation $-\log(2)/k$ [12]. Data were analyzed using SPSS 11.0 for Windows.

3. RESULTS

3.1. Herbicide concentration in paddy water

No herbicides were present in the farm paddy water and experiment before application. Figure 2 shows the concentration of herbicides detected in Farm A and the corresponding experiment of herbicide containing thiobencarb and mefenacet at different time intervals. In the farm paddy, about 98% of thiobencarb and 91% of mefenacet degraded within 1 day after application. In the experiment, 95% of applied thiobencarb and 83% of mefenacet degraded within 1 day after application. However, the dissipation rate was more rapid after 7 days of application. Both the compounds were detected until 21 days after application in the farm paddy and 28 days after application in the experiment. The calculated half-life of thiobencarb and mefenacet, respectively, were 2.93 and 4.02 days in the farm paddy, and 6.89 and 4.86 days in the experiment. The R^2 values were acceptable (Tab. II) for all the herbicides.

Along with mefenacet the herbicide pyributicarb was analyzed in Farm B. Figure 3 shows the dissipation pattern of these two herbicides in the farm paddy and the experiment. The dissipation rate of the two herbicides was faster in the farm paddy

Figure 2. Herbicide dissipation pattern in Farm A and corresponding experimental plots. Data are given $\pm$ SD (n = 4).

than the experiment (Tab. II). The calculated half-life of mefenacet and pyributicarb were 3.38 and 4.01, and 4.42 and 6.13, respectively, in the farm paddy and in the experiment.

The dissipation pattern of herbicides used in Farm C is presented in Figure 4. In the experiment, cyhalofop-butyl was not detected even after 1 day of application but it was detected in the farm paddy until 7 days after application and was within the limit of detection, 0.1 µg/L, until 14 days after application, with a calculated half-life of 0.99 days. Mefenacet persisted longer in the experiment, with a longer half-life than in the farm paddy (Tab. II).

3.2. Herbicide concentration in drainage water

Table III shows the herbicide draining from the three paddy farms. The drainage of the experimental plots was controlled

Table II. Half-life (DT_{50}), disipation rate and R^2 values of the study herbicides.

Herbicide used	Farm paddy			Experiment		
	k	R^2	DT_{50}	k	R^2	DT_{50}
Farm A	Mefenacet	0.0749	0.9504	4.02	0.0619	0.9526
	Thiobencarb	0.1028	0.9707	2.93	0.0437	0.8605
Farm B	Mefenacet	0.0846	0.889	3.38	0.0681	0.9988
	Pyributicarb	0.0748	0.833	4.01	0.049	0.8673
Farm C	Mefenacet	0.0992	0.819	3.04	0.0678	0.9818
	Cyhalo fop-butyl	0.3035	0.999	0.99		4.43

DT_{50} = half-life (in days); computed using the equation $-\log(2)/k$. k = dissipation rate; slope of the regression lines.

Figure 3. Herbicide dissipation in Farm B and corresponding experimental plots. Data are given $\pm$ SD (n = 4).

until the detection of herbicide in the water. In the drainage water of Farm A, both the herbicides mefenacet and thiobencarb were present until 14 days after application. The detection

Figure 4. Herbicide dissipation in Farm C and corresponding experimental plots. Data are given $\pm$ SD (n = 4).

amount went below $0.01 \mu\text{g/L}$ after 7 days for mefenacet and 3 days for thiobencarb. Pyributicarb and mefenacet were present until 14 days after application in the drainage water of Farm B. Mefenacet in the drainage water of Farm C was present until 21 days after application. There were significant relationships between the herbicide concentrations in paddy water and in drainage water.

Table III. Herbicide concentration in the drainage water of the farm paddy and cumulative rainfall on the sampling dates.

DAH	Farm A		Cumulative	Farm B		Cumulative	Farm C	Cumulative
	Mefenacet	Thiobencarb	rainfall	Mefenacet	Pyributicarb	rainfall	Mefenacet	rainfall
	$\mu\text{g L}^{-1}$		mm	$\mu\text{g L}^{-1}$		mm	$\mu\text{g L}^{-1}$	mm
1	162.964	179.168	13	32.44	41.003	13	242.05	19
3	117.349	3.77	97	46.557	39.715	49	44.478	55
7	0.707	<0.01	110	18	7	133	6.814	139
14	<0.01	<0.01	111	<0.01	4	140	2.688	147
21	—	—	115	—	—	141	<0.01	147
Correlation between paddy water concentration (R^2)	0.8774	0.7975		0.7189	0.6288		0.9845	
	($P < 0.005$)	($P < 0.01$)		($P < 0.006$)	($P < 0.002$)		($P < 0.000$)	

DA H = Days after herbicide application

4. DISCUSSION

The dissipation pattern of mefenacet was more or less similar in all the farm paddies. The dissipation rate was faster in Farm B and Farm C than in Farm A, as well as in the corresponding experiments. There was significant difference in dissipation of mefenacet between Farms A and B ($P < 0.007$), Farms B and C ($P < 0.05$) and Farms A and C ($P < 0.001$). Mefenacet concentration in paddy water peaked over the second day and its dissipation was rapid until the third (farm paddies) to fourth week (experiments), and the half-life of mefenacet varied from 3.04 to 4.86 days. The underlying cause might be that mefenacet has a lower water solubility (4 mg/L) and higher adsorption coefficient ($K_d = 24.07$), and for this reason much of its residues could have been adsorbed by the soil, leaving only a small portion in the water [5]. According to the study of Ferdinand et al. [5], mefenacet dissipation rates peaked at 2 to 3 days after application and were rapid until the fourth week, with a half-life of 3.1 to 4.1 days; and also there was no evidence of residue build-up, due to continuous application in the same plot. Watanabe and Takagi [20] reported that mefenacet peaked on the third day and was detected until the fourth week in their model paddy field, the rate of degradation of pyributicarb being slower with lower level concentration. Our study also reveals that the maximum concentration of the mefenacet in the farm paddies as well as in the experiment was at 1 day after herbicide application and the dissipation rate was fast until the 3rd week in the farm paddies, but up until the 4th week in the experiment. Due to lower initial concentrations and water drainage, our study showed more rapid dissipation of mefenacet than the studies of Ferdinand et al. [5] and Watanabe and Takagi [20]. In farm paddies, mefenacet degraded more rapidly than in the experiments ($P < 0.007$ for Farm A; $P < 0.039$ for Farm B and $P < 0.01$ for Farm C). There was no significant difference between the concentration of pyributicarb in the farm paddy and the experiment ($P < 0.569$).

Thiobencarb dissipated more rapidly in the farm paddy than in the experiment ($P < 0.003$). A considerable amount of thiobencarb in the drainage channel at 1 DAH indicates the runoff loss through drainage water from the paddy fields and this

may cause quick dissipation in the paddy water. Ross and Sava [17] reported significantly longer persistence in a paddy field where thiobencarb was applied as granules and the water was held for a required 6 days. The concentration of thiobencarb peaked in paddy water on day 4 at 576 ppb and did not decline significantly during the holding period [13]. However, our study farm could not maintain a water-holding period; there was rainfall even on the day of herbicide application (Tab. III). As a result, the water flowed from the paddy field to the drainage channel. The quick dissipation phenomenon in the farm paddy water resulted in a shorter half-life of thiobencarb: 2.93 days, compared with 6.89 days in the experiment. Crosby [3] reported that the field dissipation half-life of thiobencarb is 5 to 7 days. The persistence period of thiobencarb at 21 DAH in the farm paddy and 28 DAH in the experiment is congruent with the study of Watanabe et al. [22], where it was reported that the maximum concentration in paddy water was 380 ppb, and this declined to below 1 ppb between 25 and 30 days. Similar degradation rates were reported for molinate, thiobencarb and bensulfuron methyl in California paddy waters [2]. The same study of the California Rice Commission reported maximum thiobencarb degradation on the 2nd day after application, and this decreased rapidly within 10 days after application, suggesting that a minimum water-holding period is required to reduce the pesticide draining from the paddy water.

In Farm C, the half-life of cyhalofop-butyl, 0.99 days, was much higher in the paddy water, indicating longer persistence in the water than the expected 1.4–5.3 hours. The lowest measured ecotoxicological end-point for cyhalofop-butyl identified in the dossier was 0.134 $\mu\text{g/L}$, and the predicted environmental concentration (PEC) in the paddy water was 300 $\mu\text{g/L}$ and for adjacent surface water, 100 $\mu\text{g/L}$ [4]. Although mefenacet was present in the drainage channel, no cyhalofop-butyl was found. Further study is needed to examine the details of the dissipation of cyhalofop-butyl.

A considerable amount of herbicides were detected in the drainage water from the paddy fields, which correspond to the paddy water concentration representing herbicide runoff from the farm paddy (in Farm A; $P < 0.01$ for thiobencarb; $P < 0.005$

for mefenacet; in Farm B, $P < 0.006$ for mefenacet; $P < 0.002$ for pyributicarb; and in Farm C $P < 0.000$ for mefenacet). Sudo et al. [18] found that the runoff of the herbicides was concentrated in the application period due to excessive rainfall. Inao et al. [8] evaluated the pesticide paddy field model (PADDY) under two different conditions of the water management practices, continuous irrigation and drainage, and water-holding management that regulates drainage; they performed the experiment with molinate and simetryn. The concentration of both herbicides in paddy water was at the same level during the first day after application on both fields. After the second day, herbicide concentrations in the field of continuous irrigation and drainage were lower than those in the field of water-holding management. The concentration of cinosulfuron in paddy water dropped due to the effect of water flow after the opening of the water gate [6]. Many studies have reported the runoff of herbicides to the surface water in the paddy season [15, 18, 19]. Quick dissipation and the presence of herbicides in the drainage channel may be due to the effect of water runoff from the farm paddies. This may result in a reduction in the efficiency of the herbicide at killing weeds, which may in turn lead to the use of more herbicides.

In Japan, the maximum limit of some pesticides has been set up in August 2001. According to the Environmental Agency of Japan the average concentration which may not be exceeded of mefenacet, thiobencarb, pyributicarb and cyhalofop-butyl in paddy water within 150 days of applications are, respectively, 0.09 mg/L, 0.2 mg/L, 0.2 mg/L and 0.06 mg/L. The maximum limit of thiobencarb in drainage channels and public waterways (such as streams and rivers) is 0.02 mg/L, and of mefenacet in public waterways, 0.009 mg/L [11]. The maximum limits for pyributicarb and cyhalofop-butyl in public waterways are not set yet.

In conclusion, it could be said that our study farm applied herbicides using the appropriate dosage which have a short dissipation half-life in farm paddy water. The dissipation rates were slower than those in the experiment but did not persist for a length of time that may be harmful to the environment. The farm paddies have no effective drainage control measures. This was reflected in the presence of a considerable amount of herbicides in the drainage channel, even though these disappeared more rapidly than in the paddy water. Water management systems control the pesticide movement into the larger surface water bodies. In the farm paddies we studied, the recommended holding period of 10 days after application was not strictly maintained. Therefore, the herbicide ran off and/or overflowed through the drainage water. To minimize environmental pollution it is important to reduce concentrations in waterways to levels at or below acceptable concentrations, allowing time for their breakdown within the paddy field before any water is released into waterways. However, the presence of residues in drainage water indicates the potential of paddy water runoff to affect the surface water quality and the aquatic environment. The target value of these herbicides in the paddy field and public waterways may not be exceeded after 150 days of application as set by the Environmental Agency of Japan.

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