Bull Environ Contam Toxicol (2012) 88:521–525
DOI 10.1007/s00128-012-0531-0

Behavior of Bromobutide in Paddy Water and Soil After Application

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Received: 26 September 2011 / Accepted: 19 January 2012 / Published online: 2 February 2012

Abstract Behavior of the herbicide bromobutide, (RS)-2-bromo-N-(α,α-dimethylbenzyl)-3,3-dimethylbutyramide, in paddy water and soil after application to paddy fields was investigated to evaluate the degradation to bromobutide-debromo, N-(α,α-dimethylbenzyl)-3,3-dimethylbutyramide, and runoff of the herbicide. The respective maximum concentrations of bromobutide and the metabolite were 1,640–2,230 and 11.1–15.8 μg/L in the paddy water, and 2,210–4,140 μg/kg dry and 74–119 μg/kg dry in the paddy soil, respectively. The runoff ratios of the applied bromobutide from the paddy fields were calculated as 28 ± 16%. The respective mean values of the half-lives of bromobutide in the paddy water and the soil were 2.7 ± 0.34 days and 6.9 ± 2.6 days, respectively.

Keywords Herbicide · Metabolite · Paddy field · Water · Soil

Approximately 70 herbicides are applied to paddy fields for rice farming in Japan. Among those herbicides, bromobutide, (RS)-2-bromo-N-(α,α-dimethylbenzyl)-3,3-dimethylbutyramide, is a commonly used herbicide in Japan. Bromobutide can be among the most drained herbicides from paddy fields (Hasukawa et al. 2009; Kawasaki et al. 2008). Bromobutide is well known to degrade to bromobutide-debromo, N-(α,α-dimethylbenzyl)-3,3-dimethylbutyramide via photochemical reaction (Takahashi et al. 1985) and metabolism (Isobe et al. 1984). Bromobutide-debromo was detected in river water (Iwafune et al. 2010; Mitobe et al. 1999). Although variations of bromobutide in paddy waters have been reported (Hasukawa et al. 2009; Morinaka et al. 1993), neither the behavior of bromobutide-debromo in paddy water nor its behavior in paddy soil has been reported. In this paper, we describe variations in bromobutide and bromobutide-debromo concentrations both in paddy field waters and in soils after application. Then we evaluate their partitions between the paddy water and soil, and their respective decreases in paddy fields.

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Materials and Methods

The three investigated paddy fields 1–3 were located in a rice cultivation area in Niigata City, Niigata, Japan. Bromobutide was applied to paddy fields on May 23, 2009. Water and soil from the three paddy fields were sampled during May 23–June 10, 2009. Water samples were collected at four locations in paddy fields 1 and 3, and at six locations in paddy field 2. Equal volumes of the collected water from a paddy field were combined and mixed well as samples. Soil samples were collected from the 0–4 cm surface layer from a paddy field at each location. Then equal weights of these soils were combined and mixed well as samples. Water contents of paddy soils 1, 2, and 3 were 57.5 ± 6.2%, 58.3 ± 6.4% and 44.3 ± 7.2%, respectively. The soil densities were 1.29 ± 0.12 g/cm^3 (paddy soil 1), 1.28 ± 0.093 g/cm^3 (paddy soil 2) and 1.22 ± 0.10 g/cm^3 (paddy soil 3). The organic contents were estimated as the

loss upon ignition (550°C, 15 h) and calculated as the percent dry weight. The organic contents of paddy soils 1, 2 and 3 were 7.65 ± 1.05%, 8.67 ± 0.88% and 4.57 ± 0.65%, respectively. All samples were stored at 5°C in the dark, and were analyzed within 24 h after collection.

A gas chromatograph—mass spectrometer (Finnigan POLARIS Q; Thermo Electron, Waltham, MA, USA) equipped with an auto-injection system (Combi Pal; 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 InertCap 5 ms/Sil column (GL Sciences, Tokyo, Japan) was used for the gas chromatographic separation. Reagents including the standard pesticides were purchased from GL Sciences, Kanto Kagaku (Tokyo, Japan) and from Wako Pure Chemical Industries (Osaka, Japan).

Determination of bromobutide and bromobutide-debromo was performed using a previously described method (Kawata et al. 2005; Tanabe et al. 2000). The correlation coefficient (r) of each calibration curve was greater than 0.998. The linear ranges of the standard curves were 0.05–4 ng. The minimum detection limits were 0.01 μg/L for water and 5 μg/kg for soil. The overall recoveries of bromobutide and bromobutide-debromo from 500 mL of paddy water and 10 g of paddy soil were investigated by adding 0.2 μg of bromobutide and bromobutide-debromo to the water and soil. A paddy water sample (500 mL) and a paddy soil sample (10 g) were used as the blank samples. No target compounds were detected in the blank samples. The mean of overall recoveries and relative standard deviation (n = 3) of bromobutide were 82 and 4.1% from water, and 76 and 5.6% from soil, respectively. The means of overall recoveries and relative standard deviations (n = 3) of bromobutide-debromo were 83 and 2.6% from water, 87 and 8.4% from soil, respectively.

Results and Discussion

The bromobutide and bromobutide-debromo concentrations in paddy waters sampled after the application are summarized in Table 1. The maximum concentrations were comparable to those of 1,100–1,900 μg/L at paddy fields in Yamaguchi Prefecture (Morinaka et al. 1993) and those of 740–1,040 μg/L in Shiga Prefecture (Hasukawa et al. 2009), Japan. Although concentration levels of bromobutide-debromo in paddy fields were not reported, the average and the maximum concentrations of bromobutide-debromo were 8.3–9.9 and 11.1–15.8 μg/L, respectively.

The bromobutide and bromobutide-debromo concentrations in the paddy waters are shown in Fig. 1. The maximum concentrations of bromobutide were observed within 3 days after application. The bromobutide concentrations decreased to less than 5% of the maximum concentrations after 12 days, which approximates the results obtained for paddy fields in Yamaguchi (Morinaka et al. 1993) and Shiga (Hasukawa et al. 2009). However, the

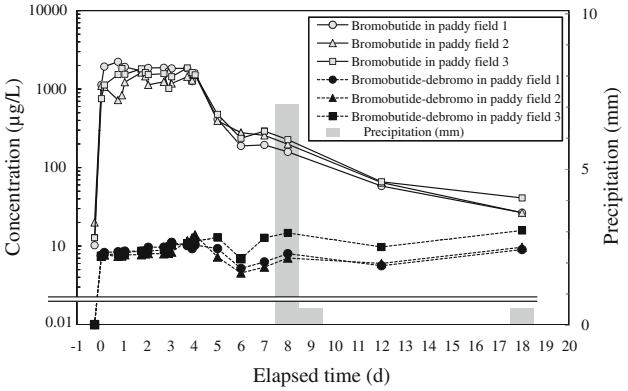

Fig. 1 Concentrations of bromobutide and bromobutide-debromo in paddy water

Table 1 Bromobutide and bromobutide-debromo in waters from paddy fields

Paddy field	n	Bromobutide					
		Concentration (μg/L)			Amount (mmol)		
		Average	Max	Min	Average	Max	Min
1	20	1,270	2,230	27	250	590	5.5
2	20	930	1,640	27	350	1,010	14
3	20	1,110	1,860	41	140	310	4.6
Paddy field	n	Bromobutide-debromo					
		Concentration (μg/L)			Amount (mmol)		
		Average	Max	Min	Average	Max	Min
1	20	8.6	11.1	5.2	2.2	3.4	0.86
2	20	8.3	13.8	4.5	4.1	6.9	2.4
3	20	9.9	15.8	6.9	1.6	2.4	0.79

Table 2 Bromobutide and bromobutide-debromo in soils from paddy fields

Paddy field	n	Bromobutide					
		Concentration (μg/kg dry)			Amount (mmol)		
		Average	Max	Min	Average	Max	Min
1	11	1,200	4,140	210	200	590	46
2	11	880	2,210	150	220	440	48
3	11	960	2,730	87	140	340	15
Paddy field	n	Bromobutide-debromo					
		Concentration (μg/kg dry)			Amount (mmol)		
		Average	Max	Min	Average	Max	Min
1	11	60	119	10	15	27	2.9
2	11	42	74	8.7	15	29	3.6
3	11	55	97	6.8	11	19	1.5

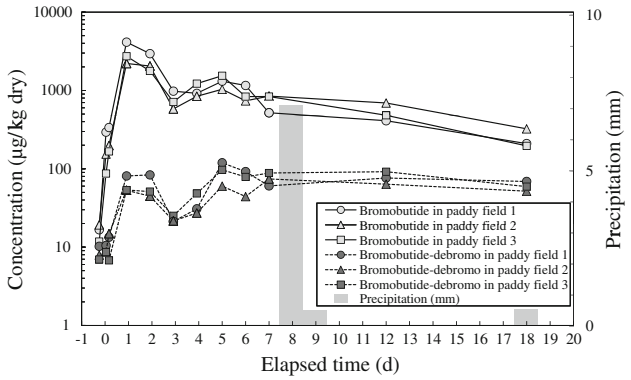

Fig. 2 Concentrations of bromobutide and bromobutide-debromo in paddy soil

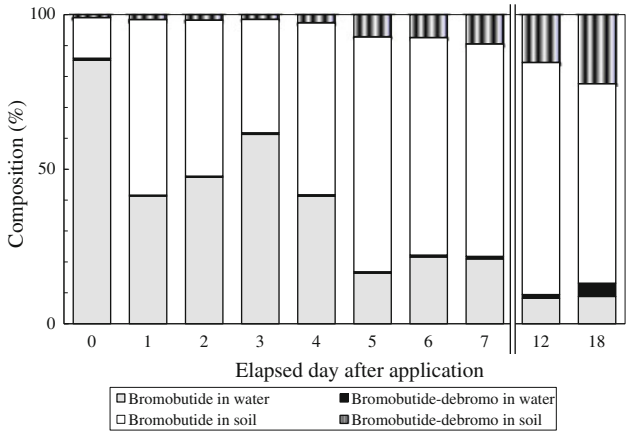

Fig. 3 Mean compositions of bromobutide and bromobutide-debromo in paddy water and soil

maximum concentrations of bromobutide-debromo were observed 3 days (paddy field 1) to 18 days (paddy field 3) after application. The bromobutide concentrations in all paddy waters at 5 days after the application decreased to around a third to a quarter of those on the previous day. This decrease was caused by the drainage of paddy water after collection of the water samples at 4 days after application.

The bromobutide and bromobutide-debromo concentrations in paddy soils sampled after application are presented in Table 2. The bromobutide and bromobutide-debromo concentrations in the paddy soils are presented in Fig. 2. The maximum concentrations of bromobutide were observed within 24 h after application. The maximum concentrations of bromobutide-debromo were observed 5 days (paddy fields 1 and 3) to 7 days after application (paddy field 2). Few reports have described the variations of bromobutide and bromobutide-debromo in paddy soil. Therefore, this study is useful to elucidate the variations in their concentrations in paddy soils after application.

Table 3 Bromobutide in runoff from paddy fields

Paddy field	Area (m^2)	Applied amount (mmol)	Runoff amount (mmol)	Runoff ratio (%)
1	2,700	580	68	12
2	4,030	770	330	43
3	1,740	380	110	29
	Mean ± standard deviation			28 ± 16

The respective variations in mean compositions of bromobutide and bromobutide-debromo in the paddy waters and soils are presented in Fig. 3. The ratio of bromobutide in paddy water decreased from 85% at 4 h after application to 8.8% at 18 days after application. The ratio decreased from 41% at 4 days after application to 16% at 5 days after application. Accordingly, the ratio of bromobutide in paddy soil increased definitively 5 days after application. This resulted from the drainage of the paddy waters, as described above. However, the ratios of bromobutide-debromo in the

Table 4 Kinetic parameters of the first-order decrease model estimated for bromobutide in paddy fields

Paddy water	k (/d)	C	n	r	p	$t_{1/2\ w}$ (d)
1	−0.290	6.17	20	−0.930	<0.01	2.4
2	−0.227	6.40	20	−0.869	<0.01	3.1
3	−0.269	5.62	20	−0.919	<0.01	2.6
		Mean ± standard deviation				2.7 ± 0.34
Paddy soil	k (/d)	C	n	r	p	$t_{1/2\ s}$ (d)
1	−0.134	6.06	9	−0.927	<0.01	5.2
2	−0.070	5.90	9	−0.839	<0.01	10
3	−0.124	5.69	9	−0.951	<0.01	5.6
		Mean ± standard deviation				6.9 ± 2.6

paddy water and soil increased from 0.7% and 1.0% at 4 h after application to 4.3% and 22% at 18 days after application, respectively. This increase was predominantly attributable to the degradation of bromobutide to bromobutide-debromo in the paddy water and soil.

Since the paddy waters were drained from paddy fields 1–3 at 4 days after application, the runoff amount of the bromobutide including the metabolite in a paddy field was calculated by subtracting the sum of the bromobutide and bromobutide-debromo amounts in the paddy waters and soils on 5 days after the application from those on the prior day. The calculated runoff amounts and the runoff ratio are presented in Table 3 together with the applied amounts of bromobutide. Runoff ratios of bromobutide based on river loads to applied amounts in the river basins (Hasukawa et al. 2009; Kawasaki et al. 2008; Sudo and Kawachi 2006) were reported as 1.60%–30.8%. The runoff ratios in paddy fields 1 and 3 were comparable to the reported values.

The organic carbon normalized soil sorption coefficient (Koc) was calculated using the following Eq. 1:

$$K\mathrm{oc} = (C\mathrm{s}/C\mathrm{w}) \times (100/C\mathrm{oc}) \quad (1)$$

where Cs and Cw represent the concentrations of bromobutide and bromobutide-debromo in the paddy soil (μg/kg) and the paddy water (μg/L), respectively, and Coc is the concentration of the organic carbon (%). The calculated Koc values of bromobutide increased to the maximum values (100, 160 and 140 mL/g in paddy fields 1, 2 and 3 at 18, 12 and 18 days after application, respectively). The average values of the calculated Koc values in the paddy fields during days 12–18 after application were 120 ± 25 mL/g (93–160 mL/g), which was 0.74 or 0.39 of the reported values of 163 and 306 (Food Safety Commission 2008). Therefore, the applied bromobutide was not distributed between the soil and water in the ratio at equilibrium during the investigated period, existing more in the paddy water than under the equilibrium condition.

The decrease of bromobutide in the water and soil can be interpreted using first-order reaction kinetics as Eq. 2:

$$\ln A = kt + C \quad (2)$$

where A signifies the amount of bromobutide in the paddy water and/or soil (mmol), k denotes the decreasing rate (/d), t is the elapsed time after the application (d), and C represents a constant. The calculated k and C values are given in Table 4. The decreasing plots of paddy waters and soils were well fitted ($p < 0.01$) to the first-order reaction given as Eq. 2. Regarding bromobutide-debromo in the paddy water and soil, no significant correlation was found between the natural logarithm of the bromobutide-debromo amount and t.

The respective half-lives of bromobutide in the water ($t_{1/2\ w}$) and soil ($t_{1/2\ s}$) were estimated using the established relations (Table 4). The half-life value of bromobutide under solar irradiation was reportedly 11 weeks in paddy water without paddy soil (Takahashi et al. 1985). The mean $t_{1/2\ w}$ value was only 0.035 of the reported half-life value. Moreover, the mean $t_{1/2\ s}$ value in the paddy soil was 0.22–0.11 of the reported half-life value for 31–64 days, in soil (Kanazawa 1996). These marked decreases of bromobutide both in water and soil in this study were attributable mainly to the distribution of bromobutide between water and soil (Fig. 3) as well as the runoff from the paddy field (Table 3).

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