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Behavior of Herbicide Pyrazolynate and its Hydrolysate in Paddy Fields after Application

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Abstract Behavior of the herbicide pyrazolynate, 4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl *p*-toluenesulfonate, in paddy water and soil after application to paddy fields was investigated to evaluate the hydrolyzation to destosyl pyrazolynate (DTP), 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole. The respective maximum concentrations of pyrazolynate and DTP were 440–1,240 and 200–260 μg/L, respectively, in the paddy water, and 610–860 μg/kg dry and 460–730 μg/kg dry in the paddy soil. The applied pyrazolynate was drained from the paddy fields as DTP. The runoff ratios of DTP from the paddy fields were calculated as 19 % ± 14 %. The respective mean values of the half-lives of pyrazolynate and DTP were 0.87 ± 0.091 and 17 ± 1.4 days in the paddy water and 2.2 ± 0.70 and 26 ± 2.1 days in the paddy soil, respectively.

Keywords Herbicide · Pyrazolate · Hydrolysate · Paddy water · Paddy soil · Runoff · Half-life

Paddy rice farming has played an important role in crop production throughout the world including Japan, where paddy fields cover a total area of 2.47 million ha, accounting for 54.2 % of all cultivated area (4.56 million ha) in FY2011. Current agricultural practices rely heavily on pesticides for rice production. Manufactured pesticides exceeded 200 varieties and 230 metric kilotons in FY2010 in Japan. Approximately 170 pesticides have been used to control paddy field weeds, fungi and pests. Their potential risk of contaminating open water by runoff from the paddy fields has posed a great concern. Approximately 70 herbicides are applied to paddy fields for rice farming in Japan. Pyrazolynate (pyrazolate), 4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl *p*-toluenesulfonate, is a common herbicide used to control both annual and perennial weeds in Japan. Pyrazolynate is rapidly hydrolyzed in water to destosyl pyrazolynate (DTP), 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole. DTP is the herbicidal entity of pyrazolynate (Yamaoka et al. 1987). Whereas pyrazolynate is only slightly soluble in water with the water solubility of 0.056 mg/L at 25°C, DTP is soluble in water with that of 415 mg/L at 25°C (Yamaoka et al. 1988b). Pyrazolynate and DTP were reported to be detected in river water (Iwafune et al. 2010). Although the variation of pyrazolynate in soil and those of DTP in water and soil have been investigated individually (Yamaoka et al. 1987, 1988a, c), few studies have reported the behaviors of pyrazolynate and DTP in actual paddy water and soil. This paper describes recent variations of pyrazolynate and DTP both in paddy field waters and soils after application, and evaluates their respective decreases in paddy fields.

Materials and Methods

The three investigated paddy fields 1–3 were located in a rice cultivation area in Niigata City, Niigata, Japan. Pyrazolynate was applied to the paddy fields on May 27, 2010. The paddy waters in the three paddy fields were drained at 15, 63 and 76 days after the application. Water and soil samples were collected during May 27–October 22, 2010 at four locations in paddy field 1 and at six locations each in

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paddy fields 2 and 3. Soil samples were collected from the 0–4 cm surface layer from a paddy field at each location, because 88 %–100 % of applied pyrazolynate and DTP were reported to remain in 0–3 cm soil from the surface (Yamaoka et al. 1988b). Equal volumes of the collected water from a paddy field were combined and mixed well as water samples. Equal weights of the collected soils were also combined and mixed well as soil samples. All samples were stored at 5°C in the dark the dark. All were analyzed within 24 h after collection.

Reagents were purchased from Kanto Kagaku (Tokyo, Japan) and from Wako Pure Chemical Industries (Osaka, Japan). A gas chromatograph–mass spectrometer (GC/MS), Finnigan POLARIS Q (Thermo Fisher, Waltham, MA), equipped with 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 quantitative analyses.

Determination of pyrazolynate and DTP was performed using the reported method (Tanizawa et al. 1987, 1988; Yamaoka et al. 1988b). The extracted DTP was tosylated to pyrazolynate with *p*-toluenesulfonyl chloride. Pyrazolynate was determined by GC/MS using perylene–d_{12} as an internal standard. The correlation coefficient (r) of each calibration curve was greater than 0.995. The minimum quantification limits were 0.1 µg/L for water and 10 µg/kg for soil. The overall recoveries of pyrazolynate and DTP from 100 mL of paddy water and 10 g of paddy soil were investigated by adding 0.2 µg of pyrazolynate and DTP to the water and soil. The mean of overall recoveries and relative standard deviation ($n = 3$) of pyrazolynate were 92 % and 11 % from water, and 76 % and 17 % from soil, respectively. The means of overall recoveries and relative standard deviations ($n = 3$) of DTP were 87 % and 15 % from water, and 65 % and 14 % from soil, respectively.

Results and Discussion

Pyrazolynate and DTP were not detected from paddy waters and soils sampled 5 h before the application. The pyrazolynate and DTP concentrations in the paddy waters and soils sampled after the application are summarized in Table 1. The ratios of the maximum amounts of pyrazolynate to the applied amounts were 25 %–38 % in paddy waters and 32 %–41 % in the paddy soils. Those of DTP to the applied amounts were 11 %–21 % in paddy waters and 37 %–53 % in the paddy soils. Moreover, the sum ratios of pyrazolynate and DTP were 35 %–40 % in the paddy waters and 56 %–78 % in the paddy soils at maximum. Regarding the DTP in paddy waters, the maximum concentrations of DTP in waters from the pot tests were 0.55 and 0.61 mg/L (Tanizawa et al. 1987). These values were equivalent to 18 %–20 % of the applied pyrazolynate amount. Namely, the results in the DTP ratio of this study were comparable to the reported values.

The variation in the mean amounts of pyrazolynate and DTP in the paddy waters and soils are presented in Fig. 1. The mean pyrazolynate amounts in the paddy water and soil were at maximum within 24 h after application. The pyrazolynate amounts in water and soil were decreased to below the detection limits at 6 and 14 days, respectively, after the application. Those of DTP fluctuated until 5 days after the application and were at maximum on 6 days after the application. The DTP amounts decreased gradually to below detection limits at 83 days in the water and 140 days in the soil after the application. Few reports have described the variations of the applied pyrazolynate and DTP in actual paddy fields. Therefore, this study is useful to elucidate the variations of pyrazolynate and DTP in paddy waters and soils after application.

Table 1 Pyrazolynate and DTP in paddy fields

Paddy field	Pyrazolynate in paddy water							DTP in paddy water						
	n[a]	Concentration (µg/L)			Amount (mmol)			n	Concentration (µg/L)			Amount (mmol)		
		Mean	Max	Min	Mean	Max	Min		Mean	Max	Min	Mean	Max	Min
1	7	350	1,240	31	88	260	5.5	15	90	260	5.4	35	140	0.51
2	7	310	840	29	75	230	3.8	14	100	220	11	38	100	2.0
3	7	180	440	28	99	260	5.5	14	80	200	10	43	110	1.4
Paddy field	**Pyrazolynate in paddy soil**							**DTP in paddy soil**						
	n	Concentration (µg/kg dry)			Amount (mmol)			n	Concentration (µg/kg dry)			Amount (mmol)		
		Mean	Max	Min	Mean	Max	Min		Mean	Max	Min	Mean	Max	Min
1	7	390	860	38	120	270	12	17	440	730	15	210	360	7
2	7	220	610	78	100	290	37	15	280	650	10	210	480	7
3	6	280	780	124	130	370	59	11	310	460	12	230	340	9

[a] Number of detected samples

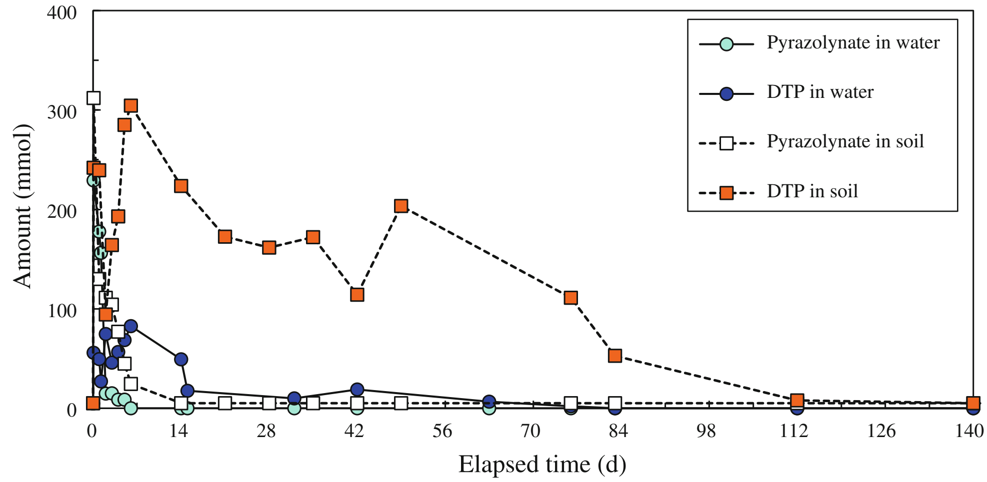

Fig. 1 Variations in mean amounts of pyrazolynate and DTP in paddy water and soil

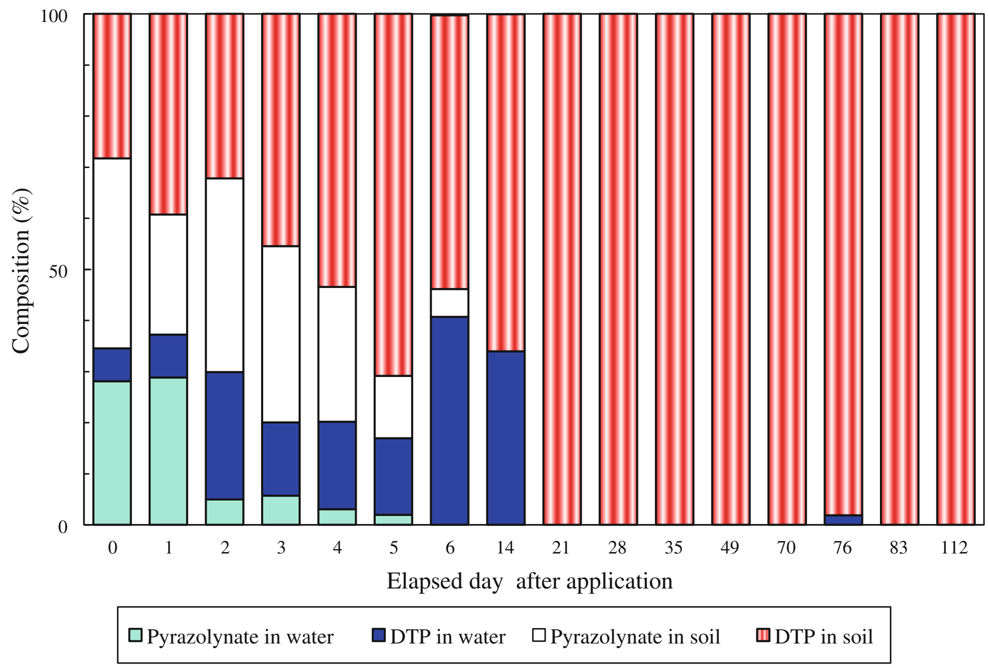

Fig. 2 Mean compositions of pyrazolynate and DTP in paddy water and soil

The respective variations in mean compositions of pyrazolynate and DTP in the paddy water and soil are presented in Fig. 2. The ratio of pyrazolynate in paddy water decreased from 28 % to 29 % within 24 h after the application to 1.9 % at 5 days after the application. That in paddy soil increased immediately to 37 % at 2 h after the application. This reflected the extremely low water solubility and the high soil sorption coefficient (7,855 and 29,830 mL/g) of pyrazolynate (Matsui et al. 2006). The value then decreased from 24 % to 38 % within 4 days after the application to 5.4 % at 6 days after the application. The DTP ratio in paddy water increased from 6 % at 2 h to 41 % at 6 days after the application; then it decreased to 34 % at 14 days. The ratio decreased dramatically to below the detection limit at 21 days. This decrease resulted from the drainage of paddy water at 15 days after the application. Accordingly, the ratio of DTP in the paddy soil increased gradually from 28 % at 2 h, and accounted for 100 % at 21 days after the application. The ratio decreased to 98 % at 76 days. The decrease suggested that a part of DTP in soil phase was dissolved in the water phase because of the high water solubility of DTP.

A part of the applied pyrazolynate and DTP could flow out from the paddy fields with the drainages of the paddy waters. The runoff events occurred on 15, 63 and 76 days

Table 2 DTP in runoff from paddy fields

Paddy field	Area (m^2)	Applied amount of pyrazolynate (mmol)	Runoff amount of DTP (mmol)	Runoff ratio (%)
1	2,700	683	25	3.7
2	4,030	911	32	3.5
3	4,070	911	22	2.4
	Mean ± standard deviation			3.2 ± 0.70

after the application. The applied herbicides were drained as DTP, because no pyrazolynate was observed in the paddy water after 6 days after the application. The runoff amount of DTP in a paddy field was calculated based on the DTP concentrations in the paddy waters and the volumes of the drained waters. The calculated runoff amounts and the runoff ratios to the applied amounts of pyrazolynate are presented in Table 2. Regarding paddy fields 1 and 2, we have reported the runoff ratios of an herbicide bromobutide as 12 % and 43 %, respectively, in the 2009 investigation (Morohashi et al. 2012b). The runoff ratios of DTP in the two paddy fields were lower than those of bromobutide. Therefore, it appears that the runoff ratio of an herbicide in a paddy field depended on the herbicide properties.

The decrease of pyrazolynate in the water and soil can be interpreted using first-order reaction kinetics as Eq. (1).

$$\ln A = kt + C \quad (1)$$

Therein, A signifies the amount of pyrazolynate in the paddy water or soil (mmol), k denotes the decreasing rate (per day), t is the elapsed time after the application (d), and C represents a constant. Figure 3 shows the ln A values versus t with the regression lines using the least-squares method. The decreasing plots of the ln A values in paddy waters and soils were fitted significantly to the first-order reaction (Table 3) given as Eq. (1). The respective half-lives of pyrazolynate in the water ($t_{1/2\ \mathrm{W}}$) and soil ($t_{1/2\ \mathrm{S}}$) were estimated using the established relations (Table 3). Yamaoka et al. (1987) reported the half-life values of pyrazolynate in water at pH 5 and 7 as 106 and 25 h, respectively. In this study, the pH values of paddy fields 1–3 were 6.1 ± 0.32, 5.8 ± 0.40 and 6.2 ± 0.49, respectively. Therefore, the $t_{1/2\ \mathrm{W}}$ value was definitely equivalent to the reported value at pH 7. The half-life values of pyrazolynate in soil were reported as 8–20 days (Matsui et al. 2006), and those in paddy soils under flooded conditions were 10 days (Yamaoka et al. 1988a). The mean $t_{1/2\ \mathrm{W}}$ value of this study was 0.11–0.28 of the reported half-life value. The decrease of pyrazolynate in this study was attributable mainly to the properties of the investigated conditions as well as to those of the soils used (Morohashi et al. 2012a).

The relation of the natural logarithm of DTP amount and t was also shown during 5–76 days for paddy water and to 112 days for paddy soil (Fig. 3), because the pyrazolynate amounts in the paddy water and soil decreased extremely compared to those in the paddy soil at 5 days after application (Fig. 1). We reported that bromobutide also decreased according to the first-order reaction kinetics in paddy water and soil, but the decreases of its metabolite bromobutide-debromo in paddy water and soil did not obey

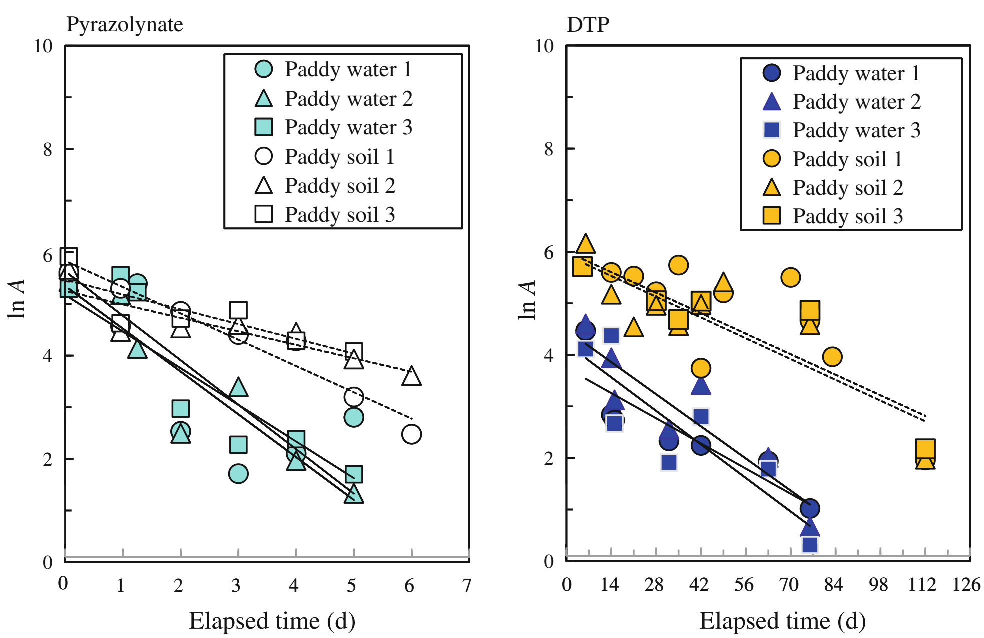

Fig. 3 Natural logarithm of pyrazolynate and DTP amounts (mmol) in paddy field versus elapsed time with regression lines using the least-squares method

Table 3 Kinetic parameters of the first-order decrease model estimated for pyrazolynate and DTP in paddy fields

Paddy field	Pyrazolynate in water						Pyrazolynate in soil					
	k (/d)	C	n	r	p	$t_{1/2\ W}$ (d)	k (/d)	C	n	r	p	$t_{1/2\ S}$ (d)
1	−0.710	5.17	7	−0.778	<0.05	1.0	−0.509	5.83	7	−0.872	<0.05	1.4
2	−0.829	5.35	7	−0.925	<0.01	0.84	−0.261	5.25	7	−0.872	<0.05	2.7
3	−0.861	5.63	7	−0.913	<0.01	0.81	−0.280	5.42	6	−0.828	<0.05	2.5
	Mean ± standard deviation				0.87 ± 0.091						2.2 ± 0.70	
Paddy field	DTP in water						DTP in soil					
	k (/d)	C	n	r	p	$t_{1/2\ W}{}^{a}$ (d)	k (/d)	C	n	r	p	$t_{1/2\ S}{}^{b}$ (d)
1	−0.0422	4.15	8	−0.867	<0.01	16	−0.0244	5.92	12	−0.736	<0.01	28
2	−0.0383	4.14	8	−0.849	<0.01	18	−0.0274	5.84	10	−0.835	<0.01	25
3	−0.0451	4.14	8	−0.886	<0.01	15	−0.0284	6.00	6	−0.884	<0.05	24
	Mean ± standard deviation				17 ± 1.4						26 ± 2.1	

[a] Half-life during 5–76 days

[b] Half-life during 5–112 days

the first-order reaction kinetics (Morohashi et al. 2012b). For DTP, the decreasing plots of the ln A values for DTP in paddy waters and soils were fitted significantly to the first-order reaction given as Eq. (1) as depicted in Fig. 3, which might result from the much higher decrease rates of pyrazolynate in water and soil compared to those of DTP. The respective half-lives of DTP in the water and soil were also estimated using the established relations (Table 3). Yamaoka et al. (1988c) reported half-life values of DTP under sunlight conditions as 6 days in paddy water and 31–34 days in soil. Although the mean $t_{1/2\ S}$ value of this study was comparable to the reported values, the mean $t_{1/2\ W}$ in this study was almost three times as long as the reported value. The marked increase of the half-life in paddy water was attributable mainly to the dissolution of DTP in soil to water.

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