Indian Journal of Weed Science **52**(4): 362–365, 2020

Print ISSN 0253-8040 Online ISSN 0974-8164

Residue dynamics and degradation behaviour of pyrazosulfuron-ethyl in the rice field environment

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Article information

DOI: 10.5958/0974-8164.2020.00072.6

Type of article: Research article

Received : 15 September 2020
Revised : 2 December 2020
Accepted : 21 December 2020

Key words

Degradation, Dissipation, Herbicide, Pyrazosulfuron-ethyl, Residues dynamics

ABSTRACT

Pyrazosulfuron-ethyl is used in rice fields to manage a range of annual and perennial weeds. Its long-term herbicide residue dynamics in rice ecosystem and degradation pattern is poorly characterized. Therefore, in the present study, field experiments were conducted for consecutive two years to investigate the residue dynamics and degradation of pyrazosulfuron-ethyl in the soil, rice plant, water and fishes in the rice field. Pyrazosulfuron-ethyl residues were found to be below the maximum residues levels (0.01 mg/kg) in the soil, rice grains, and straw. In the fishes, pyrazosulfuron-ethyl residues were in the range of 0.056- 0.013 µg/g. Half-life of pyrazosulfuron-ethyl in the soil of rice field was found to be 9.41 to 13.9 days. Results showed that pyrazosulfuron-ethyl at 25 g/ha application rate did not cause any environmental hazards and can be safely applied in the rice fields for management of annual and perennial weeds.

INTRODUCTION

Herbicides are commonly used in the modern agriculture to minimize potential yield losses by the weeds. According to an estimate, approximately 80% of applied pesticide in agricultural practices did not reach to its target and dispersed through the air, soil, and water (Sondhia 2014). As a result, they are frequently been detected in the air, surface and ground water, sediment, soil, vegetable and to some extent in the processed foods (Battanlin 2000, Sondhia 2014). In many instances herbicide applications resulted in the accumulation of residues and metabolites in the soils above the prescribed residues limits (Shalaby and Abdou 2010, Sondhia 2014). Besides this, pesticides are also found into aquatic ecosystems through runoff water.

Pyrazosulfuron-ethyl,[ethyl-5-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-1-methyl pyrazole-4-carboxylate is one of the sulfonylurea group of herbicide which is widely used to control perennial and annual weeds, especially broad-leaved weeds and sedges in the rice fields in rice growing countries as pre-emergence or early post-emergence application (Sondhia *et al.* 2013). It retards growth of weed through inhibition of acetolactate synthase (ALS), a key enzyme that catalyzes the biosynthesis of three important amino acids, *viz.* valine, leucine, and isoleucine which are essential for the protein synthesis of plants (Zhu *et al.* 2002, Sondhia 2009, Sondhia *et al.* 2013). Due to high persistence in soil, a few leguminous crops are reported to be highly sensitive to the residues of sulfonylurea herbicides (Ye *et al.* 2003, Sondhia *et al.* 2016, Sondhia 2019).

Excessive use of pyrazosulfuron-ethyl in the rice fields may have adverse effects on the agricultural production, environment and human health (Ding *et al.* 2010, Sondhia *et al.* 2016) and may significantly decrease the soil biota (Xu *et al.* 2009). In earlier studies, Zheng *et al.* (2008) demonstrated dissipation of pyrazosulfuron-ethyl in water by chemical hydrolysis. Xu *et al.* (2009) and Sondhia *et al.* (2013) reported fungal degradation of pyrazosulfuron-ethyl in the soil and identified major and minor metabolites. Singh *et al.* (2012) provided translocation of ^{14}C pyrazosulfuron-ethyl in the rice plant but did not study its complete fate in the rice ecosystem. Therefore, this study was undertaken to investigate degradation behaviour and residues dynamics of pyrazosulfuron-ethyl in the soil, plant, fishes and water under rice field environment.

MATERIALS AND METHODS

The study was conducted during rainy seasons in 2012 and 2013. In both the years, approximately

25-days old seedlings of rice Cv. '*Kranti*' were transplanted in the soil of experimental field with a row spacing of 20 x 15 cm. Pyrazosulfuron-ethyl was sprayed as a post-emergence to control mix flora of weeds in the rice field at recommended dose of 25 g/ha along with a check (no herbicide). Rice crop was raised according to irrigated conditions with the recommended package of practices. The experimental soil was found to be of clay loam texture with 67.32% sand, 10.0% silt, and clay 22.68%, pH 7.4 and organic carbon 0.85%. Commercial and analytical grade pyrazosulfuron-ethyl was purchased from United Phosphorus Limited Company, Gujarat. Analytical grade chemicals and solvents were used in the studies which were purchased from E Merck. Germany.

Collection of soil, water, plant and fish samples

Degradation of pyrazosulfuron were determined in the treated and untreated soils collected in polyethylene bags from the rice field at 0, 5, 10, 20, 30, 60, 90 days after the herbicide application and at harvest. Rice plant samples were collected on 1, 10, 20, 30, 60, and at harvest after the herbicide application. Water samples were taken at 5, 10, 20, 30, 60, 90 days after the herbicide application to evaluate pyrazosulfuron-ethyl residues as a result of runoff. Fishes were collected from the adjacent ponds to determine pyrazosulfuron-ethyl residues at 30, 60, and 100 days after the herbicide application in the rice field.

Determination of pyrazosulfuron-ethyl residues

Ten g of the soil from each sample was weighed and transferred to an Erlenmeyer flask of 250 ml capacity. Pyrazosulfuron-ethyl was then extracted and analyzed from the soil samples following methods of Sondhia *et al.* (2013). The limit of detection (LOD) of pyrazosulfuron-ethyl in the various matrixes was detected with acceptable certainty as demonstrated by Sondhia (2008) and European Commission Safety of the Food Chain Pesticides and Biocides guidelines (2015). The LOD and the LOQ for pyrazosulfuron-ethyl were found to be 0.001 and 0.01 µg/mL, respectively.

Pyrazosulfuron residues in the soil, rice, water, and fishes were determined by the HPLC attached to a Photo Diode Array Detector utilizing a C-18 column (ODS) of 250 mm length and 4.6 mm of internal diameter. A mobile phase consisted of acetonitrile: water (70:30) was used with a flow rate of 0.9 mL/ min^{-}. HPLC system was injected with standard solutions (20 µL) of pyrazosulfuron-ethyl in acetonitrile with a concentration range of 0.001 to 10 µg/mL. Detection of pyrazosulfuron-ethyl was done at a wavelength at 215 nm and peak areas (µV/sec) was measured and plotted versus concentrations (µg/ mL) and fitted to a simple linear regression to obtain an equation for the standard curve. The residues of pyrazosulfuron-ethyl in each sample were calculated based on the basis of slope of the standard curve which was found to be y=-13431x +36462 (R^2 0.99). The data were calculated as mean ± S.D and analyzed following analysis of variance technique (ANOVA). Degradation kinetics was described using a first-order reaction model: $Ct = C0 \times e^{-kt}$, where C_0 (mg kg) was the initial concentration in the soil, Ct (mg kg) was the concentration at time t (min) and k (per min) is the rate constant. The half-life *i.e.* the time of dissipation of was calculated as $t1/2 = \ln (2)/ k,$ where K is the degradation rate constant.

RESULTS AND DISCUSSION

Residue dynamics of pyrazosulfuron-ethyl in the soil of rice field

Degradation of pyrazosulfuron-ethyl in the soil of rice field is presented in **Figure 1**. After two hours of spray, the pyrazosulfuron-ethyl residues were found to be 0.0595 µg/g in the soil of rice field. Pyrazosulfuron-ethyl residues were found to be degraded rapidly from the rice soil and decreased to 0.025, 0.018 and 0.017, 0.0010 µg/g after 5, 10 and 20, 30 days, respectively. At 90 days residues of pyrazosulfuron-ethyl were found below <0.001 µg/g in the soil of rice field. However, in 2013, after two hours of application of pyrazosulfuron-ethyl, 0.095 µg/g residues were detected in the soil which dissipated to 0.0219 and 0.0088 µg/g at 20 and 30 days, respectively. At 60 and 90 days, residues of pyrazosulfuron-ethyl were reached to a level of <0.001 µg/g in the soil of rice field.

Pyrazosulfuron-ethyl residues in the water

As a result of runoff from the rice field to the adjacent ponds, an amount of 0.033 and 0.0167 µg/mL pyrazosulfuron-ethyl residues were detected in the pond water at 10 and 20 days, respectively after herbicide application in the rice field. Residues of pyrazosulfuron-ethyl in the pond water were found to be below <0.001 µg/mL after 30 days in 2012 (**Table 1**). However, in 2013, at 5 and 10 days, 0.0349 and 0.0314 µg/mL residues of pyrazosulfuron-ethyl were detected in pond water which degraded to 0.0096 µg/ mL at 20 days, respectively. Residues of pyrazosulfuron-ethyl were dissipated to below 0.001 µg/mL after 60 days in the pond water.

Residue of pyrazosulfuron-ethyl in the rice plants

An amount of 0.0116 and 0.036 µg/g pyrazosulfuron residues were found in the green plant at 10 and 30, days, respectively in 2012. Residues were found to be below the detection limit (<0.001 µg/g) at 60 days. Pyrazosulfuron-ethyl residues were also found below the detection limit (0.001µg/g) in the rice straw at harvest (**Table 1**). In 2013, residues of pyrazosulfuron-ethyl were in the range of 0.2384 to 0.012 µg/g in the green rice plants at 10 to 30 days.

Residues of pyrazosulfuron-ethyl in the fishes

In 2012, pyrazosulfuron residues as a result of runoff in the fishes were found to be 0.013 µg/g after 30 days; however, residues were degraded to below the limit of detection after 60 days. In the fishes, 0.056 µg/g residues of pyrazosulfuron-ethyl were found after 30 days in the fishes in 2013. At 60 days pyrazosulfuron-ethyl, residues in fishes were found below the detection limit (<0.001 µg/g) (**Table 1**).

Pyrazosulfuron –ethyl was found to degrade in the soil according to first order equations: y = -0.023x +1.068 (linear) and y = -0.032x +1.508 in 2012 and 2013, respectively. The degradation trends of pyrazosulfuron-ethyl residues on soil at various days, determination coefficients, and half-life are given in **Table 2**, and **Figure 1** and **2**. On the basis of dissipation equations, the half-life of pyrazosulfuron-ethyl in the soil of rice field was found to be 13.86 and 9.41 days under field conditions in 2012 and 2013, respectively.

Singh *et al.* (2012) found half-life of pyrazosulfuron approximately 5 days at 20-30 g/ha rates of applications, whereas Ishii *et al.* (2004) found half-life of pyrazosulfuron-ethyl as 11 and 1.9 days in rice field soil and water, respectively. Chu *et al.* (2002), reported half-life of pyrazosulfuron-ethyl as 16.2–24.4 days in the surface soil, 5.8–7.8 days in the bottom soil having low pH and high organic matter in a rice field experiment. The half-life found in this study in both the years was in similar range to first-order kinetics with half-life reported for other sulfonylurea herbicides such as chlorsulfuron (20-147 days), and metsulfuron-methyl (17-135 days) in soils having pH range from 3.9 to 7.0 (Sondhia 2009). In literature, degradation of sulfonylureas was reported to be less in neutral pH soils than in the acidic soils (Hultgren *et al.* 2002).

During the experiment in 2012 and 2013, total rainfall during the rice crop growth period was found to be 1309.9 and 2331.4 mm, respectively, that had a

Table 2. Rate kinetics equations, R^2 value and half-life of pyrazosulfuron-ethyl residues in the soil under rice field conditions

Year of study	Equation	R^2	DT_{50} (days)
2012	y = -0.023x + 1.068	0.88	13.9
2013	y= -0.032x+1.508	0.92	9.41

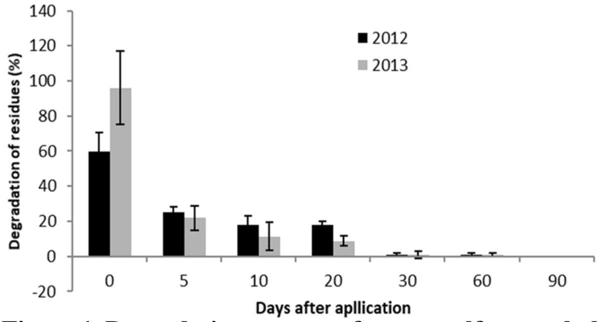

Figure 1. Degradation pattern of pyrazosulfuron-ethyl residues in the soil of rice field

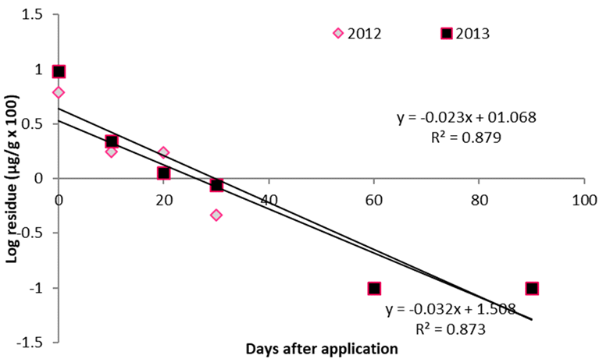

Figure 2. Dissipation rate kinetics of pyrazosulfuron-ethyl in the soil of rice field

Table 1. Residues of pyrazosulfuron-ethyl in the pond water and rice plants

Days	Residues (µg/g)					
	Pond water		Rice plants		Fishes	
	2012	2013	2012	2013	2012	2013
1	-	-	0.246*± 0.048**	0.312± 0.011	-	-
5	<0.001	0.0349± 0.010	-	-	-	-
10	0.033 ± 0.010	0.0314± 0.008	0.116± 0.010	0.238± 0.090	-	-
20	0.0167± 0.013	0.0096± 0.001	0.072± 0.010	0.163± 0.010	-	-
30	<0.001	0.0074± 0.0005	0.036± 0.006	0.012± 0.004	0.013± 0.004	0.056± 0.017
60	<0.001	<0.001	0.001	0.007± 0.001	<0.001	<0.001
90	<0.001	<0.001	<0.001	<0.001	-	-
100	-	-	-	-	<0.001	<0.001

* Mean of three replications; **Standard deviation

significant effect on residue dynamics in the soil, water, and plants. Due to continuous heavy rains in the month of June (422.3 mm) and July (613.8 mm) in 2013, more residues were reached to pond water as a result of runoff and detected even after 5 days of pyrazosulfuron–ethyl application in the rice field. Whereas in 2012 uneven rain in the month of June (130.4) and July (671.2), which caused the difference in the pyrazosulfuron-ethyl residues. Literature demonstrated that due to dry spell herbicide usually tend to adsorbed more in the soil and not moved by runoff (Suo *et al.* 2019) and hence pyrazosulfuron residues were not detected after 30 days in the pond water in 2012 (**Table 1**).

In our experiment, approximately neutral soil pH (7.4) and high organic carbon might have favored degradation of pyrazosulfuron-ethyl in the rice field by the process of hydrolysis and resulted in below detection levels of residues in the soil at harvest. Similar results were also reported by Zheng *et al.* (2013). The movement of pyrazosulfuron in the bottom layer of soil was also reported by Chu *et al.* (2002) besides its degradation via biochemical process, photolysis and through uptake by plants (Wang *et al.* 2013). In general, the degradation of pyrazosulfuron-ethyl was rapid in the soil of rice field in both the years.

Conclusion

In this study, pyrazosulfuron-ethyl was found to degrade quickly in the soil of rice field in both the years. Flooded conditions due to heavy rains, almost neutral pH and high organic carbon favored rapid degradation of pyrazosulfuron-ethyl in the soil of rice growing field and residues were not detected at harvest in the soil, grain and straw. Residues were also found below the maximum residue levels (MRL) of 0.01 mg/kg in the rice plants prescribed by Indian government under the prevention of food adulteration act and rules and therefore, pyrazosulfuron-ethyl can be considered as an effective and safe herbicide to be applied at 25 g/ha in transplanted rice to control sedges and broad-leaved weeds.

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