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Research Article

Field studies on persistence of pyrazosulfuron-ethyl in soil, ground water and residues in transplanted rice

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Summary

Field experiment was conducted at Zonal Agricultural Research center, Kathalagere, during *Kharif* 2008. To study persistence and residues of pyrazosulfuron-ethyl in soil and ground water in transplanted rice ecosystem were estimated using HPLC technique. Pyrazosulfuron-ethyl was applied at 25 g a.i. ha^{-1} and 50 g a.i. ha^{-1} with and without addition of recommended farm yard manure in transplanted rice. The study revealed that the residue of pyrazosulfuron-ethyl in soils ranged from 0.0103 and 0.0199 mg kg^{-1}, respectively with FYM at recommended and double the recommended dose on 2nd day of application. And without FYM the residues were 0.0116 and 0.0229 mg kg^{-1}, respectively. The residues were detected up to 35 days only. The half-life of pyrazosulfuron-ethyl ranged from 16.6 to 21 days. The results revealed that the residues of pyrazosulfuron-ethyl were below the detectable level in the post harvest soil, paddy grain and straw. No residues of pyrazosulfuron-ethyl were detected in ground water up to two weeks after the application of pyrazosulfuron ethyl. After two weeks the residues were detected in ground water collected from both the piezometers which were applied with recommended and double the recommended dose of pyrazosulfuron-ethyl .The residues ranged from 0.0071 to 0.0042 mg kg^{-1} between 21st and 28th day, respectively, after which the residues were below the detectable level both at recommended and double the recommended level of application. A maximum of 0.0154 mg kg^{-1} on 21st day and minimum of 0.0023 mg $kg^{-1}$of pyrazosulfuron ethyl residues on 35th day were detected in the underground water.

Key words : Pyrazosulfuron-ethyl, Half-life, HPLC

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Introduction

India is a leading producer of rice *(Oryza sativa* L.) in the world. Every year most of the yields losses occurring due to the infestation of grass, annual and perennials broad leaved weeds and sedges. There are many herbicides to control these weeds. Among them pyrazosulfuron- ethyl is a selective pre-emergence sulfonylurea herbicide, used primarily to control broadleaf weeds and some grasses. It is already established that sulfonylurea group of herbicides are very effective against various weeds and grasses (Suzuki *et al*., 1990: Umehara and Suzuki, 1992: Hamada *et al*., 1999: Chu *et al*., 2002).

This herbicide has become more popular due to its high activity at low application rates and low mammalian toxicity. Although pyrazosulfuron-ethyl would appear to be degraded rapidly in soils like other sulfonylureas herbicides (Kim *et al.,* 2003a and 2003b; Mikada *et al.,* 1996). Pyrazosulfuron-ethyl herbicide application in soil leads to various reaction in soils and environment, which determine the toxicity and persistence in the soil and plants. The breakdown of pyrazosulfuron-ethyl is largely depends on soil temperature, moisture content, organic matter and pH. The chemical will degrade faster under acidic condition, and soil with higher moisture content at higher temperature. In Karnataka pyrazosulfuron-ethyl is recommended for transplanted rice at 25 g a.i ha^{-1} and is available as Sathi (Trade name) 10 WP in 80 g packet, being extensively used in Bhadra commend area.

Resources and Research Methods

Field experiment was conducted at Zonal Agricultural Research Center, Kathalagere, during Kharif 2008. The experiment was laid out in Randomized Complete Block Design (RCBD) with six treatments and four replications. T_1: Recommended dose of pyrazosulfuron-ethyl (25 g a.i ha^{-1}), T_2: Recommended dose of pyrazosulfuron-ethyl (25 g a.i ha^{-1}) + FYM@10t ha^{-1}, T_3: Double the recommended dose of pyrazosulfuron-ethyl (50 g a.i ha^{-1}), T_4: Double the recommended dose of pyrazosulfuron-ethyl (50 g a.i ha^{-1}) +FYM 10t ha^{-1}, T_5: Hand weeding @ 30 and 45 days after transplanting and T_6: Un weeded control. The physical and chemical properties of the soil given in Table A.

Table A : Physical and chemical properties of Kathalagere soils

pH	EC	OM (g kg^{-1})	% Sand	% Silt	% Clay	CEC (c mol kg^{-1+})
7.3	0.03	12.6	70.3	10.3	19.4	24.7

Recovery test :

***Soil, water, grain and straw* :**

20 g of the soil sample was transferred in 50 ml of screw tight test tube, for which 0.01 (10 mg L^{-1}), 0.1 (100 mg L^{-1}) and 1 (100 mg L^{-1}) ml standard pyrazosulfuron-ethyl solution in methanol was added quantitatively to each flask separately. The fortified soil was analyzed for pyrazosulfuron-ethyl.

Persistence studies :

Persistence of pyrazosulfuron-ethyl was studied by collecting soils from each treatment and pooled by different treatment. The collected sample (20 g) was extracted twice with two volumes of 50% (v/v) aqueous methanol by horizontal shaking on a mechanical shaker for 1 hour. The content was centrifuged and filtered through Whatman filter paper No.1 after the soil solids settled down. The twice extracts were then combined. The combined methanol extract was transferred to 500 ml of separatory funnel and diluted with 250 ml de-ionized water and 50 ml saturated NaCl solution and 1 ml of 6 N HCl. Pyrazosulfuron- ethyl residues were then quantitatively re-extracted twice with 50 ml and 25 ml of dichloromethane by thorough shaking. The combined dichloromethane extracts were then concentrated in rotary vacuum evaporator to dryness. Pyrazosulfuron-ethyl residues were then dissolved in 5 ml n-hexane.

Chromatographic glass column (15 mm * 50 cm length) were prepared for cleanup of pyrazosulfuron-ethyl residues from other co extractives with a small plug of cotton and 2.5 g anhydrous sodium sulphate overlaid 10 g of silica gel (grade V) as the adsorbent. The columns were pre washed with 50 ml of n- hexane. Pyrazosulfuron-ethyl residues in n-hexane were quantitatively transferred to the column after repeated rinsing with n-hexane. The column was washed with 50 ml of n-hexane and ethyl acetate (3:1). The eluate was discarded; finally the column was eluted with 75 ml solvent mixture of n-hexane and ethyl acetate (1:1). The eluate was evaporated to dryness in rotary vacuum evaporator. The residues were then dissolved in acetionitrile. This solvent was evaporated to dryness and finally the volume was made up to 5 ml by repeated washing with acetionitrile. A suitable aliquot of the cleaned up sample was injected into HPLC with the help of micro-liter syringe for quantitative residue analyses.

Degradation kinetics :

The data on persistence studies have been mathematically treated and fitted in the first order exponential decay equation in order to interpret the rate of degradation.

$$Ct = Coe - kt$$

where,

Ct - the concentration (mg g^{-1}) after time t (day), Co – initial concentration (mg g^{-1}) K – Rate constant (day). Thus a plot of logarithm of concentration against time gives a straight line with slope proportional to the rate constant. Writing $t_{1/2}$ as the time taken for 50 per cent degradation or "Half life", the above equation becomes.

$$t1/2 = (0.693.K)$$

Estimation of pyrazosulfuron-ethyl residues in ground water of transplanted rice :

Initially in the experimental plot T_1 and T_3 plots were selected and a dimension of 3' X $_3$' X $_6$' pits were opened and two piezometers (PVC pipe 6" dia and 7' length with perforated holes) were installed in the paddy field in such a way that the gradient along the slope is maintained with T_1 representing recommended dose and T_3 representing double the recommended dose. Gravel and sand were packed in the lower depth of the piezometer as shown in the figure with one foot visible above the ground. Later land preparation was carried out and transplanting of paddy was taken up. Pyrazosulfuron-ethyl was applied on the 2nd day of transplanting and water samples were collected on the same day after three hrs and subsequently at weekly interval and were analyzed for residues of pyrazosulfuron-ethyl by HPLC method.

Research Findings and Discussion

Recovery studies for pyrazosulfuron-ethyl in soil, grain, straw and water are presented in the Table 1. The mean recovery of pyrazosulfuron-ethyl in soil was 91.4 per cent, grain 87.9 per cent, straw 82.1per cent and water 84.2 per cent at the fortification levels of 0.01 (10 mg L^{-1}), 0.1 (100 mg L^{-1}), and 1 (100 mg L^{-1}) ml.

Table 1 : Per cent recovery of pyrazosulfuron-ethyl by HPLC method

Sr. No.	Conc. (mg kg^{-1})	Recovery (mg kg^{-1})	Recovery (%)	Mean (%)
Soil				
1.	0.01	0.0091	91.0	
2.	0.10	0.094	94.4	91.4
3.	1.00	0.810	81.0	
Water				
1.	0.01	0.009	90.9	
2.	0.10	0.079	78.7	84.2
3.	1.00	0.820	82.8	
Grain				
1.	0.01	0.009	91.4	
2.	0.10	0.091	90.1	87.9
3.	1.00	0.830	82.3	
Straw				
1.	0.01	0.0079	79.2	
2.	0.10	0.0890	89.4	82.1
3.	1.00	0.7800	77.7	

Con = Concentration

The persistence of pyrazosulfuron-ethyl in paddy field is shown in the Table 2. The residue of pyrazosulfuron-ethyl in soils ranged from 0.0103 and 0.0199 mg kg^{-1}, respectively (T_2 and T_4) on 2nd day of application. And with out FYM the residues were 0.0116 and 0.0229 mg kg^{-1}, respectively (T_1 and T_3). The degradation of the initial residue with the time taken in both the treatments were up to 35 days. At recommended level of application the residue level ranged 0.0116 on 2nd day to 0.0012 mg kg^{-1} on 35th day with out FYM treatment and 0.0103 and 0.0019 mg kg^{-1} with FYM treatment by the end of the 28 days after treatment. At double the dose of application the residues were 0.0229 and 0.0119 mg kg^{-1} respectively (T_3 and T_4). The degradation of the initial residue with the time taken in both the treatments were up to 45 days. At double the recommended level of application the residue level ranged 0.0229 on 2nd day to 0.0016 mg kg^{-1} on 45th day with out FYM treatment and 0.01119 to and 0.0021 mg kg^{-1} with FYM treatment by the end of the 35th day after treatment and the chromatograms were presented in Fig 1.

Table 2 : Persistence of pyrazosulfuron-ethyl residues (mg kg^{-1}) in soil – field study

Days after treatments / T	T_1	T_2	T_3	T_4
2	0.0116	0.0103	0.0229	0.0199
7	0.0091	0.0084	0.0196	0.0185
14	0.0076	0.0063	0.0155	0.0139
21	0.0056	0.0030	0.0134	0.0092
28	0.0028	0.0019	0.0072	0.0052
35	0.0012	BDL	0.0024	0.0021
42	BDL	BDL	0.0016	BDL
49	BDL	BDL	BDL	BDL
56	BDL	BDL	BDL	BDL
63	BDL	BDL	BDL	BDL

BDL – Below detectable level, T – Treatments

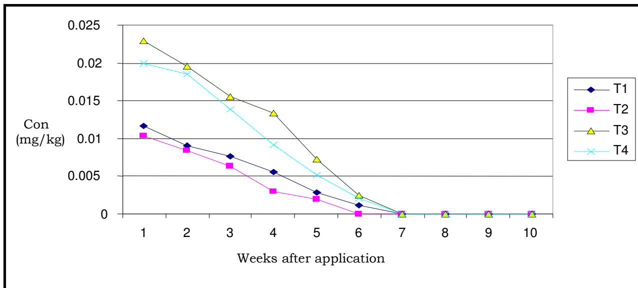

Fig. 1 : Persistence of pyrazosulfuron-ethyl residues (mg kg^{-1}) in soil- field study

Dissipation of pyrazosulfuron-ethyl in soil :

The dissipation parameters ($t_{1/2}$) were calculated from the best fit line of logarithms of residual concentration versus time for soil at both levels of treatments suggested that dissipation of pyrazosulfuron- ethyl first order kinetics ($R^2 > 0.98$) as shown in the Table 3.

Table 3 : First order kinetics of K_{deg}, R^2 and half-life ($t_{1/2}$) of experimental soil

Treatments	Quantity added (mg kg^{-1})	K_{deg} day^{-1}	R^2	$t_{1/2}$ day
Recommended dose of pyrazosulfuron-ethyl 25 g ai ha^{-1}	0.0125	0.039	0.982	17.7
Recommended dose of pyrazosulfuron-ethyl 25 g ai ha^{-1}+ FYM@10t ha^{-1}	0.0125	0.041	0.991	16.6
Double the Recommended dose of pyrazosulfuron-ethyl 50 g ai ha^{-1}	0.0250	0.031	0.986	21.8
Double the Recommended dose of pyrazosulfuron-ethyl 50 g ai ha^{-1}+FYM 10t ha^{-1}	0.0250	0.035	0.981	19.30

Initial values in soils immediately after application (2nd day) was 0.0116 to 0.0229 mg kg^{-1} for pyrazosulfuron-ethyl for recommended and double the recommended rates of application, respectively.

The half-life of pyrazosulfuron-ethyl ranged from 17.7 days for T_1, 16.6 days for T_2, 21.8 for T_3 and 19.3 for T_4 , respectively. The half-life was highest in double the recommended dose of pyrazosulfuron ethyl (50 a.i g ha^{-1}) than the recommended dose of pyrazosulfuron ethyl (25 a.i g ha^{-1}).

The K_{deg} day^{-1} ranged from 0.039 in T_1, 0.041 in T_2, 0.031 in T_3 and 0.035 in T_4.

Harvest time residues of pyrazosulfuron-ethyl in soil, grain and straw in transplanted rice :

In the present investigation the time gap between application of the herbicides and harvest of the crop was 10-12 weeks. The results revealed that the harvested materials of rice did not contain the residues of pyrazosulfuron-ethyl which is in accordance with previous reports of Anonymous (1996) and Nilanjan (2006) . The half lives of pyrazosulfuron in soil ranged from 14 to 19 days both at recommended and double the recommended level of application. Beyond 35 days after the application, the residues in soil were below the detectable level (Table 4). This suggests that the dissipation of herbicide is faster at the initial stage of crop growth period and there may not be any accumulation in the grain or straw as supported with the findings of Anonymous (1996) and Smith (1986).

Table 4 : Residue of pyrazosulfuron-ethyl in soil, grain and straw at the time of harvest in transplanted rice

Treatments	Residue in (mg kg^{-1}) Rice		
	Grain	Straw	Soil
T_1	BDL	BDL	BDL
T_2	BDL	BDL	BDL
T_3	BDL	BDL	BDL
T_4	BDL	BDL	BDL

BDL – Below detectable level

Residues of pyrazosulfuron-ethyl in ground water :

The results revealed that the mobility of herbicides was also governed by texture of the soils. With the addition of water could expand to make the column impervious thus hindering the herbicides movements. After the herbicide treatment the residues of pyrazosulfuron-ethyl were not detected initially up to 22nd day in underground water collected from Piezometers (Fig. 2 and Table 5). The residues of

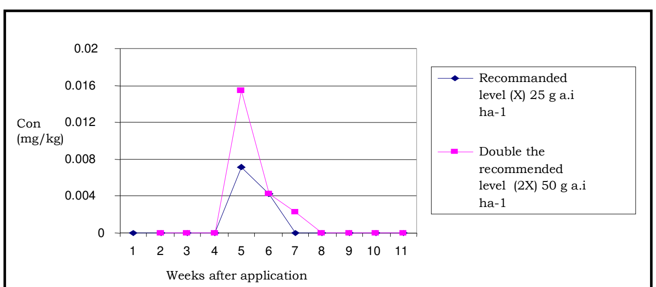

Fig. 2 : Persistence of pyrazosulfuron-ethyl residues (mg kg^{-1}) in underground water

Table 5 : Persistence of pyrazosulfuron-ethyl residues (mg kg^{-1}) in ground water (Piezometer)

Days after treatments / T	Recommended level (X) 25 g a.i ha^{-1}	Double the recommended level (2X) 50 g a.i ha^{-1}
2	0	0
7	0	0
14	0	0
21	0.0071	0.0154
28	0.0042	0.0043
35	BDL	0.0023
42	BDL	BDL
49	BDL	BDL
56	BDL	BDL
63	BDL	BDL

BDL – Below detectable level, T- Treatments

pyrazosulfuron-ethyl were in the range of 0.0071 to 0.0042 mg kg^{-1} on 22nd day to 28 days at recommended level of application. And later on 35th day, the residues were below the detectable level. In double the recommended dose, the residues were in the range of 0.0154 to 0.0023 mg kg^{-1} between 22 and 45th day. Beyond 45th day, the residues were below the detectable level. Similar results were recorded by Ferrero (2001) as there is possibility of presence of preferential ways of percolation in the treated area and important cause of preferential flow includes the occurrence of macrospores.

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