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Original Research Paper

Bispyribac Sodium Persistence in Soil, Plant and Grain in Direct Seeded Rice and its Effect on Soil Properties

T. Ramprakash†, M. Madhavi, M. Yakadri and A. Srinivas
AICRP on Weed Control, Rajendranagar, Hyderabad, India
†Corresponding author: T. Ramprakash

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ABSTRACT

A field experiment on direct-seeded rice was conducted during *kharif* 2011 and 2012 at the College Farm, ANGRAU Hyderabad, to study the influence of different doses of bispyribac sodium 10% SC (10, 15, 20, 25 and 40 g a.i/ha) on physical, physico-chemical and fertility properties of the soil. Persistence of the herbicide in soil from application to harvest of the crop and the residues in plant samples at harvest were also studied. No significant changes in physical (texture, bulk density, particle density, pore space, maximum water holding capacity), physico-chemical (pH, EC, CEC, organic carbon) and fertility properties of the soil (available N, P_2O_5 and K_2O) were noticed at any of the applied doses. Bispyribac sodium dissipation in soil followed a first-order decay process. Half-life (DT_{50}) of bispyribac sodium was 13.10 days, 10.21 days and 9.93 days at 40 g/ha, 25 g/ha and 20 g/ha doses respectively. DT_{90} values were also calculated. No detectable residues of bispyribac sodium were found in the straw or grain at the time of harvest.

INTRODUCTION

Direct seeded rice is gaining popularity among the farmers of the Andhra Pradesh state in view of the advantages viz., early maturity, low water requirement and good yield offered by this method of cultivation. However, weed management is one of the critical problems that limits the yield. Farmers use several herbicides along with other integrated approaches for weed management. Among several herbicides available, bispyribac sodium is a very popular herbicide among the farmers in view of the broad-spectrum weed control offered by this herbicide.

Bispyribac sodium, a popular post-emergence rice herbicide in Andhra Pradesh, inhibits the plant enzyme acetolactate synthase (ALS) which in turn inhibit the production of the amino acids valine, leucine and isoleucine in plants (Tranel &Wright 2002). Without these amino acids, protein synthesis and growth are inhibited, ultimately causing plant death. Bispyribac sodium is a faintly acidic compound, with a pKa of 3.05, highly soluble in water (73.3 g/L, 25°C), methanol (26.3 g/L, 25°C) and slightly soluble in acetone (WSSA 2007). Agronomic efficiency of bispyribac sodium is well established. Tachikawa et al. (1997) reported that the low application rate of 25-45 g/ha provided outstanding efficacy on *Echinochloa* sp. and this herbicide can be applied from 1 to 7 leaf stage of the weed. Results of the research work carried out by several Indian researchers (Chandraprakash et al. 2011, Mehta et al. 2010) proved suitability of this herbicide as a potential post-emergence herbicide in transplanted rice.

Due to the low potential of volatilization and the estimated rapid photo-chemical transformation, the environmental concentrations in air and the transport through air are considered negligible for bispyribac sodium. Under anaerobic conditions, bispyribac sodium is moderate to highly persistent in anaerobic flooded paddy soils (EFSA 2010). Studies in China indicated that, degradation of bispyribac sodium in soils followed first order kinetics with average half-lives in three kinds of non-sterilized paddy soils varying from 9.02 to 26.91 days (Yang Ren-bin & Zheng Li-ying 2006). Zheng Li Ying et al. (2011) reported that half-life of bispyribac sodium as 7.6-10.3 days in non-sterilized soil and 43.3-61.9 days in sterilized soil.

Research work on persistence of this herbicide in Indian, especially in Andhra Pradesh situations where the herbicide is being used on large scale is scanty. In this view, an experiment was planned to study the persistence and field dissipation patterns of this herbicide in transplanted rice.

MATERIALS AND METHODS

A field experiment was conducted during *Kharif* 2011 and 2012 at the College Farm, ANGRAU, Hyderabad. Experiment was laid out in randomized block design with seven treatments comprising different doses of the bispyribac sodium 10% SC (10 g/ha, 15 g/ha, 20 g/ha, 25 g/ha, 40 g/ha) applied at 20 days after sowing (DAS) compared with unweeded control and hand weeding treatment (20 and 40 DAS) and replicated thrice. The experiment was conducted in the same experiment plot during both the years and care was taken to impose the same treatments in the same plots. Fertilizers were applied to the plots as @ 120-60-40 kg/ha of N-P_2O_5-K_2O in the form of urea, SSP, MOP. The whole amount of P and K was applied as basal dose. N was applied in three equal splits at transplanting, tillering and PI stages. MTU-1010 (120 day duration) was used as the test variety. Sprouted rice seed was sown in the field with drum-seeder. Bispyribac herbicide treatments were imposed as a spray in the experimental plots at 20 DAT in thin film of water.

Collection of the samples: Initial soil samples were collected at the time of sowing. Soil samples were collected at 0, 1, 3, 8, 15, 30, 60 days after application and at harvest time (100 DAA) from the rice field. Samples were collected from different spots in the experimental plots in all the replications at 0-15 cm depth and were bulked together. Soil samples were air dried, passed through 2 mm sieve, homogenized and stored in sealed airtight polythene bag. These samples were stored at -20°C in a deep-freezer for residue analysis.

Soil samples collected at harvest were analysed for their physical, chemical and physico-chemical properties and organic carbon.

Soil sample analysis for physico-chemical properties: Particle size analysis of the soil was carried out by Bouyoucos hydrometer method (Piper 1966). Other physical properties of the soil viz., bulk density, particle density, pore space, maximum water holding capacity (MWHC) were determined by Keen's cup method (Bernard & Henry 1921). pH and electrical conductivity (EC) were measured in 1:2.5 soil water extract. The soil samples collected were analysed for organic carbon (%), based on rapid titrimetric method (Walkley & Black 1934), soil available N based on alkaline permanganate method (Subbaiah & Asija 1956), soil available P based on Olsen's method (Olsen et. al. 1954) and soil available K based on ammonium acetate method (Jackson 1973). CEC of the samples was estimated according to procedure described by Richards et al. (1954).

The experimental soil was dark greyish brown in colour and deep. Texture of the soil was sandy clay loam (60.2% sand, 11.6% silt and 28.0% clay). Bulk density and particle density of the soil were 1.26 and 2.64 Mg/m3 respectively. Soil was slightly alkaline in reaction, non-saline with a CEC of 20.21cmol (p^+) kg^{-1}. Organic carbon content of the soil was medium. Soil of the experiment site was low in available nitrogen, high in available phosphorus and high in available potassium.

Analysis of bispyribac sodium residues: Bispyribac sodium (sodium 2, 6-bis (4,6-dimethoxy -2- pyrimidinyloxy) benzoate) PESTANAL®, analytical standard was obtained from Fluka. The stock solution was prepared in an acetonitrile/water mixture (65:35 v/v) and kept at 4°C in a refrigerator. All working solutions were prepared daily by diluting this solution and the stock solution

Residue analysis in soil samples: Bispyribac residues in the soil samples were analysed employing the procedures outlined by Zhaeng Li Ying et al. (2005). The soil samples were extracted with 4% $NaHCO_3$ solution. The extract was partitioned with petroleum ether and dichloromethane. The aqueous phase (containing the final residue) was acidified with 1 mol/L hydrochloric acid and re-extracted with ethyl

Table: 1 Comparison of the soil properties in initial and post-harvest soil samples as influenced by bispyribac sodium.

S. No.	Soil Property	Changes in the soils property: Before Transplanting	At harvest: Bispyribac treatments	At harvest: Control
1.	Soil colour	10 YR 3/2 (Very dark greyish brown)	10 YR 3/2 (Very dark greyish brown)	10 YR 3/2 (Very dark greyish brown)
2.	Depth of the soil	95-100 cm	95-100cm	95-100 cm
3.	Texture of the soil	Sandy clay loam	Sandy clay loam	Sandy clay loam
4.	Bulk density	1.25 Mg/m^3	1.25-1.36 Mg/m^3	1.32 Mg/m^3
5.	Particle density	2.64 Mg/m^3	2.67 Mg/m^3	2.64 Mg/m^3
6.	Pore space (%)	51.27	51.29-54.11	51.87
7.	MWHC (%)	42.8	40.66-42.10	40.92
8	pH	7.75	7.71-8.05	7.96
9	EC	0.61 dS/m	0.56-0.69 dS/m	0.69 dS/m
10	CEC	22.21 cmol (p^+) kg^{-1}	19.25-20.17 cmol (p^+) kg^{-1}	21.21 cmol (p^+) kg^{-1}
11	Available nitrogen	231.6 kg/ha	198.1-205.1 kg/ha	210.1 kg/ha
12	Available P_2O_5	49.32 kg/ha	45.21-51.67 kg/ha	47.12 kg/ha
13	Available K_2O	379.82 kg/ha	365.7-386.5 kg/ha	346.2 kg/ha

Table 2: Residues of bispyribac sodium (mg/kg) in soil samples (mean of two years) collected at different intervals after application of the herbicide.

Treatments	Residues of bispyribac sodium at different days after application								
	0	1	3	8	15	30	45	60	Harvest
Bisp-Na@ 10.0 g/ha	0.026	0.021	0.020	BDL	BDL	BDL	BDL	BDL	BDL
Bisp-Na@ 15.0 g/ha	0.028	0.030	0.026	BDL	BDL	BDL	BDL	BDL	BDL
Bisp-Na@ 20.0 g/ha	0.033	0.038	0.026	0.020	BDL	BDL	BDL	BDL	BDL
Bisp-Na@ 25.0 g/ha	0.048	0.053	0.040	0.025	0.021	BDL	BDL	BDL	BDL
Bisp-Na@ 40.0 g/ha	0.066	0.068	0.051	0.034	0.029	0.020	BDL	BDL	BDL
Control	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Hand weeding	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Residues in grain, straw at harvest : BDL (Below Detectable Limit); Detectable Limit: 0.02 mg/kg

acetate. 20 μL of final solution was injected into HPLC column using mobile phase of methanol + water (75+25, V/V) containing 0.04% H_3PO_4. Quantification of the herbicide was done using UV detection at 250 nm wavelength. The results showed that the averaged recoveries of the method ranged 87.12%-93.22%, at the fortified levels of 0.02-1.0 mg/kg. The minimum detectable limits in soil were found to be 0.02 mg/kg.

Residue analysis in grain and plant samples: Rice grain and straw samples were collected from all the treatment plots at harvest. Bispyribac sodium residues in the grain and plant samples were analysed according to the procedure given by Shimin Wu & Jun Mei (2011). A HPLC equipped with a C18 reverse phase chromatographic column was attached to a DAD. Determination of analytes was performed using a mobile phase consisting of acetonitrile/water (65:35 v/v) with a flow rate of 1.0 mL/min at 30°C.

Studies were carried out to validate the method, sensitivity, repeatability, reproducibility and recovery. Fortified samples were used for precision and accuracy studies. In plant and grain samples the recoveries varied between 92.6-98.7% and 90.1-94.3%, respectively. Minimum detectable limit (detection limit) for the method adopted was 0.02 ppm.

RESULTS AND DISCUSSION

Effect of bispyribac on soil properties: Summary of changes in different properties (mean of two years) of the soil samples collected at transplanting and harvest is presented in the Table 1. There were no significant changes in soil physical (texture, bulk density, particle density, pore space, maximum water holding capacity), physico-chemical (pH, EC, CEC, OC) and fertility properties of the soil (available N, P_2O_5 and K_2O) due to application of bispyribac sodium. Statistical analysis of the pre and post-harvest samples indicated that the influence of the herbicide bispyribac sodium on soil properties was non-significant. Bera & Ghosh (2013) reported non-significant changes in soil physical, physico-chemical and fertility properties (bulk density, water holding capacity, moisture content, soil pH, EC, OC, available N, P and K) due to application of bispyribac sodium 10% SC.

Persistence of bispyribac residues in soil: In the experiment, five doses of the bispyribac sodium were tested for their persistence in the soil and grain. In the same experiment, data on weed management of the chemical was also recorded. Weed control efficiency data during both the years indicated that, satisfactory weed control was achieved with 25.0 g/ha dose. This in tune with the findings of Khaliq et al. (2013).

Details of the residues of bispyribac sodium in soil samples are presented in Table 2. Persistence of bispyribac sodium residues in the soil samples could be detected up to 30 DAA (days after application) in recommended dose (25 g/ha) treatments. The residues reached the BDL (0.02 mg/kg) after 30 DAA. When sub-optimal doses (10.0 g/ha and 15.0 g/ha) of the herbicide were used, persistence in the soil was shorter compared to the recommended dose (25.0 g/ha) and excess dose (40.0 g/ha). In 10 and 15 g/ha treatments persistence residues was recorded only up to 3 DAA. When the bispyribac sodium was applied at 40 g/ha, residue in soils samples could be detected upto 30 DAA. Residues of the test herbicide could not be detected in the soil samples at harvest stage of the crop in any of the dose applied. Yang Ren-bin & Zheng Li-ying (2006) reported increased persistence of bispyribac sodium in soil with increasing doses of the herbicide.

Dissipation trends of the bispyribac sodium: Initial detected amount (IDA) of herbicide in soil varied from 0.026 mg/kg to 0.066 mg/kg in different treatments on 0 DAA (2 hours after application). However, highest residues in soil samples were recorded at 1 DAA. This is due to time elapsed in movement of herbicide from the water to the sediment, as

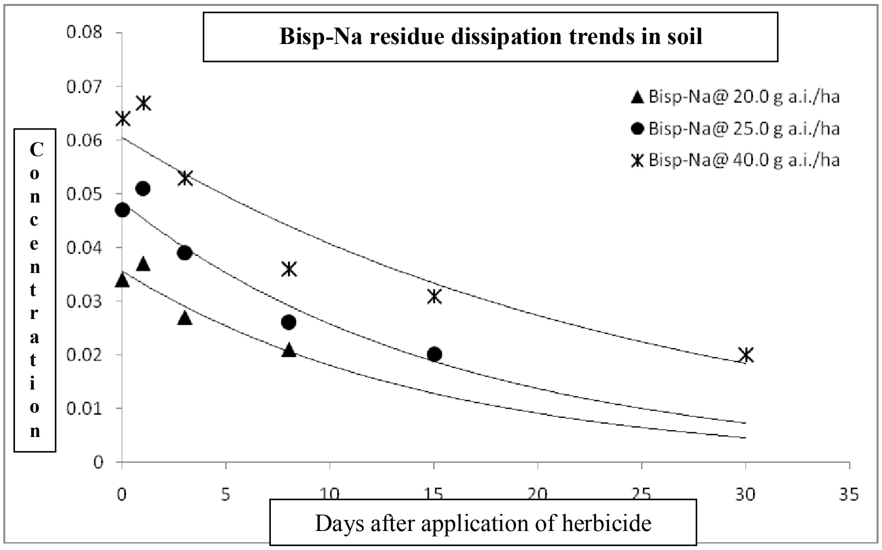

Fig. 1: Dissipation of the herbicide in soil when the herbicide was applied at different doses were applied.

the herbicide was applied when a thin film of water was present.

Dissipation of the herbicide in soil when the herbicide was applied at different doses, is presented in Fig 1. In the figure, dissipation curves of 40 g/ha, 25 g/h and 20 g/ha are only depicted. Different curves of fit were tested to predict the dissipation behaviour of the herbicide. Among the models tested (linear, polynomial, logarithmic, exponential) the exponential model was found to give better fit for field dissipation of the bispyribac sodium at 20, 25 and 40 g/ha doses. The curve fitment for 10 and 15 g doses could not be done due to data inadequacy. Mathematically, bispyribac sodium dissipation followed a first-order (or more correctly for field dissipation, pseudo first-order) decay process:

$$C=C_o exp^{-kd.t} \quad ...(1)$$

Where, *Co* is the initial concentration in soil, *C* is the concentration in the soil after t days, and K_d is the dissipation rate coefficient.

$$\log (C/C_0) = -0.4343\ K_d\ t \quad ...(2)$$

Applying Equation 2, dissipation trends of the bispyribac sodium at different doses of application was as following.

For 40 g/ha dose $y = 0.0595e^{-0.045x}$ $R^2 = 0.978$ ...(3)

For 25 g/ha dose $y = 0.0471e^{-0.066x}$ $R^2 = 0.964$ ...(4)

For 20 g/ha dose $y = 0.0334e^{-0.071x}$ $R^2= 0.982$ ...(5)

Using the above exponential equations (3, 4, 5) the half-life (DT_{50} *i.e.,* time taken, in days, for 50% dissipation of the initial detected amount) and DT_{90} (time taken, in days, for 90 % dissipation of the initial detected amount) were calculated. The DT_{90} of a herbicide is useful to understand the rotation restrictions for the sensitive crops to be taken up in a sequence. The residue level at 90% of the IDA was well below the minimum detection limit of 0.02 mg/kg. Hence, the mathematical equation provided an opportunity to assess the persistence of the herbicide to a small fraction of the applied amount.

The field dissipation at 40 g/ha application rate indicated that, the half-life (DT_{50}) was 13.10 days and DT_{90} was 51.16 days. DT_{50} was 10.21 days and DT_{90} was 34.88 days when herbicide was applied at 25 g/ha. At 20 g/ha dose, the half-life (DT_{50}) was 9.93 days and DT_{90} was 32.60 days. Dissipation trends indicated that with increasing doses of bispyribac sodium the half-life and DT_{90} increased significantly. At recommended dose of application (25 g/ha) the dissipation half-life recorded in the anaerobic field conditions was in good agreement with dissipation constants and half life recorded by APVMA (2011) in Australia; Yang & Zheng (2006) in China and EFSA (2010) in Italy.

Prolonged half-life and DT_{90} noticed in 40 g/ha dose could be due to reduced biological degradation of the herbicide at higher doses. Zheng et al. (2011) stated that, microorganisms was a critical factor that influenced bispyribac sodium depletion in soils and could accelerate greatly the degradation in soil. With the application of excess doses of bispyribac sodium the microbial population of the soil in the rhizosphere region of the transplanted *kharif* rice decreased after herbicide application, it increased at 60 DAA, which was even higher than initial application as well as hand weeding and untreated control (Bera & Ghosh 2013).

Bispyribac sodium residues in straw and grain: Rice grain and straw were analysed for bispyribac residue. No detectable residues of bispyribac sodium were found in the straw or grain at the time of harvest. HPLC analysis indicated that there were no residues of this herbicide in soil, rice grains and straw at crop harvest in transplanted and direct seeded rice (Mehta et al. 2010).

Hence, it can be concluded from this study that bispyribac sodium did not adversely influence the soil properties when used as post-emergence herbicide for control of broad spectrum weeds in rice and at recommended rates of application the residues in the soil persisted upto 15 DAA beyond which they were BDL (0.02 mg/kg).

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