Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 15	No. 4	pp. 1217-1220	2016

Original Research Paper

Dissipation and Persistence of Propaquizafop in Soil, Plant and Rhizomes in Turmeric and its Effect on Soil Properties

T. Ramprakash†, M. Madhavi and M. Yakadri***
*AICRP on Weed Control, ANGRAU, Rajendranagar, Hyderabad-30, India
**Department of Agronomy, College of Agriculture, Rajendranagar, Hyderabad, India
†Corresponding author: Ramprakash T.

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 16-11-2015
Accepted: 12-12-2015

Key Words:
Propaquizafop
Turmeric
Herbicide persistence
Half-life
Soil properties

ABSTRACT

Propaquizafop is a new graminicide herbicide recommended for control of grassy weeds in all dryland and ID crops. A field experiment was conducted during *Kharif* 2012 at the College Farm, ANGRAU, Hyderabad, on a Alfisol, to study the dissipation and persistence of varying doses of propaquizafop (25, 50, 62.5, 100 and 125g a.i/ha) in soil and turmeric. The influence of the herbicide on soil physical, physico-chemical and fertility properties was also assessed. Residues of the propaquizafop in soil and soybean were estimated on GC-ECD. Recovery of the herbicide in soil was 91.8-92.6%. In the rhizome and plant, the recovery was 88.6-92.1% and 93.6-93.8%, respectively. Limit of quantification was 0.01 mg/kg. No significant changes in physical (texture, bulk density, particle density, pore space, maximum water holding capacity), physico-chemical (pH, EC, CEC, organic carbon) and available nutrient status of the soil (available N, P_2O_5 and K_2O) were noticed in any of the applied doses of the herbicide. Application of propaquizafop @62.5 g/ha resulted in highest bio-efficiency. Propaquizafop dissipation in soil followed a first-order decay process. Half-life of the herbicide in soil increased with increasing dose. At sub-optimal doses, 50.0 g/ha, residues of propaquizafop persisted in the soil upto 15 DAA, (days after application) with a half life (DT_{50}) of 15.12 days. At the recommended dose (62.5 g/ha) half-life of propaquizafop was 17.67 days and residues reached below detectable limit (BDL) beyond 30 DAA. At doses above recommended level (100.0 and 125 g/ha), herbicide residues in the soil persisted for a longer period (45 and 60 DAA respectively) with DT_{50} of 21.29 and 29.36 DAA, respectively. No detectable residues of propaquizafop were detected in the turmeric rhizomes or plant at the time of harvest.

INTRODUCTION

Propaquizafop (2-isopropylideneamino - oxyethyl (R)-2-[4 -(6-chloroquinoxalin-2-yloxy) phenoxy] propionate) is used as a selective, post-emergence phenoxy herbicide. It is used to control annual and perennial grass weeds in potatoes, soybeans, sugar beets, peanuts vegetables, cotton and flax. The compound is absorbed from the leaf surface and moves throughout the plant. It accumulates in the active growing regions of stems and roots.

In the soil environment, propaquizafop degrades largely to the major metabolite quizalofop by hydrolysis of the ester. Further hydrolysis of the side chain occurs resulting in the minor metabolite quizalofop-phenol. Hydroxylation of the quinoxaline ring occurs to give the major metabolite hydroxy-quizalofop. Cleavage of the ether linkage leads to the formation of a series of degradates containing either the quinoxaline ring or the phenyl ring. Both series of degradates are further degraded to carbon dioxide (EFSA 2008). The existing European Union's MRL for quizalofop in rapeseed is set at 0.5 mg/kg and for the other oilseeds i.e. sunflower seed, cottonseed and soybeans, the MRL is set at 0.1 mg/kg (EFSA 2012).

In Andhra Pradesh, propaquizafop is extensively used in several crops like soybean, cotton, vegetable etc. Propaquizafop is currently being used as a sole herbicide or in tank-mix combination with other herbicides viz., pyrithiobac sodium for control of grassy weeds. This herbicide consumption has increased from 40 kilolitres (2011) to 80 kilolitres (2013) due its widespread usage (APPMA 2013). Research work on persistence of this herbicide in Indian conditions, especially in Andhra Pradesh situations where the herbicide is being used on a large scale is scanty. In this view, an experiment was planned to study the persistence and field dissipation patterns of this herbicide applied at different rates to turmeric.

MATERIALS AND METHODS

A field experiment was conducted during *Kharif* 2012 at the College Farm, ANGRAU, Hyderabad. The experiment was laid out in randomized block design with seven treatments comprising different doses of the propaquizafop 5 %

EC (50, 62.5, 100 and 125g a.i/ha) applied as post-emergence spray at 20 DAS compared with unweeded control and hand weeding treatment (20 and 40 DAS) and replicated thrice. Fertilizers were applied to the plots @180-60-120 kg/ha of N-P_2O_5-K_2O in the form of urea, SSP, MOP. In addition, FYM was applied @10 t/ha. Mydukuru (9 month duration) was used as the test variant. The crop was sown at 60 × 20 cm spacing in ridges and furrows. Propaquizafop 5 % EC herbicide was sprayed with knapsack sprayer fitted with flat-fan nozzle at 20 DAS.

Collection of soil samples: Initial soil samples were collected before sowing of the experiment. Soil samples were collected at 0, 1, 3, 8, 15, 30, 45, 60, 90, 150 days after application of herbicide (DAA) and at harvest time (270 DAA) from the turmeric 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 a sealed airtight polythene bag kept at 20°C in a deep-freezer for residue analysis. Soil samples collected before sowing and at harvest were analysed for their physical, chemical and physico-chemical properties and organic carbon to assess changes in soil properties.

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 Razkowski 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 the rapid titrimetric method (Walkley & Black 1934), soil available N based on alkaline permanganate method (Subbiah & 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 the procedure described by Richards et al. (1954).

The experimental soils were dark reddish brown in colour and moderately deep. Texture of the soil was sandy clay loam with 68.2 % clay, 8.6 % silt and 23.2 % clay. Bulk density and particle density of the soil were 1.21 and 2.64 mg/ m^3 respectively. Analysis of the physico-chemical properties of the soil indicated that the soils were neutral in their reaction, non-saline, with a CEC of 18.04 cmol(p^+) kg^{-1}. Nutrient status studies indicated that the soils were low in nitrogen, medium in phosphorus and high in available potassium.

Analysis of propaquizafop residues: Propaquizafop analytical standard was obtained from Dr. Ehrenstofer Inc. The stock solution was prepared with hexane and kept at 4°C in a refrigerator. All working solutions (0.01, 0.02, 0.05, 0.1, 02, 0.5) were prepared by diluting this solution and the stock solution

Residue analysis of soil samples: Propaquizafop residues in the soil samples and the turmeric samples by extracting the homogenized pulp of turmeric rhizome (20 g)/soil (50 g) thrice (50 + 30 +20mL) with acetone and filtered through a Buchner funnel. The filtrate was concentrated to about 30 mL in a rotary evaporator (40°C) and transferred into a 500 mL separatory funnel with 30 mL 2% Na_2SO_4 solution. This mixture was partitioned with dichloromethane 3 times (3 × 20 mL). Dichloromethane layer was dehydrated on Na_2SO_4 and concentrated to dryness. The residue was dissolved in petroleum ether and purified by Florisil cartridges. Residues were eluted with 2 mL petroleum ether-acetic ether 80:20 (v/v) and concentrated in a rotary evaporator. The residue was re-dissolved in 2 mL n-hexane for GC-ECD analysis.

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

S. No	Soil Property	Changes in the soils property		
		Before sowing	At harvest	
			Propaquizafop treatments	Control
1.	Soil colour	5 YR 3/4(Dark reddish brown)	5 YR 3/4(Dark reddish brown)	5 YR 3/4(Dark reddish brown)
2.	Texture of the soil	Sandy clay loam	Sandy clay loam	Sandy clay loam
3.	Bulk density	1.27 Mg/m^3	1.21 -1.29 Mg/m^3	1.26 Mg/m^3
4.	Particle density	2.64 Mg/m^3	2.64 Mg/m^3	2.64 Mg/m^3
5.	Pore space (%)	48.21	46.25-49.26	48.2
6.	MWHC (%)	34.26	33.89-35.26	35.12
7.	pH	6.91	6.78-7.12	7.06
8.	EC	0.41 dS/m	0.38-0.26 dS/m	0.66 dS/m
9.	CEC	20.21 cmol(p^+) kg^{-1}	19.24-21.11 cmol (p^+) kg^{-1}	20.66 cmol (p^+) kg^{-1}
10.	Available nitrogen	212.8 kg/ha	208.2 – 222.8 kg/ha	211.1 kg/ha
11.	Available P_2O_5	40.05 kg/ha	42.43 - 44.22 kg/ha	44.12 kg/ha
12.	Available K_2O	356.1 kg/ha	351.9 - 366.2 kg/ha	352.2 kg/ha

Recovery of the herbicide in the soil was 91.8-92.6%. In the rhizome and plant, the recovery was 88.6-92.1% and 93.6 to 93.8%, respectively. Limit of quantification (LOQ) was 0.01 mg/kg.

RESULTS AND DISCUSSION

Effect of propaquizafop on soil properties: Summary of changes in different properties of the soil samples collected at planting 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 propaquizafop. Statistical analysis of the pre and post-harvest samples indicated that the influence of the herbicide propaquizafop on soil properties was non-significant.

Persistence of propaquizafop residues in soil: In the experiment, five doses of the propaquizafop were tested for their persistence in the soil, rhizome and plant. 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 62.5 g/ha dose.

Details of the residues of propaquizafop in soil samples are presented in Table 2. Persistence of propaquizafop residues in the soil samples could be detected up to 30 DAA (days after application) in recommended dose (g/ha) treatments. The residues reached the BDL (0.01 mg/kg) after 45 DAA. When sub-optimal doses (25.0 g/ha and 50.0 g/ha) of the herbicide were used, persistence in the soil was shorter compared to the recommended dose (62.5 g/ha). In 25 and 50.0 g/ha treatments persistence residue was recorded upto 15 and 30 DAA. Propaquizafop applied at 100 g/ha and 125 g/ha resulted in longer persistence (45 and 60 DAA respectively). 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. EFSA (2012) reported increased persistence of propaquizafop in soil with increasing doses of the herbicide.

Dissipation trends of the propaquizafop: Initial detected amount (IDA) of herbicide in soil varied from 0.028 mg/kg to 0.067 mg/kg in different treatments on 0 DAA (2 hours after application). Dissipation of the herbicide in soil when applied at different rates is presented in Fig. 1. Different curves of fit were tested to predict the dissipation behaviour of the herbicide. Among the models tested (linear, polynomial, logarithmic and exponential), the exponential model was found to give better fit for field dissipation of the propaquizafop at 25, 50, 62.5, 100.0 and 125 g/ha doses. Mathematically, propaquizafop dissipation followed a first-order (pseudo first-order) decay process:

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

Where C_o is the initial concentration in soil, C is the concentration in the soil after t days, and K_d is the dissipation rate coefficient. The linearized equation (1) is:

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

Applying equation (2), dissipation trends of the propaquizafop at different doses of application was as following:

25.0 g/ha dose $y = 0.026e^{-0.04x}$ $R^2 = 0.98$ ...(3)

50.0 g/ha dose $y = 0.030e^{-0.03x}$ $R^2 = 0.93$ ...(4)

62.5 g/ha dose $y = 0.039e^{-0.03x}$ $R^2 = 0.92$ ...(5)

100.0 g/ha dose $y = 0.055e^{-0.03x}$ $R^2 = 0.99$ ...(6)

125.0 g/ha dose $y = 0.060e^{-0.02x}$ $R^2 = 0.98$ ...(7)

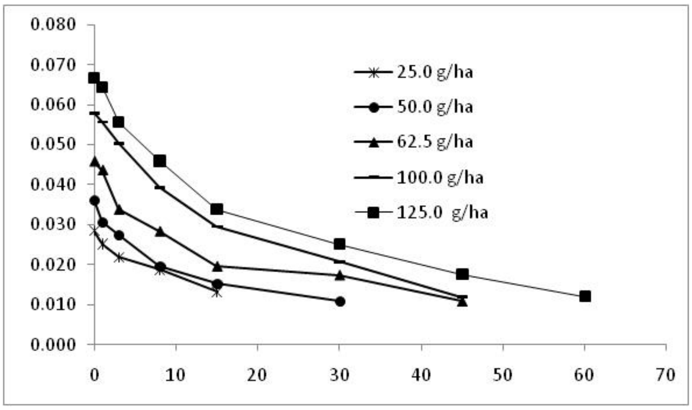
Using the above exponential equations (3 to 7) the half-life (DT_{50} i.e. time taken, in days, for 50 % dissipation of the initial detected amount) was calculated. The field dissipation at doses above the recommended rate of application (100 g/ha) and double the recommended rate indicated that, the half-life (DT_{50}) was 21.29 and 29.36 days, respectively. DT_{50} at lower than the recommended rate of application were 16.93 and 15.12 days respectively, at 25 and 50 g a.i./

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

Treatments	Residues of propaquizafop at different days after application									
	0	1	3	8	15	30	45	60	90	Harvest
Propaquizafop @ 25.0 g/ha	0.028	0.025	0.022	0.019	0.013	BDL	BDL	BDL	BDL	BDL
Propaquizafop @ 50 g/ha	0.036	0.031	0.027	0.020	0.015	0.011	BDL	BDL	BDL	BDL
Propaquizafop @ 62.5 g/ha	0.046	0.044	0.034	0.028	0.020	0.017	0.011	BDL	BDL	BDL
Propaquizafop @ 100 g/ha	0.058	0.056	0.050	0.039	0.030	0.021	0.012	BDL	BDL	BDL
Propaquizafop @ 125 g/ha	0.067	0.064	0.056	0.046	0.034	0.025	0.017	0.012	BDL	BDL
Control	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Hand weeding	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Residues in rhizome and plant at harvest: BDL (Below Detectable Limit)
Detectable Limit: 0.01 mg/kg

Concentration



Days after application of herbicide

Fig. 1: Propaquizafop residue dissipation trends in soil.

ha half-life of propaquizafop in soil at field rate application, was 17.67 days. Dissipation trends indicated that with increasing doses of propaquizafop, the half-life increased significantly. At recommended dose of application (50 g/ha) the dissipation half-life recorded in the aerobic field conditions was in good agreement with dissipation constants and half life recorded by Hee et al. (1996).

Prolonged half-life noticed in 100 g/ha and dose could be due to reduced biological degradation of the herbicide at higher doses. Hee et al. (1996) stated that, micro-organisms, especially fungi (*Fusarium* spp.), was a critical factor that influenced quizalafop depletion in soils and could accelerate greatly the degradation in soil. Application of pre and post emergence herbicides in jute affected the total bacteria, actinomycetes and fungi population in soil initially, but the microbial population improved gradually and reached to normal level by harvest of jute (Sarkar & Majumdar 2013). Even though, there is no universally accepted classification of pesticide environmental persistence, propaquizafop can be categorized as slightly persistent in the soil by using Roberts (1996) classification based on the mean half-life of the pesticide in the soil.

Propaquizafop residues in straw and grain: Turmeric rhizomes and plants were analysed for propaquizafop residues at the time of harvest. No detectable residues of propaquizafop were found in the haulms or rhizomes at the time of harvest. Jiye Hu et al. (2010) established the safe usage of quizalofop in potato and other crops.

CONCLUSION

It can be concluded from this study that propaquizafop did not adversely influence the soil properties when used as post-emergence herbicide for control of grassy weeds in turmeric and at recommended rates of application the residues in the soil persisted upto 45 DAA beyond which the residues reached the BDL (0.01 mg/kg).

REFERENCES

APPMA 2013. Andhra Pradesh Pesticide Manufacturer's Association Herbicide consumption Data.

Bernard, A. Keen and Henry Razkowski 1921. The relation between the clay content and certain physical properties of a soil. Journal of Agricultural Sciences, 11: 441-449.

EFSA 2008. European Food Safety Authority Scientific Report. Conclusion on the peer review of quizalofop-P, 205: 1-216.

EFSA 2012. Reasoned opinion on the modification of the existing MRLs for quizalofop-P in oilseed rape, sunflower, cotton and soybean. EFSA Journal, 10(12): 01-28

Hee, K.K., Bong, K.Y., Injin, P. and Yong, T.S. 1996. Fate of herbicide quizalofop in soil. Koren Journal of Environmental Agriculture, 15(4): 488-493.

Jackson, M.L. 1973. Soil Chemical Analysis. Prenctice Hall of India Pvt. Ltd., New Delhi.

Jiye, Hu., Deng, Z., Chang, L., Zhixin, Z. 2010. Simultaneous analysis of herbicide metribuzin and quizalofop-p-ethyl residues in potato and soil by GC-ECD. Chromatographia, 72: 701-706.

Olsen, S.R., Cole, C.V., Watanabe, F.S. and Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Circular of US Dept. of Agriculture, 939.

Piper, C.S. 1966. Soil and Plant Analysis. International Science Publishers, New York, 47-49.

Richards, L.A. 1954. Diagnosis and improvement of saline and alkali soils. Agricultural Hand Book No. 60. United States Department of Agriculture (USDA), Washington.

Roberts, T.R. 1996. Assessing the fate of agrochemicals. Journal of Environmental Science and Health, 31(3): 325-335.

Sarkar, S. and Majumdar, B. 2013. Herbicidal effect on weed growth, crop yield and soil microbes in olitorius jute (*Corchorus olitorius* L.). Journal of Tropical Agriculture, 51(1-2): 23-29.

Subbiah, B.V. and Asija, G.L. 1956. A rapid procedure for determination of available nitrogen in rice soils. Current Science, 31: 196.

Walkley, A.J. and Black, I.S. 1934. Estimation of organic carbon by chromic acid titration method. Soil Science, 37: 29-38.