Journal of Crop and Weed, 12(3):154-159(2016)

Studies on persistence and dissipation of propaquizafop in soils under laboratory simulated conditions

D. K. HAZRA, R. KARMAKAR, DURGESH AND [1]A. BHATTACHARRYA

AINP on Pesticide Residues, Directorate of Research, Research Complex Building,
[1]Deptt. of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya,
Kalyani-741235 , Nadia, West Bengal

Received : 09-11-2016; Revised : 22-12-2016; Accepted : 25-12-2016

ABSTRACT

The persistence of propaquizafop was studied in two different soils (Canning-saline soil and Jhargram-red & lateritic soil) under controlled laboratory simulated conditions. Propaquizafop was fortified at 2 and 4 µg g^{-1} and samples were drawn, extracted and analyzed upto 90 days at regular intervals. Dissipation of propaquizafop was followed first order kinetics irrespective of any treatment and soil type. Calculated half-life values were found to be in the range of 25.29-27.63 days irrespective of dosage of application. Higher dissipation rate had been observed in Canning soil.

Keywords: Dissipation, fortification, persistence, propaquizafop, residue

Perfect soil-applied herbicides should control weeds for the necessary time, then instantly degrade, never move off-site into soils, surface water or groundwater (Di *et. al*., 2002) or be present to affect the growth of subsequent crops. Propaquizafop (2-isopropylideneamino-oxyethyl (R)-2-[4-(6-chloroquinoxalin-2-yloxy) phenoxy] propionate), a graminicide from the aryloxyphenoxy propionate group (fops) (Tomlin, 1997), used at very low rate (50-200 gm a.i.ha^{-1}) to control a wide range of important grass weed species at various growth stages (Mitchell *et. al*., 2003, Khan *et al*. 2003, Vesik *et al*., 1997)). Roy *et. al*. (2005) studied the persistence of Clodinafop (same group) in wheat soil @ 30, 60 and 90 gha^{-1} and found that the initial deposits goes below detectable after 15 days of application irrespective of treatments. But there was little information available on the persistence and dissipation of propaquizafop in open soil environment as well as laboratory-simulated conditions. No systemic work has been reported on the persistence of propaquizafop in soils of West Bengal, India also so, the present experiment was undertaken.

MATERIALS AND METHODS

Chemicals and reagents

Technical grade Propaquizafop (97.9%) was obtained from M/S Indofil Chemical Company, Mumbai and stored at –10°C in a deep freezer. All solvents and other chemicals used were of analytical reagent grade. All common solvents were redistilled in all glass apparatus before use. The suitability of the solvents and other chemicals were ensured by running reagent blanks before actual analysis.

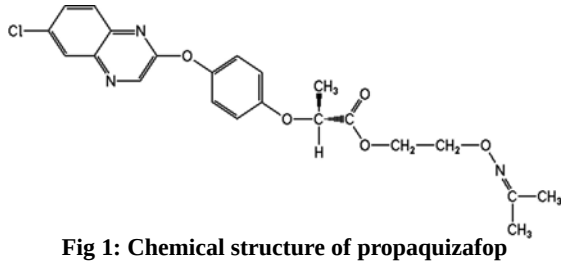

Fig 1: Chemical structure of propaquizafop

Preparation of soil sample

During 2004-05, laboratory simulation study on persistence behavior of propaquizafop was under taken in soils of various physic-chemical properties (Table 1). Soils samples were collected from i) Jhargram- (Red & Lateritic soil, Alfisol), Regional Research Station, BCKV, Midnapore, West Bengal and ii) Canning-(Saline soil), Regional Research Station, BCKV, 24 Parganas (South), West Bengal, India, following standard methodology of soil sampling. Mention the reference followed for determination of physic chemical properties of the soil.

Table1: Physico-Chemical Properties of Saline and Red & Lateritic Soils

Properties	Location	
	Canning	**Jhargram**
pH	7.6	5.1
Organic matter (%)	3.4	5.1
CEC (meqv. $100g^{-1}$)	14.86	11.36
Initial moisture (%)	3.4	3.9
Water holding capacity (%)	46.12	53.12
Sand (%)	48.95	55.21
Silt (%)	18.39	19.88
Clay (%)	32.66	24.91

E-mail: dipakipft@gmail.com

Preparation of propaquizafop standard solutions

Percent purity of Propaquizafop standard was checked by High Performance Liquid Chromatography (HPLC). A standard stock solution of 10 µg ml^{-1} was prepared in HPLC acetonitrile. The standard solutions required for calibration curve (0.05, 0.25, 0.5, 0.75 and 1.0 µg ml^{-1}) were prepared from the stock solution by serial dilutions with same solvent. All standard solutions were stored at -4^{0}C before use.

Application of propaquizafop in soil samples

Finely sieved (85 mesh) air-dried sub soil samples (50 gm) were taken in an amber glass bottles after following standard quartering techniques. Propaquizafop standard was fortified at lower dose of 2 µg g^{-1} and higher dose of 4 µg g^{-1} and compared with control soil samples. The treatments were replicated thrice.

Sampling

Soil samples were drawn at 0 (after 2 hours of application), 1, 3, 7, 15, 30, 45, 60 and 90 days after Propaquizafop application.

Extraction and cleanup

Soil samples drawn at different day's interval were dispended in 100 ml acetonitrile and shaken in a mechanical shaker for three hours. The content of each sample thus obtained was filtered in a Buchner funnel through Whanman filter paper (42 micron) with 50 ml of same solvent. The filtrate was reduced by rotary low pressure vacuum evaporator at 40^{O}C to 50ml and concentrated extract was transferred to a seperatory funnel. Thereafter the acetonitrile phase was partitioned thrice with hexane (100+50+50) ml. The hexane layers were discarded and acetonitrile layers were collected by passing over anhydrous sodium sulphate. The combined organic layer was evaporated to dryness by low pressure rotary vacuum evaporator at 40^{O}C. The extract was dissolved in 2 ml hexane and subjected to column clean up using 10 g aluminum oxide layer sandwiched between 2 g layer of anhydrous Na_2SO_4. First of all the extract was cleaned with 50 ml of hexane to discard it (Fig 2). Finally the column was eluted with 50 ml acetonitrile and dried in rotary vacuum evaporator at 40^{O}C to reconstitute propaquizafop residues for HPLC analysis after syringe filtration (0.2 micron).

Analysis of propaquizafop

Final analysis of Propaquizafop residues in soil samples was carried out by HPLC (Shimadzu) coupled with LC-10 ATvp pump and SPD-10A detector connected to CBM-101 module using CR LC10 software and following RPC-18 (Reversed Phase Column, Phenomenex, 250 x 4.6 mm, 5µm) using mobile phase of acetonitrile : water (9:1), 235e ^{max} and flow rate of 1.5ml min^{-1} with retention time of 5.46 min. HPLC detection has proven to be a good for Propaquizafop determination because no deviation step is needed.

Limit of detection (LOD) and limit of quantification (LOQ)

Limit of detection (LOD) is the lowest concentration of analyte detectable by an analytical method and is expressed in concentration unit. Limit of quantification (LOQ) is the lowest solute concentration that can be determined with acceptable precision and accuracy, under the stated experimental conditions. It is also expressed in concentration unit (Sanjay *et al*. 2011). To determine the limit of detection of the equipment for Propaquizafop, a blank sample was run under the experimental conditions to obtain the detector baseline noise. A detectable ion should produce a signal that is at least three times the baseline noise [that is, signal-to-noise (S/N) ratio = 3] (Maštovská and Lehotay, 2003). The LOD of Propaquizafop was determined by running serially diluted solutions of the herbicide standard at the set chromatographic conditions and finding the concentration at which S/N = 3. The limit of detection was observed to be 0.01 µg g^{-1} with limit of quantification 0.05 µg g^{-1} for soil substrate.

Recovery experiment

As the quantitative determination of pesticide in soil is directly related to the evaluation and interpretation of data, a reliable method is required which can be reproducible and can be applicable to different commodities. To evaluate the efficiency and reliability of the analytical method adopted, the recovery experiment was carried out by fortifying the untreated soil samples (50 g) with 0.05, 0.25 and 0.5 µgg^{-1} of analytical standard Propaquizafop (Fig 4 and 5). The recovery tests were carried out on three replicates at each spiked level.

Identification and quantification

Pesticide residue is identified if the retention time matched that of the standard and the relative abundance is within 10% of that of the standard (Ogah *et al*. 2012). Identified graminicide was quantified using the external standard method of comparing sample peak area with that of the pesticide standard under the same conditions. Each sample was analyzed three times and the mean values obtained. The pesticide content of each sample was calculated as:

Substrate (Soil)
↓
Air-dried sub soil samples were sieved finely (85 mesh)
↓
Weighed 50 ± 0.1 g sample into each in amber glass bottles (250 ml)
↓
Propaquizafop standard was fortified @ 2 and 4 µg g^{-1}
↓
Soil samples were drawn at different intervals
↓
Dispensed in 100 ± 0.1 ml acetonitrile, capped well and shaken in mechanical shaker
↓
Solvent portion was filtered in a Buchner funnel
↓
Filtrate was reduced by rotary low pressure vacuum evaporator at 40^{O}C to 50 ml
↓
Concentrated extract was partitioned thrice with hexane (100+50+50) ml
↓
Combined layers were collected over anhydrous sodium sulphate
↓
Organic layer was evaporated at 40°C to dryness and subjected to column clean up
↓
Column was eluted with 50 ml acetonitrile and dried in rotary vacuum evaporator at 40^{O}C
↓
Reconstituted propaquizafop residues for HPLC analysis after syringe filtration.

Fig. 2 : Flow Chart of extraction and cleanup methodology for propaquizafop estimation

$$\text{Residue in ppm } (\mu g.g^{-1}) = \frac{A_1 \times V_1 \times W_1}{A_1 \times V_1 \times C} R_f$$

Where,

A_1 = Area of the compound in sample.

A_2 = Area of the compound in standard.

V_1 = Total volume of sample in ml

W_1= Concentration of standard injected (µg ml^{-1})

V_2 = Injected volume of the sample in µl

C = Total weight of the soil sample in gm.

R_f = Recovery factor

RESULTS AND DISCUSSION :

Analytical instrument calibration (Linearity)

Quantification of propaquizafop residues was performed after checking the detector linearity of HPLC. In most of the chromatographic procedures, a linear relation is observed between detector response (y) and analyte concentration (x). This can be expressed as a linear regression equation: y = a + bx (Sanjay *et al*. 2011). The linearity of a method is a measure of range within which the results are directly, or by a well defined mathematical transformation, proportional to the concentration of analyte in samples within a given range. The detector linearity curve (Fig. 2) was obtained by plotting the peak areas of standards injected against the concentration levels (0.05, 0.25, 0.5, 0.75 and 1.0 µg ml^{-1}) of the standard after serial dilution. The results obtained by curve correspond to: y = 79535 xs + 6339, r^2 = 0.996

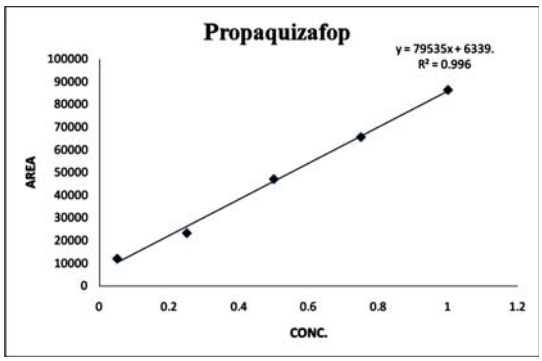

Fig. 3: Detector linearity of propaquizafop in HPLC

The average recoveries of three injections obtained for propaquizafop at all concentrations were determined in the range of 94.02–98.30% (Table 2). The results were encouraging and suggested that the method could be extended to more substrates. Moreover, it is simple, efficient, and easy to adopt in laboratories engaged in pesticide residue analysi *Identification and Quantification*

Pesticide residue is identified if the retention time matched that of the standard and the relative abundance is within 10 per cent of that of the standard (Ogah *et. al*. 2012).

Table 2: Recovery Study of propaquizafop in soils having physicochemical properties

Soil types	Amount fortified ($\mu g\ g^{-1}$)	% Recovered amount			Average recovery (%)	RSD (%)	Overall average recovery (%)
		R1	R2	R3			
Canning-Saline Soil	0.05	107.44	96.76	98.66	100.96	5.64	98.30
	0.25	101.39	90.78	88.06	93.41	7.54	
	0.50	99.64	103.60	98.38	100.54	2.71	
Jhargram-Red & Lateritic Soil	0.05	92.65	86.54	87.98	89.06	3.59	94.02
	0.25	97.18	97.52	99.01	97.90	1.00	
	0.50	94.69	94.40	96.24	95.11	1.04	

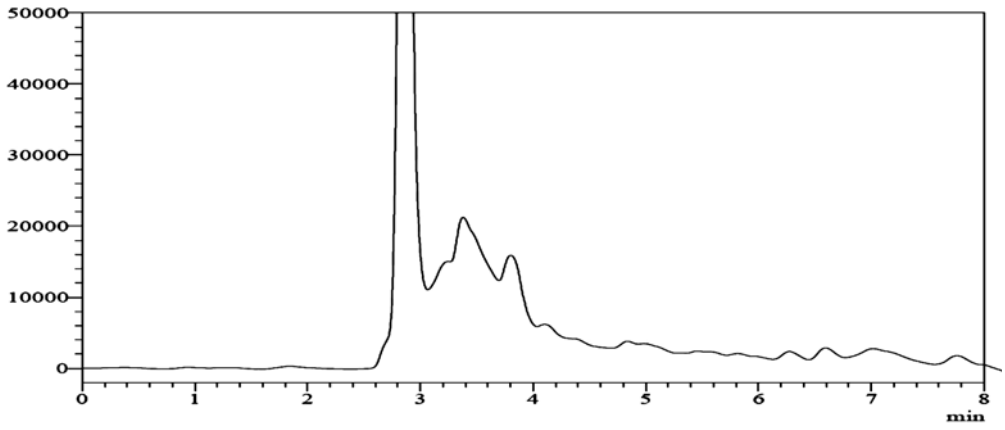

Fig. 4: HPLC chromatogram of control canning soil sample

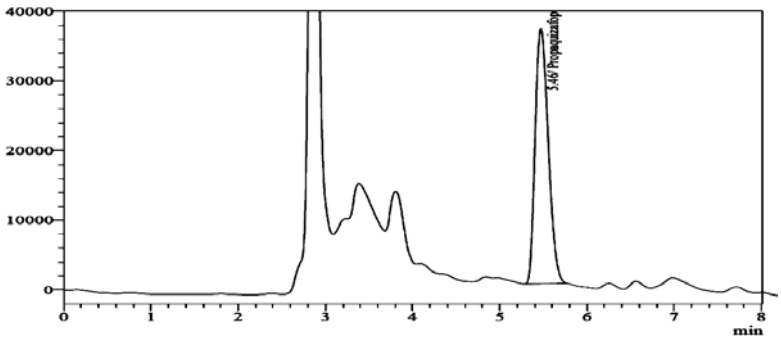

Fig. 5: HPLC chromatogram of canning soil sample fortified at 0.5 µg g-1

Table 3: Dissipation of propaquizafop in Canning-saline soil and Jhargram-red & lateritic soil under laboratory simulated condition

Soil Types	Level of fortification	Residues (µg g^{-1}) Recovered ± RSD (n=3)*								
		0d	1d	3d	7d	15d	30d	45d	60d	90d
Canning Soil	2	1.66±4.21	1.56±3.84	1.36±5.88	1.26±6.34	1.14 ±2.63	0.88±4.54	0.59±13.55	0.32±12.50	0.12±2.51
	4	3.47±1.72	3.23±1.54	2.75±2.54	2.49±3.21	2.24±2.67	1.80±5.00	1.17 ± 5.12	0.60 ± 1.59	0.28±10.71
Regression Equation ,Y= 3.223- 0.0119x, r^2 Value = 0.957 ; Half Life (Days) 25.29										
Regression Equation ,Y= 3.52-0.0116x, r^2 Value = 0.938 ; Half Life (Days) 25.95										
Jhargram-Soil	2	1.78±3.37	1.69±1.77	1.39±3.59	1.23±4.06	0.98±4.08	0.75±8.00	0.42 ± 9.52	0.24 ± 2.83	0.12±3.33
	4	3.55±2.25	3.32±1.90	2.75±2.18	2.56±2.34	2.03±2.95	1.57±3.18	0.84 ± 8.33	0.68±10.29	0.32±8.75
Regression Equation ,Y= 3.21-0.013x, r^2 Value = 0.908 ; Half Life (Days) 26.15										
Regression Equation ,Y= 3.50- 0.0113x, r^2 Value = 0.918 ; Half Life (Days) 25.29										

** n=number of three replicates, RSD= Relative Standard Deviation*

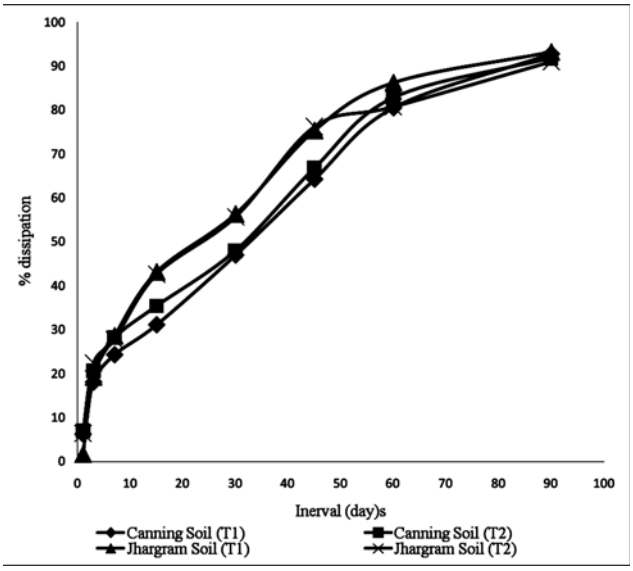

Fig. 5 : Dissipation of propaquizafop in Canning soil and Jhargram soil under laboratory simulated condition

Persistence and dissipation

Data on persistence/dissipation of Propaquizafop in Canning and Jhargram soils (Table 3) showed that herbicide residues dissipated progressively with increment of time irrespective of dosage and soil type. The initial deposits (residues recovered after two hours of application) were 1.66µg g^{-1} and 3.47µg g^{-1} in Canning and 1.78µg g^{-1} and 3.55µg g^{-1} in Jhargram soil at low (2µg g^{-1}) and high (4µg g^{-1}) dosage of applications, respectively. The residues progressively declined beyond 90 days in both soils with more than 90 per cent of dissipation. Comparatively slower dissipation was observed in red & lateritic soil than that exhibited in saline soil.

The residue data was subjected to first order kinetics ($C_t = Co\ e^{-kt}$), where C_t is concentration after a lapse of

time 't'; C_0 is apparent initial concentration and 'k' is the dissipation constant (Fig. 5). Half-life values were calculated from regression equation using the formula ($T_{1/2}$ = 0.693/K) (Vijay *et. al.* 2011). Calculated half-life values were 25.29 and 25.95 days in Canning soil and 26.15 and 27.63 days in Jhargram soil at 2 µg g^{-1} and 4 µg g^{-1} levels of fortification, respectively. This type of dissipation also correlated with the earlier research work of Roy *et al*. (2005) for another aryloxyphenoxy propionate group (fop) herbicide *i.e.* Clodinafop. The difference in the persistence of propaquizafop in two soil types may be attributed to the difference in their physico-chemical properties (Table 1) especially due to organic matter percentage difference, which was 3.4 per cent in Canning soil as compared to 5.1 per cent in Jhargram soil. As reported in the literature, the organic matter firmly adsorbs the herbicide molecules, rendering them non-available to microbial degradation and other losses as leaching, volatilization etc, resulting in the increased persistence of herbicide (Prado *et al.*, 2002,).

From this study, it might, therefore be stated that the rate of dissipation of Propaquizafop would more or less similar in both the soil types and slightly slower in Jhargram soil than that of Canning soil (saline).

ACKNOWLEDGEMENT

We are very much thankful to M/s Indofil Chemical Company, Mumbai for financial assistance. The infrastructural facilities provided by Bidhan Chandra Krishi Viswavidyalaya are also thankfully acknowledged.

REFERENCES :

Di HJ., and Alymore-LAG. 2002., Modeling the probabilities of groundwater contamination by pesticides. *J. Soil Sci. Soc. Amer*. **61** : 17-23.

Khan P. and Lendin S. 2003. Effects of the herbicides propaquizafop and primisulfuron-mehtyl on Salix plants and weeds in energy plantations. *Biomass-Bioenergy*.**12**: 25-33.

Maštovská K. and Lehotay S. .2003. "Practical approaches to fast gas chromatography- mass spectrometry. *J. Chromatography* ; **1000** : 153-80.

Mitchell P.W. and Adoryan ML. .2003. Evaluation of the efficiency of Propaquizafop herbicide on the control of weeds occurring in a peanut (*Arachis hypogaea* L.) crop. *Cientifica-Jaboticabal*. **27** : 223-27.

Ogah C.O. and Coker H.B. 2012. Quantification of organophosphate and carbamate pesticide residues in maize. J. App. Pharma. Sci. **2** : 93-97.

Prado R., Menendez J., Brown H., Cussans GW., Devine M.D, Duke SO. and Helweg A. 2002 . Metabolism of propaquizafop in chlorotoluron-resistant and succeptible biotypes of *Alopecurus myosuroides*. Proc. 2nd Int. Weed Control Cong. Copenhagen, Denmark, 25-28th June : 1-4 : 517-21.

Roy S. and Singh S.B., 2005. Phototransformation of clodinafop-propargyl. *J. Env. Sci. Health.* **40** : 525-34.

Sahoo S. K., Battu R.S., and Singh B., 2011. Development and validation of QuEChERS method for estimation of propamocarb residues in tomato (*Lycopersicon esculentum* Mill) and soil. *Amer. J. Analytical Chem.*, **2** : 26-31

Tomlin C.D.S., 1997. *The Pesticide Manual*, British Crop Protection Council, Surrey, U.K.

Lopez V., Sugranes F. and Alsina J.M., 1997. Agil, a new post emergence grass killer for application in narrow-leaved crops and in garlic and onions. *Proc. 1993 Cong. Spanish Weed Sci. Soc.*, Lugo, Spain, 1-3 December, pp. 322-27.

Gajbhiye V. T., Gupta S., Mukherjee I., Singh S. B., Singh N., Dureja P., and Kumar Y., 2011. Persistence of Azoxystrobin in/on grapes and soil in different grapes growing areas of India . *Bull Env. Contamination Toxico*. **86** : 90–94.