https://doi.org/10.33307/entomon.v47i2.711
ENTOMON 47(2): 127-134 (2022)
Article No. ent. 47204

Persistence of cyantraniliprole in sandy loam soil and effect of organic manure amendment

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ABSTRACT: The persistence of cyantraniliprole, a new systemic insecticide of the class anthracitic diamide, was studied under the laboratory conditions in sandy loam soil and the soil amended with farmyard manure (0.5%), after spiking at 1, 2 and 4 µg kg^{-1} levels in three different soil moisture regimes *viz.* air dry, field capacity level and also in saturated conditions. Degradation was comparatively faster in saturated than at field capacity and air dry condition. There was an increase in the persistence with increase in the spiking concentration. The persistence of cyantraniliprole was dependent on soil moisture condition, organic matter content and concentration of cyantraniliprole used. © 2022 Association for Advancement of Entomology

KEYWORDS: Degradation, farmyard manure, soil moisture regimes, concentration

INTRODUCTION

Pesticides are chemicals intended for preventing, destroying, repelling, or mitigating any pest during the production, shipment, transit, storage or distribution of any food or agricultural product. Only 10 per cent of the applied pesticide reaches the targeted pest and remaining 90 per cent will get transported through air, soil and water (Moses *et al*., 1993). The pH of soil, type of clay, extent of organic matter, amount of pesticide reaching the environment and moisture regime are the most important parameters influencing the transfer and transformation pathway of pesticide in soil (Worrall *et al*., 2001). The length of time a chemical remains in soil without losing the molecular integrity, physical, chemical and biological characteristics through which it is transported and distributed is termed as "soil persistence" (Navarro *et al*., 2007) of that chemical. Half-life is used to evaluate the persistence. Some pesticides those are resistant to transformation last longer in the soil, posing a greater risk to the environment and subsequent crop. Pesticides and their toxic metabolites persisting in soil is a major global concern since it leads to an increase in hazardous load in the ecosystem (Luo *et al*., 2008; Das and Mukherjee, 2012).

Cyantraniliprole (Benevia) is a novel broad spectrum systemic insecticide of anthranilic diamide category. Its mode of action is ryanodine receptor activation; hence it is coming under Insecticide Resistance Action Committee (IRAC) group 28. Documented half-life of cyantraniliprole in soil under aerobic condition is 16.20-89.4 days (PPDB, 2019). In India it is registered for utilisation in six crops including grapes, pomegranate, chilli, tomato, cabbage and gherkins for the control of both

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lepidopteran and dipteran pests (CIBRC, 2021). Even though highly effective against agricultural pests, cyantraniliprole is highly toxic to aquatic and benthic vertebrates and honey bees. The major metabolites are IN- J9Z38 and IN-JCZ38. The mobility of the compound was found to be moderate with a water solubility of 14.2 mg l^{-1}, the dissipation kinetics of cyantraniliprole in soil given main emphasis and was done in sandy loam soils characterized by low clay content, high porosity and faster leaching. Hence the present study aims to investigate the effect of various moisture regimes on persistence of cyantraniliprole.

MATERIALS AND METHODS

Soil required for the study was sampled (0-15 cm top soil) using tube auger and spade from Kazhakkuttam, Thiruvananthapuram, Kerala, India with no recent history of pesticide application. The soil was ground, shade dried and sieved through a 2 mm mesh screen. The physico-chemical properties of the soil *viz*. pH, organic carbon, and percentage of sand, silt and clay fractions (textural analysis) in the soil, the major nutrients were estimated adopting standard analytical procedures.

Analytical standard of cyantraniliprole (99.2% purity) was procured from Bayer Crop Science (Frankfurt, Germany). Cyantraniliprole (Benevia 10.26 % OD), was obtained from M/S Bayer CropScience. The reagents such as methanol, acetonitrile used were of analytical and HPLC grade. The chemicals PSA, NaCl, Na_2SO_4 and $MgSO_4$ were activated at 450° C for 4h before use. The organic manure for the soil amendment was dry powdered cow dung which was procured locally.

The Dionex Ultimate 3000 UHPLC system (Thermo Scientific) was used for chromatographic separation using column Accucore a Q column (100 x 2.1, 2.6µ) maintained at a temperature of 30 °C. Elution was done using two elutents (solvent mixtures). The mobile phase consisted of [A] 0.1 per cent formic acid + 5 mM ammonium formate in water; [B] 0.1 per cent formic acid + 5 mM ammonium formate in methanol. The flow rate was maintained at 0.30 ml min^{-1} and 6 minutes run time. Then the effluent from LC was introduced into Thermo Scientific TSQ Quantiva mass spectrometer. The source parameters were, ion source type is H-ESI (Heated electrospray ionization), Sheath gas, 60.00 (Arbitrary units), Auxillary gas, 5.00 (Arbitrary units) and Sweep gas, 1.00 (Arbitrary units) with ion transfer tube temperature, 320 °C and ion spray voltage source of 3800 V (positive ion). The vaporization temperature is 200 °C. The residues were quantified in MS/MS system (Rao and Davidson, 1980).

Studies on the persistence and dissipation of cyantraniliprole in normal sandy loam soils and 0.5 per cent dry farm yard manure (FYM) amended soil were performed under different conditions *viz*., air dry, field capacity and saturation at three levels (1, 2 and 4 mg kg^{-1}) in the laboratory incubation condition. The commercial formulation of cyantraniliprole (Benevia) was used for the study. For conducting the laboratory study, one kg each of the normal soil and FYM amended soil maintained at air dry, brought to field capacity (90 ml kg^{-1} of sandy loam) and in saturated condition (2-3 cm layer of water) were taken in conical flask and spiked separately at 1, 2 and 4 mg kg^{-1} levels of cyantraniliprole, homogenized and kept aside for 2 hours (0^{th} day). Whole apparatus is kept under incubation chamber. Ten gram soil was taken from the conical flask in triplicate and analyzed for residue estimation of cyantraniliprole. Likewise, samples were drawn on 1^{st}, 3^{rd}, 5^{th}, 7^{th}, 10^{th}, 15^{th}, 20^{th} and 30^{th} day after application for estimation of residues and to identify the metabolites formed if any. Residues of cyantraniliprole persisting at different time intervals were estimated, from which the half-life was calculated.

The general procedure for pesticide residue analysis is sample collection, extraction, clean-up and estimation. The extraction and clean-up of residues of cyantraniliprole from soil was performed by QuEChERS method, wherein soil samples were extracted using acetonitrile and the efficiency of extraction was assessed. For this a 10 g of soil samples were weighed in 50 ml centrifuge tube, to which, 4 g magnesium sulphate, 1 g sodium chloride and 20 ml acetonitrile were added. The mixture

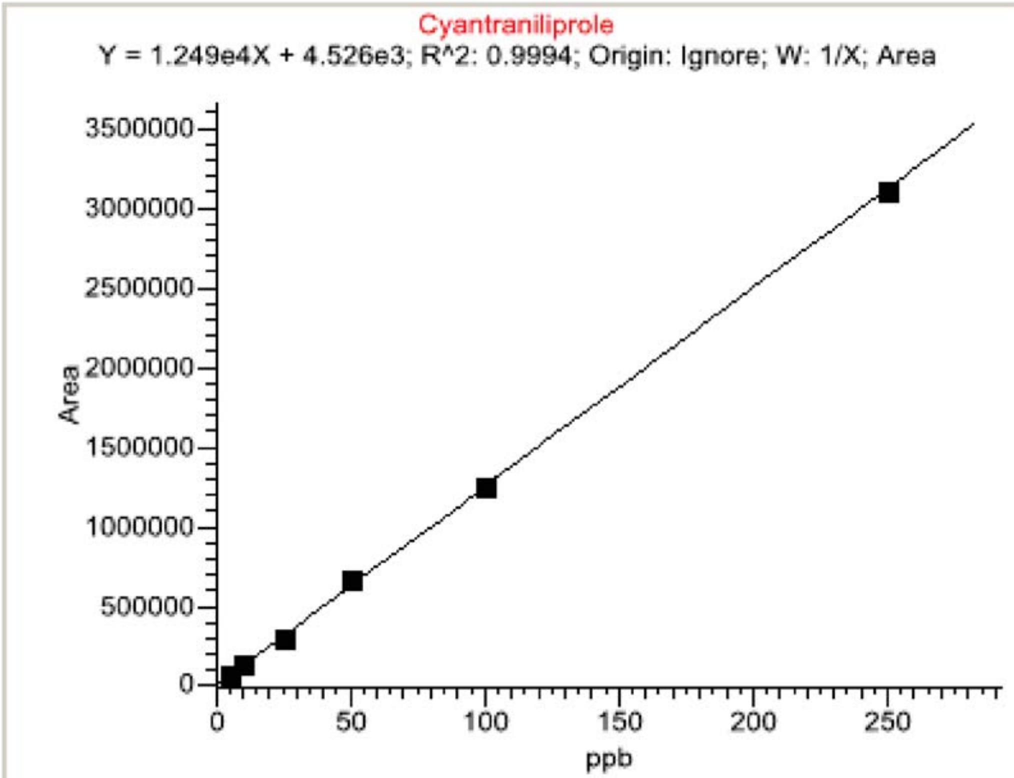

Fig. 1 Calibration curve (Linearity Curve) showing $R^2 = 0.9994$

shaken for 2 minutes in a vortex shaker and was centrifuged for 4 minutes at 3300 rpm. Ten ml supernatant was transferred to a 15 ml centrifuge tube using a micropipette and 0.25 g primary secondary amine and 1.5 g magnesium sulphate were added and was shaken for 30 seconds in a vortex followed by centrifugation at 4400 rpm for 10 minutes. After the centrifugation, 4 mL of the cleaned supernatant extract was transferred to a turbo tube and evaporated to dryness at 40°C using turboVap. The dry residue was redissolved in methanol and the volume was made up to 1ml, filtered through 0.22µm poly vinylidene fluoride (PVDF) syringe filter and collected in a glass vial and injected to UHPLC for estimation and confirmation of residues.

The single laboratory analytical method was validated in terms of linearity, specificity, limit of quantitation, limit of detection, accuracy and precision as per European Union guidelines (Sante, 2021) prior to real samples analysis. For recovery studies, untreated soil samples were fortified at 0.01, 0.05 and 0.1 mg l^{-1}. Linearity was assessed with the coefficient of correlation (R^2) derived from 5-point calibration. Absence of any peak at or near propinquity of retention time of the target molecule indicates the specificity of the method. The lowest concentration with signal to noise (S/N) of 3:1 was considered as the limit of detection (LOD) and the S/N of 10:1 was considered as the limit of quantification (LOQ) reliable linearity within a range of 0.01 to 1 µg ml^{-1}. The accuracy was expressed in terms of recovery (%) and the relative standard deviation of repeatability (RSDr %) was accounted as the precision of the method. The recovery of cyantraniliprole from soil was determined by analyzing the fortified samples in triplicate. The residue dissipation and half-life of cyantraniliprole were subjected to statistical analysis outlined by Hoskins (1961). $C_t = C_o e^{-kt}$, where C_t indicates concentration of cyantraniliprole at time t, C_o shows the initial deposits after application and k indicates rate constant of degradation. The half-life ($t_{1/2}$) is expressed as the time required to reach the half of

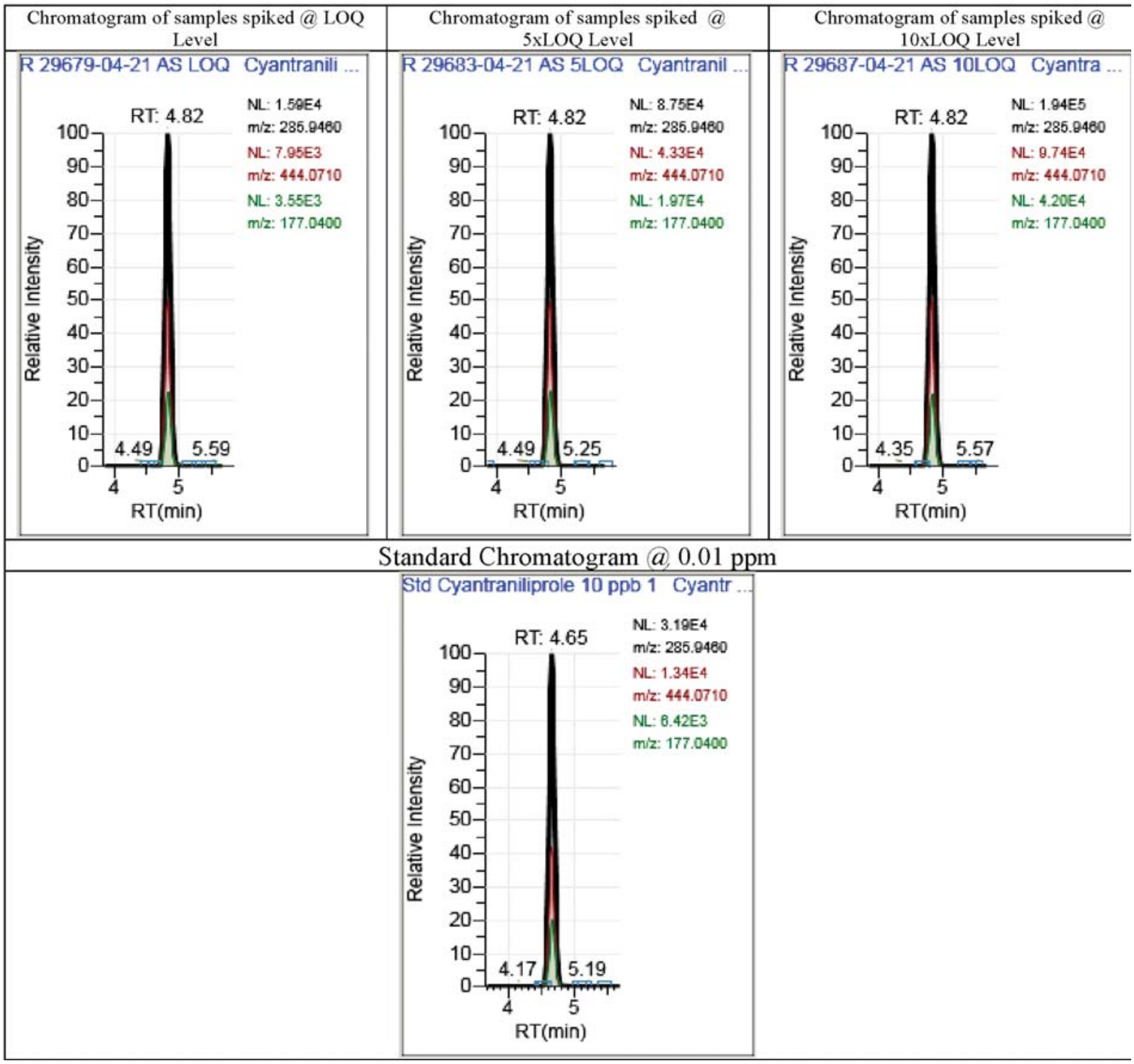

Fig.2 Chromatograms of spiked samples at three different levels

Table 1. Mass depending parameters in LC-MS/MS

Retention time (min)	Precursor ion *Q1*	Product ion *Q3*	Collision energy	Quantitative/ qualitative
4.82	475.04	177.04	42.815	Quantitative
		285.946	13.539	Qualitative
		444.071	19.455	Qualitative

initial concentration and was calculated from the equation, $t_{1/2} = \ln (2) / k$.

RESULTS AND DISCUSSION

The residues were quantified in MS/MS system. The compound dependent parameters of cyantraniliprole are retention time (min), precursor ion Q1, product ion Q3 and collision energy (Table 1). To validate the suitability of the analytical method for the experimental samples, various analytical parameters were tested, including recovery, precision, linearity, quantitation limit (LOQ) and detection limit (LOD). The values of recovery experiment obtained in the validation indicated the efficiency of the method adopted for extraction and clean-up of residues. The method showed a good linearity from 0.001–0.25 mg kg^{-1} with coefficient of correlation, R^2 value greater than 0.9994 (Fig.1).

The soil used for the study was sandy loam in texture with a proportion of 65.9 per cent sand, 22.3 per cent silt and 11.8 per cent clay content. The bulk density and particle density of the soil were 1.59 and 2.63 Mg m^{-3}, respectively. The water holding capacity was found to be 18.21 per cent. The soil was found to be moderately acidic with a pH of 5.97. The organic matter content of the soil was 0.84 per cent. The availability of primary nutrients in the soil was 177.89 kg ha^{-1} of available nitrogen, 61.04 kg ha^{-1} of available phosphorous, 148.6 kg ha^{-1} of available potassium. The secondary nutrients such as calcium, magnesium and sulphur were found to be 182, 55.7 and 3.0mg kg^{-1} respectively. Thus, the soil was found to be low in available nitrogen, medium in available potassium and high in available phosphorus. The secondary nutrients were found to be deficient in soil (Table 2). The recovery of cyantraniliprole from soil samples fortified at 0.01, 0.05 and 0.1 mg kg^{-1} (Fig. 2) varied from 81.35, 86.56 and 90.26 per cent with RSD of 1.52, 3.25 and 5.11 per cent. Since recoveries were more than 80 per cent, and the RSD values below 20, the method was selected for extraction and estimation.

At 1, 2 and 4 mg kg^{-1} the half - lives were 27.60, 28.25, 30.45 days at air dry condition, respectively whereas it was 24.83, 25.44, 25.94 days at field capacity soil moisture conditions and 18.50, 20.33, 22.31 days at saturated conditions, respectively in normal soil. The data on the metabolism of cyantraniliprole under laboratory condition revealed that no major metabolites were detected in the soil in the experiment conducted for assessing the persistence of cyantraniliprole. In all the three soil conditions, slower dissipation of cyantraniliprole was observed in soils amended with 0.5per cent FYM as the half-life values increased to 28.21, 29.29, 32.44 days in air dry condition, 25.66, 25.97, 26.24 days in field capacity condition and 19.07, 21.15 and 23.73 days in saturated soil condition at 1, 2, 4 mg kg^{-1} levels of fortification. Soil moisture regimes do have an influence on the persistence in the soil and also for the soil amended with FYM. Maximum persistence of cyantraniliprole was observed in 4

Table 2. Physical and chemical properties of the soil

Parameters	Properties
Texture	Sandy loam
Sand (%)	65.90
Silt (%)	22.30
Clay (%)	11.80
Bulk density (Mg m^{-3})	1.59
Particle density (Mg m^{-3})	2.63
Porosity (%)	39.54
Field moisture (%)	8.20
Water holding capacity (%)	18.21
Hydraulic conductivity (mL min^{-1})	0.4
pH	5.97
Electrical conductivity (dS m^{-1})	0.30
Cation exchange capacity (cmol (+) kg^{-1})	4.30
Anion exchange capacity (cmol (+) kg^{-1})	1.21
Organic matter (%)	0.81
Available nitrogen(kg ha^{-1})	177.89
Available phosphorus (kg ha^{-1})	61.04
Available potassium (kg ha^{-1})	148.60
Exchangeable calcium (mg kg^{-1})	182.00
Exchangeable magnesium (mg kg^{-1})	55.70
Exchangeable sulphur (mg kg^{-1})	3.00

Table 3. Persistence of cyantraniliprole in soil

DAA	Residues (mg kg^{-1})					
	Sandy loam soil			0.5% FYM amended soil		
	T1 (1 mg kg^{-1})	T2 (2 mg kg^{-1})	T3 (4 mg kg^{-1})	T4 (1 mg kg^{-1})	T5 (2 mg kg^{-1})	T36(4 mg kg^{-1})
Air dry soil						
0	0.68±0.05	1.29±0.2	2.96±0.7	0.96±0.09	1.71±0.09	3.25±1.1
1	0.67±0.04	1.28±0.02	2.93±0.3	0.92±0.1	1.69±0.2	3.23±0.6
3	0.65±0.02	1.26±0.06	2.91±0.08	0.89±0.1	1.65±0.01	3.21±0.3
5	0.62±0.05	1.19±0.10	2.63±0.2	0.81±0.08	1.58±0.1	3.15±0.2
7	0.59±0.04	1.08±0.04	2.41±0.03	0.75±0.04	1.49±0.05	3.09±0.4
10	0.50±0.06	0.96±0.2	2.06±0.3	0.67±0.06	1.27±0.07	2.98±0.2
15	0.47±0.02	0.87±0.20	1.87±0.2	0.60±0.1	1.18±0.1	2.54±0.1
20	0.41±0.10	0.71±0.05	1.75±0.08	0.53±0.03	0.98±0.04	2.27±0.1
30	0.33± 0.02	0.68±0.01	1.62±0.01	0.48±0.01	0.91±0.01	1.73±0.09
$t_{1/2}$(days)	27.60	28.25	30.45	28.21	29.29	32.44
Field capacity soil						
0	0.61±0.01	1.13±0.6	2.43±0.1	0.65±0.01	1.17±0.1	2.41±0.2
1	0.57±0.02	1..09±0.6	2.41±0.3	0.63±0.04	1.10±0.1	2.35±0.1
3	0.51±0.01	1.01±0.6	2.37±0.3	0.57±0.05	1.03±0.02	2.21±0.5
5	0.48±0.01	0.94±0.7	2.31±0.07	0.51±0.01	0.96±0.01	2.13±0.5
7	0.41±0.02	0.85±0.4	2.24±0.05	0.49±0.02	0.87±0.03	1.76±0.4
10	0.38±0.01	0.79±0.5	1.98±0.1	0.41±0.01	0.81±0.07	1.53±0.1
15	0.31±0.02	0.62±0.4	1.69±0.4	0.37±0.02	0.68±0.05	1.37±0.2
20	0.29±0.01	0.58±0.3	1.51±0.1	0.34±0.04	0.61±0.01	1.29±0.06
30	0.27±0.03	0.53±0.1	1.12±0.4	0.29±0.03	0.54±0.01	1.17±0.1
$t_{1/2}$(days)	24.83	25.44	25.94	25.66	25.97	26.24
Saturated soil						
0	0.93±0.03	1.26±0.03	2.52±0.3	0.95±0.01	1.30±0.07	2.60±0.1
1	0.91±0.05	1.21±0.02	2.49±0.2	0.93±0.02	1.28±0.01	2.57±0.4
3	0.87±0.08	1.12±0.07	2.35±0.1	0.89±0.06	1.16±0.07	2.51±0.1
5	0.75±1.1	1.02±0.01	2.19±0.3	0.75±0.03	1.09±0.05	2.35±0.1
7	0.61±0.07	0.93±0.01	2.02±0.1	0.69±0.03	0.96±0.03	2.14±0.02
10	0.58±0.01	0.86±0.04	1.84±0.2	0.60±0.02	0.87±0.02	1.89±0.04
15	0.51±0.07	0.71±0.01	1.58±1.1	0.53±0.01	0.79±0.02	1.61±0.06
20	0.48±0.07	0.63±0.04	1.34±0.02	0.49±0.01	0.71±0.04	1.45±0.02
30	0.29±0.02	0.45±0.01	1.02±0.2	0.31±0.01	0.47±0.01	1.14±0.03
$t_{1/2}$(days)	18.50	20.33	22.31	19.07	21.15	25.73

DAA - Days after application

mg kg^{-1} fortified amended soil under air dry condition (Table 3).

The results are in accordance with the earlier findings of study of persistence of chlorpyriphos by George *et al.* (2007) where higher organic matter application increased the persistence and also persistence was found increasing with the increase in concentration of applied chemical. The increased retention of pesticide by the organic matter reduced its amount in soil solution and thus making it available for microbial degradation. The effect of moisture was prominent and longer persistence was observed under dry conditions followed by field capacity moisture and submerged condition (Gupta *et al.*, 2008).The study on persistence and degradation of cyantraniliprole under various moisture regimes also showing similar results with higher persistence in air dry condition and the half-life obtained were 33, 28.9 and 18.2 days for air dry, field capacity and saturated condition respectively (Kumar and Gupta., 2020).

A faster dissipation of cyantraniliprole occurred in saturated soil conditions, could probably‘ be due to the anaerobic condition. Kulshrestha and Singh (1992) also reported a faster dissipation of pendimethalin under submerged soil conditions. Similarly, Smith *et al.* (1995) also reported faster dissipation of cyfluthrin under anaerobic soil conditions and George *et al.* (2007) reported faster degradation in flooded condition. The amended soil with 0.5 per cent organic matter showed an increase in the half-life at various concentration levels. Similarly, a higher persistence of fipronil was obtained in organic matter rich soils than in sandy loam soils (Mohapatra *et al.*, 2010).

The moisture status of the soil affected the persistence of cyantraniliprole. From first day of application to 30 th day of application the residue concentration was found reducing. The half- life of the compound was found reducing when the moisture content was increased and the highest half-life was obtained for the soil under air- dry condition and the lowest under the saturated soil condition. As the concentration of fortification increased, the half-life also increased. The persistence data also revealed that the half-life was found slightly increased in the soil amended with farmyard manure in all the three soil conditions. None of the major metabolites of cyantraniliprole were detected in the persistence study.

ACKNOWLEDGEMENT

The authors wish to express the gratitude to AINP on Pesticide Residues, College of Agriculture, Kerala Agricultural University, Vellayani, for providing necessary research facilities for conduct of the study.

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(Received September 27, 2022; revised ms accepted May 23, 2022; published June 30, 2022)