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Dissipation Kinetics of Chlorantraniliprole in Soils of Sugarcane Ecosystem

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Abstract Dissipation kinetics of chlorantraniliprole was studied in sandy loam soils of sugarcane ecosystem by adopting a rapid analytical method. The recovery of chlorantraniliprole was 91.67 % when extracted with ethyl acetate as against only 65.58 % in acetonitrile-based extraction. An additional cleanup step with primary secondary amine did not enhance the recovery significantly over the no-cleanup method. The ethyl acetate-based extraction followed by direct quantification in HPLC (High-performance liquid chromatography) without any cleanup facilitated rapid quantification of chlorantraniliprole residues. The LOQ (limit of quantification) of the method was 0.01 µg/g. The half-life of chlorantraniliprole was 6.50 and 6.81 days for the recommended and double the recommended doses, respectively.

Keywords Chlorantraniliprole · Residue · Dissipation · Sugarcane

India, though occupies the prestigious second place in cane area and sugar production (Solomon 2011), the productivity in the country has been hovering around 66 t/ha since the last two decades. Insect pests are among the few important constraints which limit the productivity of sugarcane to a considerable extent. Termites are among the 20 major pests posing serious threat to sugarcane cultivation in India. They are alone responsible for 33 % loss in cane yield and 4.5 % reduction in sugar recovery (Directorate of Sugarcane Development 2012). Several insecticides are being used for the management of termites infesting sugarcane crop. Chlorantraniliprole, the first member of the new class, anthranilic diamide is one among the important insecticides recommended as soil drench (Central Insecticide Board and Registration Committee 2009). Chlorantraniliprole holds great promise in pest management as it exhibits outstanding insecticidal properties by activating a novel target, the ryanodine receptors with low mammalian toxicity (Lahm et al. 2007; Sattelle et al. 2008). The dissipation of chlorantraniliprole has already been studied in rice, corn and tomato crop ecosystems at varied levels of field doses under different edaphoclimatic conditions by adopting unique analytical methods (Dong et al. 2011; Xu et al. 2010; Malhat 2012; Malhat et al. 2012). However, information on the dissipation kinetics of chlorantraniliprole in the soils of sugarcane ecosystem is lacking among the published research work. Hence, an attempt was made to study the persistence and dissipation kinetics of chlorantraniliprole applied as soil drench in sandy loam soils of sugarcane ecosystem by employing a simple, sensitive and rapid analytical method.

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Materials and Methods

Analytical standard chlorantraniliprole (purity, 98.3 %) was purchased from Sigma-Aldrich Pvt. Ltd., Bengaluru, India. Primary secondary amine (Bondesil-PSA, 40 µm particle size) was procured from Agilent Technologies, USA. Organic solvents used in the study were of HPLC

(High-performance liquid chromatography) grade and purchased from Thomas Baker (Chemicals) Ltd., Mumbai, India. Analytical reagent grade anhydrous $MgSO_4$ and NaCl were procured from HiMedia Laboratories Pvt. Ltd., Mumbai.

Stock solution (1,000 μg/mL) of chlorantraniliprole was prepared by accurately weighing 25 mg of analyte in volumetric flask (certified A class) and dissolving it in 25 mL of methanol. The stock solution was stored in dark vial at 4°C. A working standard of 100 μg/mL was prepared by appropriate dilution of the stock solution, from which the calibration standards (0.005–1.0 μg/mL) were prepared by serially diluting with mobile phase (methanol–water, 60:40, v/v).

Field experiment was conducted at Sugarcane Breeding Institute (Indian Council of Agricultural Research), Coimbatore, India in a randomised block design with three treatments replicated five times. The treatment details are as follows: T_1: chlorantraniliprole 18.5 % SC 100 g a.i./ha (recommended dose); T_2: chlorantraniliprole 18.5 % SC 200 g a.i./ha (double the recommended dose); T_3: untreated check. The insecticide was applied as soil drench over cane setts (variety Co-86032) using 1,000 L of spray fluid per ha with the help of rose can at the time of planting. It was also ensured that the experimental plots had no previous history of chlorantraniliprole application. The physicochemical properties of the experimental soil were: pH 8.5, EC 0.85 dS/m, organic carbon 0.45 % and texture sandy loam. The crop was grown by following standard agronomical practices.

Soil samples were collected from 0 to 15 cm depth of soil from the day of application (2 h after application) till 45 days after treatment. The samples (1 kg) collected from 15 randomly selected spots in each treatment were pooled, air dried, ground and then passed through 2 mm sieve. The soil samples collected on 0, 1, 3, 5, 7, 10, 15, 21, 30 and 45 days after treatment were extracted immediately after sampling.

A well-homogenised representative soil sample of 10 g was placed into a 50 mL screw-capped oak ridge tube. The target analyte was extracted separately with 20 mL of acetonitrile and ethyl acetate. The oak ridge tube was closed tightly and shaken vigorously for 1 min to ensure better interaction between the solvent and the sample. Then, 1 g of NaCl and 4 g of $MgSO_4$ (anhydrous) were added to the sample, vortexed for 1 min and centrifuged (Superspin R-V/FA; Plasto Crafts, Mumbai, India) at 5,000 rpm for 10 min at room temperature. The supernatant (4 mL) was either concentrated under gentle stream of nitrogen (15 psi) in Turbovap LV (Caliper Life Sciences, Russelsheim, Germany) at 40°C and reconstituted in 0.5 mL of mobile phase for analysis in the HPLC without any cleanup or subjected to cleanup with the sorbent as detailed below.

Dispersive solid phase extraction (d-SPE) cleanup with primary secondary amine (PSA) was compared with no-cleanup in terms of analyte recovery and interference from the study matrix. After centrifugation at 5,000 rpm for 10 min as described above in the extraction, 8 mL of supernatant was transferred to 15 mL centrifuge tube containing PSA (25 mg/g of matrix) and anhydrous $MgSO_4$ (150 mg/g of matrix). The extract was vortexed for 30 s and then centrifuged at 3,000 rpm for 10 min. The supernatant (4 mL) was transferred to test tube and concentrated to near dryness under a gentle stream of nitrogen in the Turbovap LV as described earlier. The residue was reconstituted in 0.5 mL of mobile phase and thus, the amount of sample in the final extract was equivalent to 2 g/0.5 mL.

Residues of chlorantraniliprole were detected and quantified in HPLC (Shimadzu LC-8A) equipped with diode array detector (Shimadzu SPD-M 10A). Reversed-phase C18 column (250 mm × 4.6 mm, 5 μm; Phenomenex, USA) was used to separate the target analyte. HPLC pump was run in the isocratic mode to discharge the mobile phase (methanol–water, 60:40, v/v) at a constant flow rate of 1 mL/min. The mobile phase was sonicated in ultrasonicator (Ultrasonic LC 60 H; Elma, Germany) for 15 min before using it for the HPLC analysis. The injection volume was 20 μL and the residues were detected at 230 nm. The retention time of chlorantraniliprole was 9.8 min.

The performance of the instrument and the method was evaluated by considering the validation parameters viz., linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy. Calibration curve was drawn by plotting the mean peak area against the corresponding concentration ranging from 0.005 to 1.0 μg/mL of the target analyte in mobile phase. The accuracy of the method was checked by routine recovery assay at three levels of fortification (0.01, 0.05 and 0.1 μg/g) each replicated thrice along with a control. The fortified samples were equilibrated and processed by adopting the method standardised in the present study. The precision of the method in terms of repeatability was determined on the basis of relative standard deviation (RSD %).

Persistence data was fitted into first-order dissipation kinetics $C = C_o e^{-kt}$. where, C = concentration after a lapse of time t, C_o = apparent initial concentration and k = rate constant. The first-order equation provided a satisfactory fit for the data ($R^2 > 0.9$) and half-life was calculated based on this. All other statistical analyses including the Duncan's multiple range test were performed in SPSS Statistics version 17.0.

Results and Discussion

The recovery of chlorantraniliprole was 91.67 % when extracted with ethyl acetate (without any cleanup) as against only 65.58 % in acetonitrile extraction. The less

Table 1 Residues of chlorantraniliprole in the soils of sugarcane ecosystem

DAT/ Half-life	Recommended dose (100 g a.i./ha)		Double the recommended dose (200 g a.i./ha)	
	Residue (μg/g) ± SD	Dissipation (%)	Residue[a] (μg/g) ± SD	Dissipation (%)
0	0.208 ± 0.007	–	0.461 ± 0.014	–
1	0.189 ± 0.008	9.29	0.412 ± 0.016	10.62
3	0.177 ± 0.008	14.91	0.356 ± 0.007	22.86
5	0.141 ± 0.010	31.99	0.291 ± 0.020	36.96
7	0.110 ± 0.008	46.92	0.233 ± 0.021	49.40
10	0.059 ± 0.003	71.66	0.132 ± 0.007	71.29
15	0.048 ± 0.002	76.91	0.098 ± 0.003	78.74
21	0.020 ± 0.001	90.61	0.048 ± 0.003	89.49
30	0.010 ± 0.001	95.25	0.024 ± 0.003	94.82
45	BDL	–	BDL	–
Half-life	6.50 days		6.81 days	

DAT days after treatment, *SD* standard deviation, *BDL* below detectable limit

[a] Mean of three replicates

recovery of chlorantraniliprole in acetonitrile-based extraction may be attributed to its poor solubility in acetonitrile (0.711 ± 0.072 g/L, United States Environmental Protection Agency 2008). Though the d-SPE cleanup with PSA significantly enhanced the recovery of chlorantraniliprole in acetonitrile-based extraction (69.72 %), it was still below the acceptable range of recoveries as prescribed by the European Commission (European Commission 2010). Conversely, the recovery in PSA-based cleanup (92.72 %) was on par with no-cleanup method (91.67 %) when ethyl acetate was used as the extraction solvent. Hence, ethyl acetate-based extraction followed by direct quantification in the HPLC without any cleanup was adopted to study the dissipation pattern of chlorantraniliprole applied for the management of termites in the sugarcane ecosystem.

A very good linearity was observed for the target analyte as the coefficient of determination (R^2) was 0.9998. The LOQ of the method was 0.01 μg/g based on 20 μL injection of the final extract containing 2 g of sample/0.5 mL. The precision and accuracy of the method were ascertained by recovery assays. The recoveries of chlorantraniliprole were 92.54 ± 2.89 %, 100.05 ± 2.38 % and 101.70 ± 1.68 % at 0.01, 0.05 and 0.1 μg/g level of fortification, respectively. The acceptable range of recoveries for trace residue analysis has been fixed between 70 % and 120 % with RSD of ±20 % (European Commission 2010). Thus, the method optimised in the present study provided satisfactory level of precision and accuracy.

The initial deposits of chlorantraniliprole in the soil were 0.208 and 0.461 μg/g when applied at 100 and 200 g a.i./ha, respectively. The residues reached below the detectable limit (<0.01 μg/g) at 45 days after treatment (DAT) irrespective of the doses applied (Table 1). The dissipation pattern of chlorantraniliprole followed first-order kinetics with a good fit (Fig. 1). Half-life of chlorantraniliprole in the soil during the period under study was 6.50 and 6.81 days for the recommended and double the recommended doses, respectively. The dissipation kinetics of chlorantraniliprole has already been studied in corn, rice and tomato ecosystems under different edaphoclimatic conditions. The half-life of chlorantraniliprole in the soils of corn ecosystem was 12.6 and 23.1 days for the same dose applied in two different environments (Dong et al. 2011). It was only 3.66 days in the soils of tomato ecosystem (Malhat et al. 2012) as against 16 days in the rice field ecosystem (Zhang et al. 2012).

This article describes the dissipation kinetics of chlorantraniliprole in the soils of sugarcane ecosystem. Ethyl acetate-based extraction followed by direct quantification in the HPLC without any cleanup has been shown to facilitate rapid determination of chlorantraniliprole residues in soils. The LOQ of the method was 0.01 μg/g. The half-life of chlorantraniliprole was 6.50 and 6.81 days for the recommended and double the recommended doses, respectively in the near-alkaline sandy loam soils of tropical climatic condition.

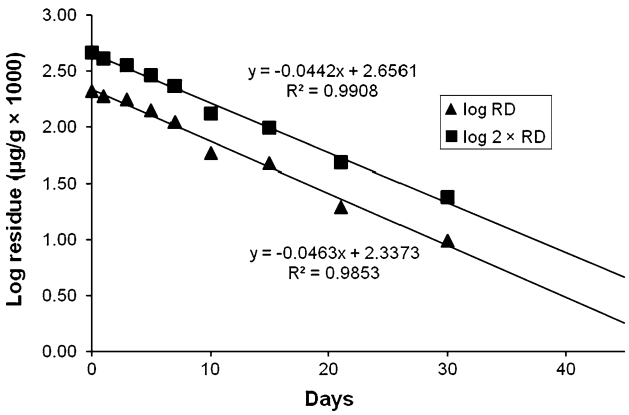

Fig. 1 Dissipation pattern of chlorantraniliprole residues in the soils of sugarcane ecosystem

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References

Central Insecticide Board and Registration Committee (2009) Major uses of pesticides registered under the insecticides act, 1968. http://www.cibrc.nic.in/mupi.pdf. Accessed 25 May 2012

Directorate of Sugarcane Development (2012) Major insect pest management of sugarcane crop. http://dsd.dacnet.nic.in/PestManage.htm. Accessed 25 May 2012

Dong F, Xu J, Liu X, Li J, Li Y, Kong Z, Shan W, Zheng Z, Zheng Y (2011) Determination of chlorantraniliprole residues in corn and soil by UPLC–ESI–MS/MS and its application to a pharmacokinetic study. Chromatographia 74:399–406

European Commission (2010) Guidance document on pesticide residue analytical methods. Document No. SANCO/825/00/rev. 8.1/16/11/2010. http://ec.europa.eu/food/plant/protection/resources/guide_doc_825-00_rev7_en.pdf. Accessed 25 May 2012

Lahm GP, Stevenson TM, Selby TP, Freudenberger JH, Cordova D, Flexner L, Bellin CA, Dubas CM, Smith BK, Hughes KA, Hollingshaus JG, Clark CE, Benner EA (2007) Rynaxypyr: a new insecticidal anthranilic diamide that acts as a potent and selective ryanodine receptor activator. Bioorg Med Chem Lett 17:6274–6279

Malhat FM (2012) Determination of chlorantraniliprole residues in grape by high-performance liquid chromatography. Food Anal Methods. doi:10.1007/s12161-012-9400-z

Malhat F, Abdallah H, Hegazy I (2012) Dissipation of chlorantraniliprole in tomato fruits and soil. Bull Environ Contam Toxicol 88:349–351

Sattelle DB, Cordova D, Cheek TR (2008) Insect ryanodine receptors: molecular targets for novel pest control chemicals. Invert Neurosci 8:107–119

Solomon S (2011) The Indian sugar industry: an overview. Sugar Tech 13:255–265

United States Environmental Protection Agency (2008) Pesticide fact sheet: Chlorantraniliprole. http://www.epa.gov/opprd001/factsheets/chloran.pdf. Accessed 05 June 2012

Xu P, Ren Y, Zhou Z, Liu A, Zhang H (2010) Determination of chlorantraniliprole in vegetables, fruits and grains by SPE clean-up and LC-UV. Chromatographia 72:763–766

Zhang JM, Chai WG, Wu YL (2012) Residues of chlorantraniliprole in rice field ecosystem. Chemosphere 87:132–136