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Degradation pattern and risk assessment of chlorantraniliprole on berseem (*Trifolium alexandrinum* L.) using high performance liquid chromatography

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HIGHLIGHTS

- Chlorantraniliprole is effective for the control of *Helicoverpa armigera.*
- Chlorantraniliprole was extracted and cleaned up by QuEChERS and analyzed by HPLC.
- The residues reached below determination limit in 10 days at higher dosages.
- Half-life of chlorantraniliprole on berseem was observed to be 0.93–1.33 days.
- The residues of chlorantraniliprole reached below MPI on 0 days of treatment.

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ABSTRACT

The persistence pattern of chlorantraniliprole on berseem leaves and its risk assessment for the safety of cattle were studied. QuEChERS method was used for the extraction and cleanup of samples and the residues of chlorantraniliprole were estimated using high performance liquid chromatography (HPLC) and confirmed by Liquid Chromatograph–Mass Spectrometer (LCMS–MS). The dissipation studies on berseem were carried out by application of chlorantraniliprole at five different dosages i.e. 11.6, 17.1, 23.1, 34.7 and 46.2 g a.i. ha^{-1}. Average initial deposits of chlorantraniliprole were found to be 0.47, 0.61, 0.78, 1.15 and 1.31 mg kg^{-1}, respectively. The residues reached below determination limit (BDL) of 0.01 mg kg^{-1} in 5, 7, 7, 10 and 10 days for 11.6, 17.1, 23.1, 34.7 and 46.2 g a.i. ha^{-1} dosages, respectively. Half-life ($t_{1/2}$) of chlorantraniliprole on berseem was observed to be 0.93, 1.14, 1.06, 1.00 and 1.33 days, respectively, at 11.6, 17.1, 23.1, 34.7 and 46.2 g a.i. ha^{-1}. It was found that the theoretical maximum residue contributions (TMRC) values reached below maximum permissible intake (MPI) on 0 day in berseem samples treated with chlorantraniliprole. These studies, therefore suggest that the use of chlorantraniliprole formulation at different dosages does not seem to pose any hazards to the consumers and a waiting period of one day is suggested to reduce the risk before consumption of berseem leaves. These data could provide guidance for the proper and safe use of this pesticide on berseem in India.

1. Introduction

Chlorantraniliprole (CAP), [3-bromo-N-[4-chloro-2-methyl-6-[(methyl amino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide], is a new insecticide that belongs to the anthranilic diamide class of chemistry (Fig. 1). It is used as an active ingredient in many different formulations. This compound has novel mode of action for synthetic insecticides called ryanodine receptor activators (Cordova et al., 2007) which are critical for muscle contraction. As the insect and mammalian ryanodine receptors are structurally different, chlorantraniliprole exhibits remarkable selectivity and safety for mammals (Lahm et al., 2007). This insecticide is extremely potent against lepidopterous pests, including those resistant to neonicotinoid and pyrethroid insecticides. The synthetic organic pesticides begin to degrade as soon as they are synthesized. The breakdown of principle components may be caused by harsh environmental conditions or chemical interactions (Sanz-Asensio et al., 1997). Therefore, dissipation studies for a given crop in the open field conditions of each growing area are necessary to test.

Berseem (*Trifolium alexandrinum*) is an important winter season fodder crop of the central, north, northwest and northeastern part

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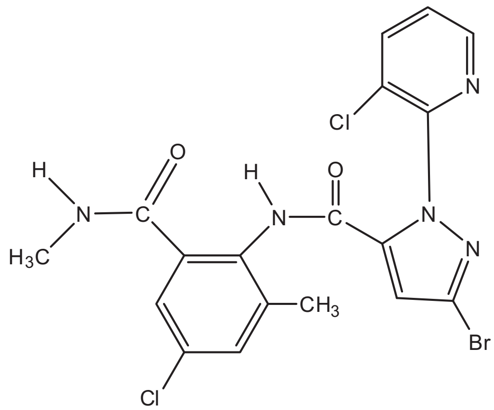

Fig. 1. Structure of chlorantraniliprole.

of India. It has wide adaptability among farmers because of its fast growth, high production mow and fresh forage production with good quality and quantity (Shrestha et al., 1996). It is estimated to be cultivated in an area of around 2 million ha with green fodder yield ranging from 60 to 120 t/ha. The low production of berseem in the country could be attributed to several factors, the most important being the damage caused by the insect pests. So the productivity of the crop can be increased by the control of insect pests with the use of insecticides. The studies on the behavior of chlorantraniliprole on various commodities like cauliflower (Kar et al., 2013), corn and soil (Dong et al., 2011), cowpea (Vijayasree et al., 2013), grapes (Malhat, 2012), rice (Zhang et al., 2012) and tomatoes (Malhat et al., 2012) have been carried out but no study has been reported on the fate of chlorantraniliprole in berseem fodder crop.

Most of the methods currently available for extracting the pesticides rely on liquid–liquid extraction and the partition process which is time consuming or solvent extraction using a mixture of solvents most of which are hazardous. However, more affordable methods have been developed recently, based on Quick, Easy, Cheap, Effective, Rugged and Safe methods (QuEChERS), first reported in 2003 (Anastassiade et al., 2003); which are becoming popular methods for sample extraction, due to their safety, simplicity, affordability, effectiveness, efficiency and dependability of the results. Many of these methods have been given official recognition as standard procedures for detection of pesticide residues in fruits and vegetables. QuEChERS has been frequently used for all type of samples, such as fat, oil, fruit, vegetables, rice and bread (Anastassiades et al., 2007; Diez et al., 2006). Therefore, in the present study, the QuEChERS method was applied using high-performance liquid chromatograph (HPLC) with photodiode array (PDA) detector system for the determination of residue levels and study of dissipation behavior of chlorantraniliprole in berseem.

2. Materials and methods

2.1. Chemicals and reagents

The technical grade analytical standard of chlorantraniliprole (purity 98.1%) was procured from M/s Sigma Aldrich, India. The formulation (Coragen 18.5 SC) was obtained from M/s E.I. DuPont, India Pvt. Ltd., Gujarat, India. Analysis of acetonitrile (HPLC grade) extract of the formulation showed only chlorantraniliprole and none of its metabolic products and was found to be accurate with respect to its active ingredient.

Solvents like ethyl acetate, acetonitrile (HPLC grade), water (HPLC grade), sodium chloride (ASC reagent grade $\geqslant$99.9%) and analytical grade activated anhydrous $MgSO_4$ were obtained from Merck, Darmstadt, Germany. Sodium sulfate anhydrous (AR grade) was procured from S.D. Fine Chemicals, Mumbai. Primary Secondary Amine (PSA) Sorbent and activated graphitic carbon black (GCB, 400 mesh) were obtained from Varian, Mumbai and Supelco, Bellfonte, USA, respectively. All common solvents were redistilled in all-glass apparatus before use. The suitability of the solvents and other chemicals was ensured by running reagent blanks before actual analysis.

2.2. Preparation of standard solution

A standard stock solution of chlorantraniliprole (1 mg mL^{-1}) was prepared in HPLC grade acetonitrile. The standard solutions required for constructing a calibration curve (2.00, 1.50, 1.00, 0.50, 0.25 and 0.10 μg mL^{-1}) were prepared from stock solution by serial dilutions with HPLC grade acetonitrile. All standard solutions were stored at 4 °C before use.

2.3. Instruments

The quantification of chlorantraniliprole residues was done by using high performance liquid chromatography (HPLC). The high performance liquid chromatograph (Model DGU-2045) equipped with reverse phase (RP) C_{18} column and photo diode array (PDA) detector, dual pump was supplied by M/S Shimadzu Corporation, Kyoto, Japan. The HPLC column, a Luna 5 μm C_{18} column (250 × 4.6 mm size, 5.20 ± 0.30 μm particle size, 2.20 ± 0.30 (90%/10%) particle distribution, 95 ± 15 A° pore diameter, 430 ± 40 $m^2\ g^{-1}$ surface area, <55.0 ppm metal content, 19.00 ± 0.70% total carbon and 3.25 ± 0.50 μmoles m^{-2} surface coverage) was obtained from M/S Spincotech Pvt. Ltd. Chennai, India. The sample injector was equipped with a 20 μL loop. For instrument control, data acquisition and processing, LC Solution software was used.

The residues of chlorantraniliprole were confirmed using a MSD sciex Applied Biosystem API 2000 Q-Trap mass spectrometer. The LC–MS was operated in the positive ion mode using multiple reaction monitoring (MRM) *i.e.* Declustering Potential (DP), Focusing Potential (FP), Entrance Potential (EP) and Collision Cell Entrance (CEP) of the transitions m/z 484.1 → 453.3 and m/z 484.1 → 286.0. Collision energy (CE) and collision cell exit potential (CXP) were optimized for each transition monitored. The experimental conditions were as follow; ionspray voltage (IS) 5500 V; curtain gas 10 psi; temperature 150 °C; ion source gas (1) 50 psi ion; source gas (2) 50 psi. Declustering potential and collision energy were optimized for each transition monitored.

2.4. Field experiment

Berseem crop (variety: BL-42) was raised during October 2011 at Entomological Research Farm, Punjab Agricultural University, Ludhiana following recommended agronomic practices (Anonymous, 2012). There were six treatments i.e. control and five dosages i.e. 11.6, 17.1, 23.1, 34.7 and 46.2 g a.i. ha^{-1} and three replications for each treatment arranged in a randomized block design (RBD), and size of the each plot was 50 m^2.

The application of chlorantraniliprole (Coragen 18.5 SC) was made at flowering stage. There were six treatments i.e. control and five dosages *i.e.* 11.6, 17.1, 23.1, 34.7 and 46.2 g a.i. ha^{-1}. Pesticide was sprayed as foliar application with the help of an ASPEE Knapsack sprayer fitted with hollow cone nozzle.

About 1 kg berseem leaf sample was collected randomly at 0 (1 h), 1, 3, 5, 7 and 10 days after the application of the insecticide. The berseem leaf samples were collected from each plot separately, packed in polyethylene bags and brought to the laboratory for