Bull Environ Contam Toxicol (2010) 85:419–422
DOI 10.1007/s00128-010-0101-2

Persistence Behaviour of Thiamethoxam and Lambda Cyhalothrin in Transplanted Paddy

Suhrid Ranjan Barik · Pritam Ganguly · Samir Kumar Kunda · Ramen Kumar Kole · Anjan Bhattacharyya

Received: 31 January 2010 / Accepted: 30 July 2010 / Published online: 12 August 2010

Abstract A field study was conducted in Pre-Kharif season 2007 on paddy to determine the persistence of thiamethoxam (12.6%) and lambda cyhalothrin (9.4%) [in a 'Readymix' formulation Alika 247 ZC], following the application of 33 g. a.i. ha^{-1} (T_1) and 66 g. a.i. ha^{-1} (T_2). Spraying of insecticide was done during milking stage of the crop (63 days after transplantation). Thiamethoxam and lambda cyhalothrin residues were estimated by HPLC and GLC respectively. The half-life values were 5.2–5.8 and 4.8 days for thiamethoxam and lambda cyhalothrin respectively. No residue was detected in the harvested paddy, straw, grain, and soil samples.

Keywords Alika 247 ZC · Thiamethoxam · Lambda cyhalothrin · Paddy

Paddy (*Oryza sativa*) is one of the most important food crops in the world. Insect pests (insects which cause economic damage to agriculture) are one of the major biological constraints for production of paddy. Several chemicals have been used since long time to control the major insect pests of paddy like BPH, GLH, Stem borer etc. The frequent use of certain insecticides leading to the development of insecticide resistance is not uncommon (Endo et al. 1987; Endo and Kazano 1988). To combat such situation, simultaneous administration of two or more toxic chemicals in ready mix formulation has become popular and are available in the market viz. endosulfan 29.75% + deltamethrin 0.75%, acephate 25% + fenvelarate 3%, chlorpyriphos 50% + cypermethrin 5%, ethion 40% + cypermethrin 5%, quinalphos 20% + cypermethrin 3%, triazophos 35% + deltamethrin 1% etc. The study of joint action of insecticides is important for the possible extension of the use of the toxicant and also for minimizing their toxic residues in non target organisms.

A new readymix insecticide formulation Alika 247 ZC, consists of thiamethoxam 12.6% and lambda cyhalothrin 9.4%, is going to enter in the Indian market by Syngenta India Ltd. Thiamethoxam [3-{(2-chloro-5-thiazolyl) methyl} tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine] is the first commercial neonicotinoid insecticide (Fig. 1) from the thianicotinyl subclass and acts by binding to nicotinic acetylcholine receptors. It exhibits exceptional systemic characteristics and provides excellent control of a broad range of commercially important pests. Thiamethoxam is effective against paddy white backed plant hopper (Javaregowda and Naik 2005), wheat aphids, without showing any phytotoxicity on the wheat plants (Srinivasa Babu and Sharma 2003). Thiamethoxam is also used for seed treatment to control aphids, jassids and thrips (Vadodaria et al. 2001). It was also reported to have termiticidal properties (Delgarde and Rouland-Lefevre 2002) and anti-feedant action (Acda 2007). Low use rates, flexible application methods, excellent efficacy, long-lasting residual activity and favourable safety profile make this new insecticide well-suited for modern integrated pest management programmes in many cropping systems (Maienfisch et al. 2001).

Lambda cyhalothrin [α-cyano-3-phenoxybenzyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate] is one of the well known synthetic pyrethroids (Fig. 2). It is a non-systemic insecticide with contact and

S. R. Barik · P. Ganguly · S. K. Kunda · R. K. Kole · A. Bhattacharyya (✉)
Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal 741252, India
e-mail: anjan_84@rediffmail.com

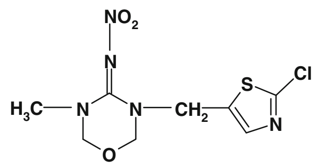

Fig. 1 Structure of thiamethoxam

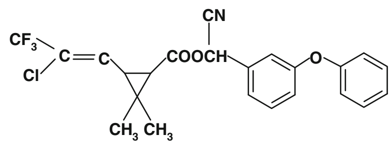

Fig. 2 Structure of lambda cyahalothrin

stomach action as well as repellent properties. It gives rapid knockdown activity to control of a wide spectrum of insects pests like aphids, thrips, lepidopteran larvae, coleopteran larvae and adults in cereals, ornamentals, potatoes, vegetables, cotton and other crops. It provides good control of insect borne plant viruses and insect pests in public health.

The present field study on transplanted paddy (in transplanted paddy, seedlings are first grown in seedbeds before they are transplanted in the fields) has been made to understand the dissipation pattern as well as residual fate of these two compounds (thiamethoxam and lambda cyhalothrin) in paddy plant, grain, husk, straw and field soil, when these are applied simultaneously in the form of a readymix insecticide formulation Alika 247 ZC following a single application @ 33 g. a.i. ha^{-1} (T_1) and @ 66 g. a.i. ha^{-1} (T_2) along with untreated control (T_3).

Materials and Methods

A field study to determine the persistence of a 'Readymix' formulation Alika 247 ZC was conducted at the University Research Farm, Bidhan Chandra Kishi Viswavidyalaya, West Bengal, India in Pre-kharif season 2007 on paddy [variety- Khitish (IET- 4094)]. Alika 247 ZC was applied with the help of Knapsack sprayer equipped with WFN 62 nozzle @ 33 g. a.i. ha^{-1} (T_1) and @ 66 g. a.i. ha^{-1} (T_2) along with untreated control (T_3) in Randomized Block Designed plots. The area of each plot was 20 m^2. The spacing was 30 cm × 20 cm (between row to row and plant to plant respectively). Three replications were used for each treatment. Fertilizers (N, P_2O_5 and K_2O) were applied @ 60, 30 and 30 kg ha^{-1} respectively. Irrigations were given as and when required. Spraying of insecticide was done once only during milking stage of the crop (63 days after transplantation).

Green foliage samples of paddy plant were collected at 0 (2 h after spraying), 1, 5, 10 and 15 days after application of the insecticides for dissipation study. Paddy straw, grain and soil samples were also collected at the time of harvest following standard sampling procedures. Paddy green foliage (2 kg) samples were collected from 5–7 places randomly in each treatment plots replication wise on each date of sampling. Samples from untreated control plots were also collected in the same way. Paddy straw (0.5 kg), grain (1 kg), soil (1 kg) samples were taken at the time of harvest. Soil samples were collected from a depth of 6" with the help of soil auger. Plant samples were chopped, soil samples were air dried and grains were grinded to facilitate extraction of the pesticides using organic solvent. A valid representative sample of soil (100 g) and plant (50 g each for green foliage, grain and straw) for each compound was prepared separately by quartering technique in the laboratory and taken for residue analysis. Samples were extracted immediately after collection as far as practicable. Extracts were cleaned up immediately after extraction as far as possible.

In order to estimate thiamethoxam residue, the plant sample (50 g) was blended with 150 mL of acetonitrile: water (9:1) for 2–3 min in a blender and filtered through Whatman No. 1 filter paper fitted in a Buchner funnel under pump suction. The solid residue was washed using 150 mL acetonitrile. Soil sample (100 g) was taken in 500 mL conical flask and 200 mL of acetone: water (9:1) was added into the flask and kept overnight. The soil sample was then shaken in a mechanical shaker for 3 h followed by filtration of the extracts in Buchner funnel using suction and 100 mL of the same extracting solvent was used for washing (50 + 50 mL). The filtrates, both from plant and soil sample were then concentrated separately in rotary vacuum evaporator at 40°C and transferred to separatory funnels. These were then diluted with 150 mL saturated aqueous NaCl solution (10%) for partitioning with 200 mL dichloromethane (100 + 50 + 50). The combined organic phases were collected by passing over anhydrous Na_2SO_4 and evaporated in rotary vacuum evaporator at 40°C. Final volumes were reconstituted with HPLC grade methanol. Then, a representative portion of 3 mL was taken from it and transferred to solid phase extraction cartridge ODS-C_{18} and it was eluted with methanol (HPLC grade). The volume of the collected fraction both from plant and soil samples were made up to 3 mL for final estimation of thiamethoxam residues by HPLC (Model HP 1050 series), coupled with UV–VIS detector (Agilent 1100 series). Reverse Phase C_{18} column (250 × 4.6 mm; Thermo Hypersil ODS, 5 μ) was used for chromatographic separation with methanol: water (1:1) as the mobile phase at a flow rate of 1 mL min^{-1}. Under these working conditions thiamethoxam was detected (at $\lambda_{max} = 255$ nm) at the retention time of 3.47 min. The LOD and LOQ of the method were determined as 0.01 and 0.02 ppm, respectively, for both plant and soil samples.

Table 1 Dissipation of thiamethoxam in paddy plant

Dose	Mean (μg g^{-1}) ± SD (% dissipation) on day					$T_{1/2}$ (Days)	Regression equation (r^2)
	0	1	5	10	15		
T_1	0.50 ± 0.02	0.36 ± 0.01 (28)	0.20 ± 0.01 (60)	0.11 ± 0.01 (78)	0.06 ± 0.01 (88)	5.19	$y = 2.6410–0.0580x$ (0.9852)
T_2	0.83 ± 0.02	0.69 ± 0.01 (16.87)	0.45 ± 0.06 (45.78)	0.23 ± 0.01 (72.29)	0.14 ± 0.01 (83.13)	5.85	$y = 2.9045–0.0515x$ (0.9975)

In order to estimate lambda cyhalothrin residue, plant sample (50 g) was added with 200 mL of acetonitrile: water (9:1) and kept overnight. The mixture was blended for 2–3 min in a blender and filtered using Buchner funnel fitted with Whatman No. 1 filter paper spread with Celite powder under pump suction with repeated washing using the same solvent. Soil sample (100 g) was taken in 500 mL conical flask and 200 mL acetone: water (9:1) was added into the flask and kept overnight. The mixture was then shaken in a mechanical shaker for 3 h and the extract was filtered through Buchner funnel using pump suction. The residual soil was washed thoroughly using the same extracting solvent (50 + 50 mL). The extracts, both from plant and soil samples were then concentrated in rotary vacuum evaporator at 40°C separately. The concentrated extracts were diluted with 150 mL saturated aqueous NaCl solution (10%) and the diluted extract was partitioned with 200 mL hexane (100 + 50 + 50). The organic phase was collected by passing over anhydrous Na_2SO_4. The concentrated hexane extract was ready for column chromatography. The column (2.5 cm ID, 65 cm length) was packed with 10 g mixture of florisil (80–120 mesh) and silica gel (60–120 mesh) in the ratio of 1:1. Then the extract was transferred to the column and eluted with 150 mL mixture of hexane: acetone (9:1). The eluted fraction was concentrated in rotary vacuum evaporator at 40°C. The final volume was reconstituted with distilled hexane for analysis of lambda cyhalothrin residues by GLC (Model Chemito GC 1000) coupled with Electron Captured Detector. DB-5 Column (30 m × 0.53 mm ID (Mega bore), 1.5 μm film thickness) was used with Oven, Injector and Detector temperatures maintained at 260, 275 and 300°C, respectively. Carrier gas (N_2) flow was 60 mL min^{-1}. Under these working conditions lambda cyhalothrin was detected at the retention time of 3.04 min. The LOD and LOQ of the method were 0.01 and 0.03 ppm, respectively, for both plant and soil samples.

Recovery studies were carried out to establish the reliability of the analytical methods and to know the efficiency of extraction, partitioning and clean up steps. The substrates viz. paddy plant, straw, grain and soil were fortified separately with analytical grade thiamethoxam at the level of 0.02, 0.1, and 1.0 μg g^{-1} and with lambda cyhalothrin at the level of 0.03, 0.1 and 1.0 μg g^{-1}, respectively. Residue analysis was carried out following the above described methods. The amount of thiamethoxam and lambda cyhalothrin recovered from different substrates was analyzed by HPLC and GLC respectively.

Results and Discussion

The average recovery of thiamethoxam from paddy plant, straw, grain and soil was 88.0%, 90.3%, 95.5% and 95.0% respectively and that for lambda cyhalothrin, it was 86.4%, 90.1%, 95.9% and 101.0% respectively. All these values were found to be very satisfactory. Moreover, the chromatograms of the recovered samples were found to be free from interferences when compared with the respective control samples. Therefore, the adopted methods were in good order for the determination of thiamethoxam and lambda cyhalothrin residues in soil, grain, plant and straw samples of paddy.

The residue data of thiamethoxam in paddy plant at different day's interval are represented in Table 1. The initial deposits (2 h after spraying) of thiamethoxam in plant samples were found to be 0.50 μg g^{-1} at the recommended dose (T_1), and 0.83 μg g^{-1} at double the recommended dose (T_2). However, no residue was detected in the untreated control (T_3) samples of paddy plant. The residues of thiamethoxam in plant samples declined progressively with time. About 40%–60% of the initial residue was dissipated after 5 days of application which further increased to 83%–88% after 15 days irrespective of the application doses. The dissipation of thiamethoxam followed first order reaction kinetics. The calculated half-life values of thiamethoxam in paddy foliage were found to be 5.2 days for T_1 and 5.8 days for T_2 (Table 1). No residue of thiamethoxam was detected in paddy, straw, grain, and soil samples collected at harvest (Table 2).

Table 2 Harvest time residue of thiamethoxam in paddy straw, grain and field soil

Dose	Substrate		
	Straw	Grain	Field soil
T_1	BDL	BDL	BDL
T_2	BDL	BDL	BDL

BDL below detectable limit

Table 3 Dissipation of lambda cyhalothrin in paddy plant

Dose	Mean (μg g^{-1}) ± SD (% dissipation) on day					$T_{1/2}$ (Days)	Regression equation (r^2)
	0	1	5	10	15		
T_1	0.26 ± 0.02	0.12 ± 0.01(53.9)	BDL	BDL	BDL	–	
T_2	0.83 ± 0.02	0.69 ± 0.01 (16.9)	0.45 ± 0.06 (45.8)	BDL	BDL	4.81	$y = -0.0626x + 0.8543$ (0.9851)

BDL below detectable limit

Table 4 Harvest time residue of lambda cyhalothrin in paddy straw, grain and field soil

Dose	Substrate		
	Straw	Grain	Field soil
T_1	BDL	BDL	BDL
T_2	BDL	BDL	BDL

BDL below detectable limit

The residue data of lambda cyhalothrin in paddy plant at different day's interval are represented in Table 3. The initial deposits (2 h after spraying) of lambda cyhalothrin in plant samples were found to be 0.26 μg g^{-1} at the recommended dose (T_1), and 0.41 μg g^{-1} at double the recommended dose (T_2). No residue was detected in the untreated control (T_3). The residues of lambda cyhalothrin in plant samples also declined progressively with time. More than 50% of initial residues of lambda cyhalothrin were dissipated just after one day application for single dose. Thereafter, the residues reached below detectable limit in plant samples after 5 days in case of T_1 and after 10 days of spraying in case of T_2. The nature of dissipation of lambda cyhalothrin in paddy samples could be explained in terms of first order reaction in case of T_2 and the calculated half life value was found to be 4.81 days. No residue was detected in paddy, straw, grain, and soil samples collected at harvest (Table 4).

The present investigation revealed the less persistence nature of both the insecticides thiamethoxam and lambda cyhalothrin in paddy with the half life of 4–6 days. Moreover, no residue was detected in the harvest samples of paddy straw, grain and field soil. Therefore, the ready-mix formulation of thiamethoxam and lambda cyhalothrin may not pose any residual toxicity problem. Based on these findings, the use of Alika 247 ZC may be advocated for the control of broad spectrum insects in Paddy.

Acknowledgments We are very much thankful to M/S Syngenta India Ltd., Mumbai for sponsoring the research program.

References

Acda MN (2007) Toxicity of thiamethoxam against Philippine subterranean termites. J Insect Sci 7(26):1–6

Delgarde S, Rouland-Lefevre C (2002) Efficacy of actara® 25WG on three species of Brazilian termite (Isoptera, Nasutitermitinae) crop pests. Sociobiology 40:699–710

Endo S, Kazano H (1988) Insecticide susceptibility of rice leaffolder larvae *Cnaphalocrocis medinalis* Guenee in Kyushu district. Proc Assoc Plant Prot Kyushu 34:106–108

Endo S, Kazano H, Masuda T (1987) Insecticide susceptibility of rice leaf roller larvae *Cnaphalocrocis medinalis* Guenee. Appl Entomol Zool 22:145–192

Javaregowda, Naik LK (2005) Bioefficacy of thiamethoxam 25 WG against Paddy white backed plant hopper (WBPH) and their natural enemies. Pestology 29:31–33

Maienfisch P, Angst M, Brandl F, Fischer W, Hofer D, Kayser H (2001) Chemistry and biology of thiamethoxam: a second generation neonicotinoid. Pest Manag Sci 57:906–913

Srinivasa Babu K, Sharma AK (2003) Bioefficacy of a new molecule, thiamethoxam against foliar aphids of wheat (*Triticum aestivum*). Indian J Agr Sci 73:574–575

Vadodaria MP, Patel UG, Patel CJ, Patel RB, Maisuria IM (2001) Thiamethoxam (Cruiser) 70 WS: a new seed dresser against sucking pests of cotton. Pestology 25:13–18