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A Comparative Study on the Persistence of Imidacloprid and Beta-Cyfluthrin in Vegetables

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Abstract In an effort to compare the persistence of imidacloprid and beta-cyfluthrin, when applied through a ready mix formulation, Solomon 300 OD @ 200 and 400 mL ha^{-1} in the fruits of brinjal, tomato and okra, the present study has been made. The study indicated that the dissipation of these insecticides irrespective of fruits followed concentration dependent first order kinetics. The degradation constant and half live value of beta-cyfluthrin varies between −0.287 and −0.642 day^{-1} and 1.07 and 2.41 days while that of imidacloprid between −0.21 and −0.34 day^{-1} and 1.98 and 3.30 days respectively suggesting that the persistence of beta-cyfluthrin is lower than that of imidacloprid in fruits of these vegetables. Moreover, the persistence of these insecticides when compared between different fruits, it is highest in brinjal followed by tomato and least in okra, a probable clue of which has been proposed based on the non-enzymatic antioxidant content of the fruits.

Keywords β-Cyfluthrin · Imidacloprid · Tomato · Brinjal · Okra

In recent years there is overwhelming evidence to indicate that consumption of fruits and vegetables, lowers the incidence of several non-communicable diseases including cancer, cardio- and neuro-vascular disorders (Ames et al.1993; Kris-Etherton et al. 2002) because of their antioxidative potential (Kaur and Kapoor 2001). India is the second largest producer of vegetables in the world (Lal and Pandey 2011) and West Bengal ranks first in vegetables production among the states of India. Hot and humid climate leads to a substantial loss in vegetables production in the country. However, this loss has declined to 17.5 % from 23.3 % in post green revolution era due to technological changes in the area of insecticide use pattern (Dhaliwal et al. 2010). As a result of such technological changes, Solomon 300 OD, a ready mix formulation containing 9 % beta-cyfluthrin and 21 % imidacloprid has been recommended for use in brinjal, tomato and okra to control jassids, aphids, whiteflies and fruit and shoot borer, prevalent during the vegetative and reproductive stages of these vegetables. There are some reports on the persistence of these insecticides in brinjal (Mandal et al. 2010), mango (Mohapatra et al. 2011), tomato (Romeh et al. 2009), tea (Gupta et al. 2008) and chick and pigeon pea (Mukherjee et al. 2007). However, the data relating to persistence behavior of this two insecticides and their safety evaluation under West Bengal agro-climatic condition in fruits of brinjal, tomato and okra appear to be scanty. In the light of background information, a comparative study on the persistence of imidacloprid and beta-cyfluthrin in fruits of these three vegetables and a probable clue in determining their persistence behavior has been made.

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Materials and Methods

Analytical standards of imidacloprid and beta-cyfluthrin with 98.6 % and 98.8 % purity respectively as well as their ready mix formulation Solomon 300 OD containing 9 % beta-cyfluthrin and 21 % imidacloprid were supplied by M/S Bayer Crop Science Ltd., Mumbai. All the chemicals were of analytical grade and the solvents were glass distilled before use. The field studies were conducted at the experimental farm of the University during the rabi season, 2008–2009. Each of the three vegetables, grown in an area of 100 sq.m in a randomized block design with three replication, was sprayed with Solomon 300 OD @ 200 and 400 mL ha^{-1} which corresponds to 42 and 84 g of imidacloprid and 18 and 36 g of beta-cyfluthrin, at the 50 % fruiting stage followed by another two application at 7 days interval. About 1 kg fruit from each of the treated plots as well as from untreated control collected at 0, 1, 3, 5, 7, 10 and 15 days after final application, were processed for residue analysis of each of these insecticides.

For the extraction of insecticides, fruit samples were homogenized at 2,000 rpm (10 min) in a Robot Coupe Blixer. Homogenized sample (10 g) taken in a 50 mL centrifuge tube and following dispense with 10 mL each of acetonitrile and ethylacetate separately for imidacloprid and beta-cyfluthrin respectively, was again homogenized at 13,000 rpm in a Silent Crusher. The homogenate after addition of 4 g magnesium sulfate and 1 g sodium chloride was vortexed for 5 min in a rotospin and then centrifuged at 10,000 rpm for 10 min. The supernatant (1 mL) was subjected to dispersive solid phase cleanup (dSPE) with the addition of 50 mg primary secondary amine (PSA) and 150 mg anhydrous magnesium sulfate. The mixture was vortexes for a min. and then centrifuged at 5,000 rpm for 5 min for beta-cyfluthrin. In case of imidacloprid, 2 mL of the extract, after evaporated to dryness using nitrogen, was made to 1 mL with acetonitrile and dispersive SPE clean up was done by adding 50 mg PSA and 150 mg anhydrous magnesium sulfate. It was vortexes and centrifuged at 5,000 rpm for 1 min. The supernatant obtained in each case, was subjected to analysis for beta-cyfluthrin and imidacloprid using GC and HPLC respectively.

Imidacloprid residue was measured by a HPLC (Agilent 1200) equipped with BDS Hypersil column (RP-18, 25 cm × 0.46 mm i.d., 5 µm) and UV detector set at 275 nm. The aqueous solution of 30 % acetonitrile was used as mobile phase for samples of tomato and okra and that of 20 % in case of brinjal at a flow rate of 1 mL min^{-1} which resulted retention times of 7.33 and 9.203 min, respectively. The beta-cyfluthrin residue was analyzed by GC (Agilent, HP 6890A) mounted with ECD and capillary column (BPX-608, 25 m × 0.32 mm × 0.40 µm) at a column temperature of 270°C held for 20 min followed by post run at 280°C for 5 min while the detector and injector temperatures were set at 300 and 275°C respectively. The retention time was recorded as 16.268 min.

Results and Discussion

The validity of the method (Anastassiades et al. 2003) for the determination of imidacloprid and beta-cyfluthrin residues, employed in the present study, is checked by fortifying each of these insecticides separately in the respective fruit extracts of vegetables at levels of 0.01, 0.05 and 0.10 mg kg^{-1} corresponding to 1, 5 and 10 times of Limit of Quantification (LOQ). The LOD found to be 0.005 mg kg^{-1}. The overall mean recovery of imidacloprid varies between 87 % and 95 % with the increasing order of okra > brinjal > tomato while that of beta-cyfluthrin between 91 % in brinjal and okra and 95 % in tomato. The trends relating to residues in different fruits following application of imidacloprid @ 42 and 84 g ai. ha^{-1} and beta-cyfluthrin @ 18 and 36 g a.i. ha^{-1} is shown in Figs. 1 and 2, respectively. No residues of imidacloprid and beta-cyfluthrin were detected in any analyzed

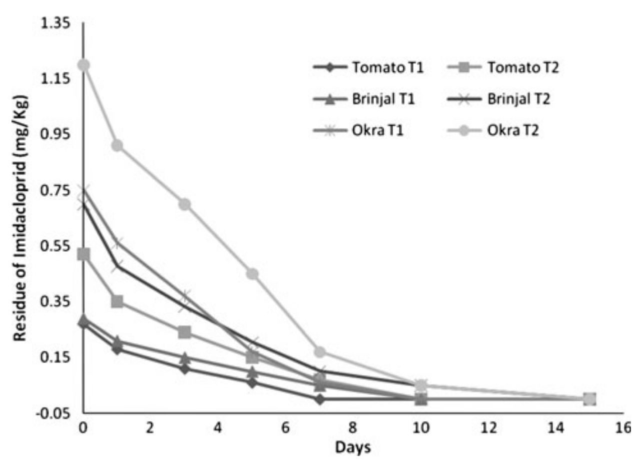

Fig. 1 Persistence and dissipation of imidacloprid in tomato, brinjal and okra fruit after application @ 42 (T1) and 84 (T2) g. ai. ha^{-1}

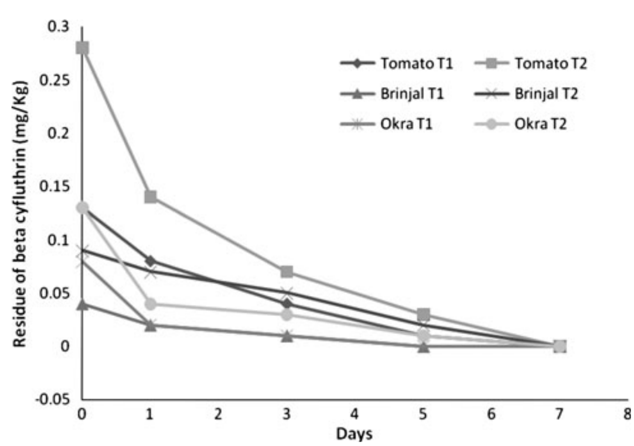

Fig. 2 Persistence and dissipation of beta-cyfluthrin in tomato, brinjal and okra fruit after application @ 18 (T1) and 36 (T2) g. ai. ha^{-1}

Table 1 Degradation dynamics parameters of beta-cyfluthrin and imidacloprid in tomato, brinjal and okra

Pesticide	Substrate	Dose	Regression equation	Determination coefficient (R^2)	Correlation coefficient (r)	Degradation constant (day^{-1})	Half life t½ (days)
β-Cyfluthrin	Brinjal	T1	$y = -0.193x + 1.559$	0.964	−0.90783	−0.444	1.56
		T2	$y = -0.125x + 1.982$	0.949	−0.99587	−0.288	2.41
	Tomato	T1	$y = -0.215x + 2.140$	0.976	−0.94845	−0.495	1.40
		T2	$y = -0.186x + 2.397$	0.986	−0.91149	−0.428	1.61
	Okra	T1	$y = -0.279x + 1.774$	0.862	−0.78783	−0.642	1.07
		T2	$y = -0.196x + 1.990$	0.907	−0.83127	−0.451	1.54
Imidacloprid	Brinjal	T1	$y = -0.091x + 2.448$	0.981	−0.91223	−0.210	3.30
		T2	$y = -0.114x + 2.836$	0.993	−0.89411	−0.262	2.64
	Tomato	T1	$y = -0.126x + 2.411$	0.994	−0.84461	−0.290	2.38
		T2	$y = -0.116x + 2.706$	0.983	−0.88866	−0.267	2.59
	Okra	T1	$y = -0.152x + 2.926$	0.969	−0.87647	−0.350	1.98
		T2	$y = -0.135x + 3.164$	0.956	−0.92021	−0.311	2.23

control fruit samples. The initial deposit of imidacloprid and beta-cyfluthrin, dependent on dosage applied, varies between 0.27 and 1.20 mg kg^{-1} with the increasing order in okra > brinjal > tomato and 0.04 and 0.28 mg kg^{-1} with the highest amount in tomato followed by okra and brinjal respectively. The comparison of initial deposits obtained in the present study with earlier reports (Mohapatra et al. 2011; Mandal et al. 2010; Mukherjee et al. 2007; Gupta et al. 2008) is made difficult by the differences in rates of application as well as vegetables concerned. The difference in rank order of initial deposit with respect to fruits and insecticides is probably related to differences in interaction between insecticide and fruits as determined by nature of the chemical and surface properties of fruit cuticle (Bates 1990). The residues of imidacloprid and beta-cyfluthrin dissipated following concentration dependent first order kinetics with greater degradation constant for beta-cyfluthrin, varying from −0.287 to −0.642 day^{-1} than imidacloprid, from −0.21 to −0.34 day^{-1} (Table 1) and reached below detectable level within 7–10 and 5–7 days respectively after final application. Accordingly, the half live of beta-cyfluthrin, varying between 1.07 and 2.41 days irrespective of fruits, is lower as compared to imidacloprid (1.98–3.30 days), which seem to be related to greater photolability of the former (Spurlock and Lee 2008). The half live of imidacloprid in brinjal recorded as 3.30 and 2.64 days at lower and higher doses, agrees well with the report of Mandal et al. (2010). The dissipation pattern of imidacloprid and beta-cyfluthrin when compared to different fruits under study produced a similar rank order with greater persistence in brinjal followed by tomato and okra. As the vegetables are grown simultaneously under same environmental condition, the physical factors affecting persistence of these chemicals in different fruits appear to be same. The difference in persistence of either imidacloprid or beta-cyfluthrin with respect to different fruits provides a probable clue to the involvement of non-enzymatic antioxidants rather than enzyme mediated reactions that pesticides undergo in plants which is in well agreement that persistence are enhanced by the presence of antioxidants as reported by Pico and Kozmutza (2007). As with abiotic stress, pesticides exert oxidative stress in plants (El-Gendy et al. 2010), in spite of having enzymatic antioxidants, leading to the generation of active oxygen species (AOS) at elevated rates. These radical species, because of their greater positive reduction potential than oxygen, either oxidize the foreign chemical viz. pesticides or reduced by non-enzymatic antioxidants. Among the fruits examined in the present study, brinjal possess highest contents of non-enzymatic antioxidants followed by tomato and okra as shown by their in vitro antioxidant activity (Ali et al. 2011). Thus AOS, generated as a result of pesticide stress are scavenged in the increasing order of brinjal > tomato > okra. Consequently, the pesticides undergo oxidation more readily in okra followed by tomato and brinjal leading to observed rank order in persistence of these chemicals.

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