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Behavior of Beta Cyfluthrin and Imidacloprid in/on Mango (*Mangifera indica L.*)

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Abstract Residue persistence of beta cyfluthrin and imidacloprid on mango was carried out after giving spray application of the combination formulation, beta cyfluthrin 9% + imidacloprid 21% (Solomon 300 OD) 3 times at the fruit formation stage. The treatments were, untreated control, standard dose of 75 g a.i. ha^{-1} and double dose of 150 g a.i. ha^{-1}. Initial residues of beta cyfluthrin on mango fruits were 0.04 and 0.12 mg kg^{-1} from treatments at the standard and double doses, respectively. The residues dissipated with the half-life of 2.4 and 2.6 days and persisted for 5 days only. Initial residues of imidacloprid on mango fruits were 0.14 and 0.18 mg kg^{-1} from treatments at the standard and double doses, respectively. Imidacloprid residues degraded with the half-life of 3.06 and 4.16 days, respectively and persisted for 10 days. Mature mango fruits at harvest were free from residues of both insecticides. A safe pre-harvest interval of 8 days is recommended for consumption of mango fruits after treatment of the combination formulation.

Keywords Beta cyfluthrin · Half-life · Imidacloprid · Mango · Pre-harvest interval

Mango (*Mangifera indica L.*), the king of the fruits is the most important, delicious tropical seasonal fruit of India. Various insects and diseases infest mango trees during all season, especially during flowering. Of all the mango pests, mango hopper, *Idioscopus niveosparsus* (Leth.) is considered the most serious and widespread pest throughout the country and it significantly reduces the fruit yield by 25–60% (Anonymous 2008). *Idioscopus clypealis* Lethierry, *Idioscopus nitidulus* (Walker) and *Amritodus atkinsoni* Lethierry are the most common and destructive species of hoppers which cause heavy damage to mango crop (Anonymous 2006). Beta cyfluthrin, cyano (4-fluoro-3-phenoxyphenyl) methyl-3-(2, 2-dichloroethenyl)-2, 2-dimethyl-cyclopropane carboxylate, is an enriched isomeric form of the two biologically active diastereoisomeric pairs of isomers of cyfluthrin. It belongs to the fourth generation synthetic pyrethroid and has a broad spectrum of activity against numerous species of insects in particular lepidopterous insects (Kumari et al. 2008). Formulations containing beta cyfluthrin alone or co-formulated with other compounds, are registered for use on a wide variety of crops including mango in over 50 countries (Anonymous 2007).

Imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine), a neonicotinoid, is one of the most widely used insecticides in the world. It is applied as seed treatment, soil drench, foliar spray, and as tree injection to a large variety of crop and non-crop plants. Imidacloprid was found to be more effective in controlling mango hoppers, *Amritodus atkinsoni* and *Idioscopus* spp. compared to the conventional insecticides like endosulfan, malathion, carbaryl, cypermethrin and azadirachtin. (Indumathi and Savithri 2003). Imidacloprid is effective at all doses tested including the lowest dose of 0.2 mL L^{-1} in controlling mango hopper (Verghese 2000). Samanta et al. (2009) have conducted study on the efficacy of imidacloprid to control of mango hoppers *Amritodus atkinsoni* Leth., *Idioscopusclypealis* Leth and *I. neveasparsus.* Imidacloprid controlled hoppers effectively and increased

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the yield significantly. The combination product of beta cyfluthrin (9%) along with imidacloprid (21%) is introduced in India by Bayer Crop Science Ltd as Solomon 300 OD and recommended for use against mango hopper. However, to our knowledge no information is available on the residue persistence of beta cyfluthrin and imidacloprid on mango, under semi arid tropical climatic condition of India. This study was therefore conducted to evaluate the residue persistence of beta cyfluthrin and imidacloprid on mango following the foliar application of the combination product.

Materials and Methods

Beta cyfluthrin (93% purity), imidacloprid (98.6% purity) and its combination formulation Solomon 300 OD was obtained from Bayer Crop Science Limited, India. Standard solution of beta cyfluthrin was prepared with acetone; imidacloprid was prepared with gradient HPLC grade acetonitrile and suitably diluted to obtain the working standards. All reagents and solvents used were of analytical and gradient HPLC grade.

Residue study of beta cyfluthrin and imidacloprid on mango was carried out at the experimental farm of Indian Institute of Horticultural Research, Bangalore, India during February–June 2009 on mango variety, Totapuri. For every treatment 10 trees were selected. The spray volume taken was 1,000 L ha^{-1}. The treatments were untreated control, recommended dose, 75 g a.i. ha^{-1} (beta cyfluthrin 22.5 + imidacloprid 52.5 g a.i. ha^{-1}) and double dose, 150 g a.i. ha^{-1} (beta cyfluthrin 45.0 + imidacloprid 105 g a.i. ha^{-1}) of the combination formulation Solomon 300 OD. Untreated control trees were sprayed with water. The first spray application was given at the fruit development stage, further 2 sprays were given at 10 day intervals using triple action/hollow cone nozzle sprayer. After the third spray, residue analysis of beta cyfluthrin and imidacloprid was carried out on 0 (1 h), 1, 3, 5, 7, 10, 15, 20, 25, 30 days and at harvest (60 days after last spray).

Mango fruit samples, 500 g approximately from each tree was harvested, pooled together and brought to the laboratory for processing. From each treatment 5 kg mango samples were collected. The mango fruits were cut into small pieces, mixed in a Waring blender and a representative 50 g sample (3 replicates) was processed for analysis of beta cyfluthrin and imidacloprid separately. At the time of harvest matured mango fruits (whole fruit) and pulp (after peeling of the fruits) were analysed. At harvest soil samples were collected from 3 × 3 grid and 30 cm depth with a total 10 sampling sites. Soil samples were mixed thoroughly, air dried and passed through 2 mm sieve. A representative 100 g sample in triplicates was processed for residue analysis of beta cyfluthrin and imidacloprid separately.

Extraction and clean up of beta cyfluthrin residues in mango fruits was carried out in the following manner. A 50 g portion of mango representative sample was homogenized with 100 mL acetonitrile in a Waring blender and filtered under vacuum through a Buchner funnel. The container and the filter cakes were washed twice with 50 mL acetonitrile and the combined extracts were collected in a 500 mL flask. The acetonitrile fraction was concentrated under reduced pressure in a rotary vacuum evaporator. The aqueous extract was transferred into a 1 L separatory funnel and diluted with 80 mL of distilled water. The aqueous phase was partitioned thrice with 50 mL hexane after adding 25 mL saturated sodium chloride solution and dried over anhydrous sodium sulphate. The combined hexane fraction was concentrated to 5 mL and subjected to column chromatography. The column was packed with 7 g of florisil in between 1 inch layer of sodium sulphate. Beta cyfluthrin residues were eluted with 100 mL of 5 + 5 (v v^{-1}) hexane:acetone, concentrated to dryness and redissolved in 5 mL of n-hexane for analysis by gas liquid chromatography (GLC). A represantative 100 g soil sample in triplicate was taken and processed in a similar manner without column cleanup.

A gas chromatogram (Shimadzu GC-2010) equipped with an electron capture detector (ECD) was used for analysis of beta cyfluthrin residues in mango and soil. One milliliter sample was injected with an auto sampler (AOC-20i auto injector). A capillary column, Agilent DB-5 (30 m × 0.25 mm i.d.) was used and the injector was kept in split mode with split ratio of 5. Ultra pure nitrogen was used as carrier gas at a flow rate of 1.0 mL min^{-1}. The oven temperature was initially maintained at 140°C with hold time of 5 min and programmed at 4°C min^{-1} to 250°C with hold time of 5 min and at 10°C min^{-1} to 280°C with hold time of 10 min. Injector and detector temperatures were maintained at 280 and 300°C. Under the above conditions retention times of isomers of beta cyfluthrin were 35.09 and 35.2 min. The chromatogram of untreated control, pure standard, spiked, field sample and harvest sample of mango are given (Fig. 1). The residue data was subjected to statistical analysis according to Hoskins (1961) to compute the residual half-life ($t_{1/2}$) and pre-harvest interval.

Extraction and clean up of imidacloprid residues in mango fruits was carried out in the following manner. A 50 g portion of mango representative sample was homogenized with 100 mL acetonitrile in a Waring blender and filtered under vacuum through a Buchner funnel. The container and the filter cakes were washed twice with 50 mL acetonitrile and the combined extracts were collected in a 500 mL flask.

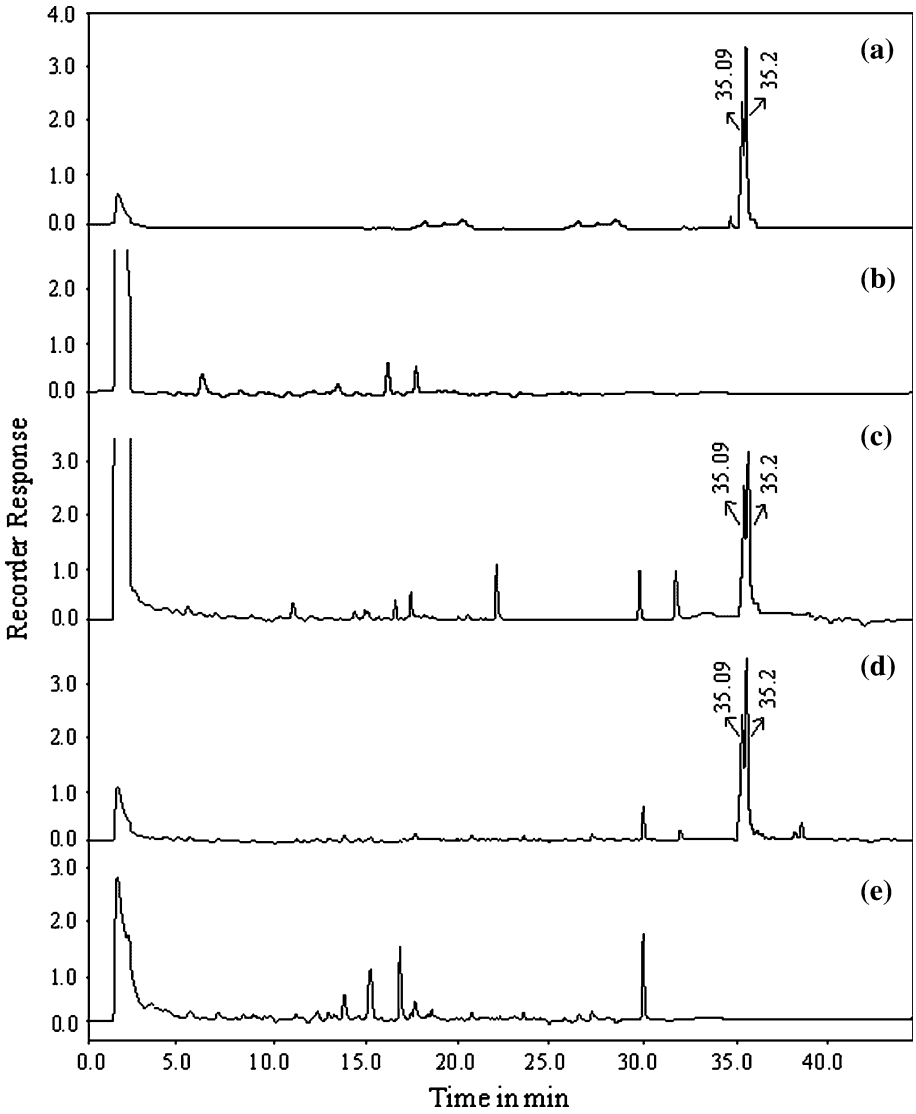

Fig. 1 GLC chromatogram of mango whole fruit, **a** pure standard of beta cyfluthrin; **b** untreated control; **c** spiked with beta cyfluthrin; **d** field sample after spray; **e** sample at harvest

The acetonitrile fraction was concentrated under reduced pressure in a rotary vacuum evaporator. The aqueous extract was transferred into a 1 L separatory funnel and diluted with 80 mL of distilled water. The aqueous phase was partitioned thrice with 50 mL 5 + 5 (v v^{-1}) mixture of hexane:ethyl acetate after adding 25 mL saturated sodium chloride solution. The combined solvent fraction was dried over anhydrous sodium sulphate, concentrated to 5 mL and subjected to column chromatography. The column was packed with 5 g of florisil in between 1 inch layer of sodium sulphate. Imidacloprid residues were eluted with 100 mL of gradient HPLC grade acetonitrile. The elute was concentrated to 5 mL and analyzed by high pressure liquid chromatography (HPLC). A represantative 100 g soil samples in triplicate was taken and processed in a similar manner without column cleanup.

Analysis of the imidacloprid residues in mango was carried out with Shimadzu HPLC Prominence LC 20 AT with a photo diode array (PDA) detector at wavelength of 270 nm. The column used was MERCK, Lichrosphere, RP-18 (250–4 mm i.d. S.S., 5 μm). The residues of imidacloprid were estimated using a mobile phase of acetonitrile:water (40:60, v v^{-1}) with a flow rate of 1 mL min^{-1} and injection volume of 20 μL. With these operating parameters the retention time of imidacloprid was 5.06 min. The chromatogram of untreated control, pure standard, spiked, field sample and harvest sample of mango are given in Fig. 2. The residue data was subjected to statistical analysis according to Hoskins (1961) to compute the residual half-life ($t_{1/2}$) and pre-harvest interval. Recovery studies were carried out in order to establish the reliability of the analytical method for the present study by spiking mango whole fruit, pulp and soil with beta cyfluthrin and imidacloprid @ 0.01, 0.1, 0.5 and 1.0 mg kg^{-1}. The spiked samples in 5 replications were processed as per methodology described above for both the insecticides.

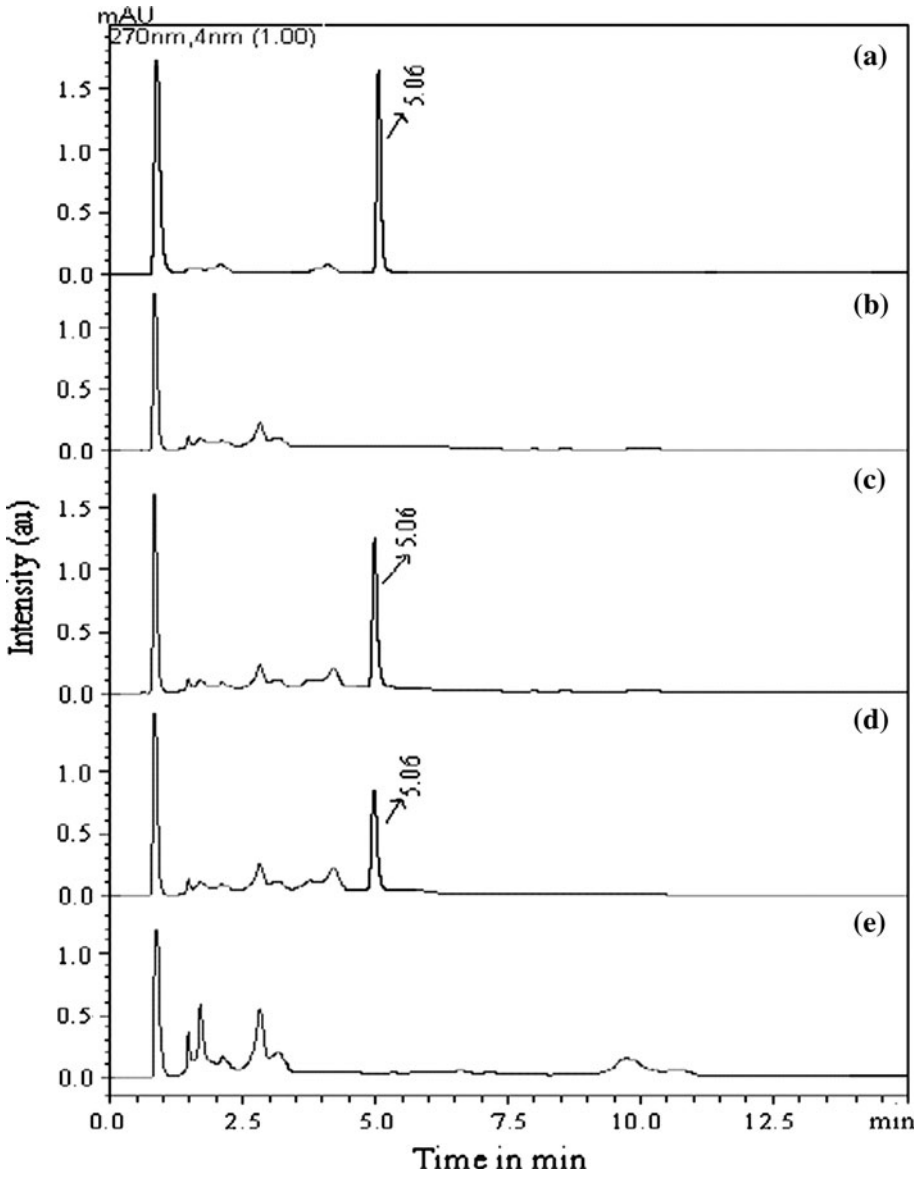

Fig. 2 HPLC chromatogram of mango whole fruit, **a** pure standard of imidacloprid; **b** untreated control; **c** spiked with imidacloprid; **d** field sample after spray; **e** sample at harvest

Results and Discussion

Recovery study of beta cyfluthrin showed that the recovery in mango whole fruit was in the range of 89.22–91.54%, in pulp 88.35–91.5% and in soil 90.32–91.44%. In mango whole fruit the recovery of imidacloprid was in the range of 83.55–85.74%, in pulp 84.68–86.37% and in soil 89.56–90.24% (Table 1). The limit of quantification of the method was 0.01 mg kg^{-1} for both the insecticides.

Residues of beta cyfluthrin were evaluated in/on mango fruits after giving spray application of the combination formulation beta cyfluthrin 9% + imidacloprid 21% (Solomon 300 OD). Initial residues of beta cyfluthrin on mango fruits were 0.044 and 0.122 mg kg^{-1} from treatment at 22.5 and 45 g $a.i^{-1}$, respectively (Table 2). The residues persisted up to 5 days only from both the treatments and dissipated at the half-life of 2.44 and 2.64 days, respectively. The maximum residue limit (MRL) of beta cyfluthrin on mango is fixed at 0.02 mg kg^{-1} by all mango importing countries from India. Based on this value and the persistence study, the safe pre-harvest interval (PHI) for consumption of mango fruits is recommended as 2.5 and 7.0 days, respectively. Beta cyfluthrin residues in mature/ripe mango fruits harvested 60 days after spray application was below the quantifiable limit of 0.01 mg kg^{-1}. Soil collected from mango field (under the canopy) was also free from beta cyfluthrin residues (Table 2).

Initial residues of imidacloprid in mango fruits were 0.143 and 0.182 mg kg^{-1} from treatment at the recommended and double the recommended doses of 52.5 and 105 g a.i. ha^{-1}, respectively. Dissipation of imidacloprid residues from mango fruits was gradual and the residues

Table 1 Recovery study of beta cyfluthrin and imidacloprid residues on mango and soil at various spiking levels

Level of spiking (mg kg^{-1})	Average residue recovered (%) ± SD					
	Beta cyfluthrin			Imidacloprid		
	Mango whole fruit	Mango pulp	Soil	Mango whole fruit	Mango pulp	Soil
0.01	89.22 ± 3.54	88.35 ± 4.63	90.32 ± 4.61	83.55 ± 2.65	84.68 ± 3.74	89.56 ± 1.68
0.10	90.72 ± 4.67	90.34 ± 3.86	90.88 ± 3.76	84.31 ± 3.15	85.23 ± 4.85	88.32 ± 3.54
0.50	90.48 ± 5.83	89.42 ± 5.83	91.04 ± 4.81	85.68 ± 4.52	86.08 ± 2.66	89.71 ± 4.02
1.00	91.54 ± 4.76	91.51 ± 4.76	91.44 ± 3.84	85.74 ± 2.85	86.37 ± 1.95	90.24 ± 3.62

Average of five replicate analyses

Table 2 Residues of beta cyfluthrin and imidacloprid in/on mango fruit and soil

Days after treatment	Untreated control	Average residue recovered (mg kg^{-1}) ± SD			
		Beta cyfluthrin @ 22.5 g a.i. ha^{-1}	Beta cyfluthrin @ 45.0 g a.i. ha^{-1}	Imidacloprid @ 52.5 g a.i. ha^{-1}	Imidacloprid @ 105 g a.i. ha^{-1}
0	BDL	0.044 ± 0.002	0.122 ± 0.005	0.143 ± 0.005	0.182 ± 0.007
1	BDL	0.030 ± 0.003	0.088 ± 0.004	0.122 ± 0.004	0.158 ± 0.007
3	BDL	0.014 ± 0.001	0.044 ± 0.004	0.098 ± 0.004	0.121 ± 0.004
5	BDL	0.011 ± 0.001	0.034 ± 0.002	0.049 ± 0.003	0.093 ± 0.005
7	BDL	BDL	BDL	0.030 ± 0.003	0.064 ± 0.004
10	BDL	BDL	BDL	BDL	0.033 ± 0.004
Mature mango fruit at harvest	BDL	BDL	BDL	BDL	BDL
Mango pulp at harvest	BDL	BDL	BDL	BDL	BDL
Soil at harvest	BDL	BDL	BDL	BDL	BDL

Average of three replicate analyses, *BDL* below detectable limit <0.01 mg kg^{-1}

persisted up to 7 and 10 days, respectively. The residues dissipated at the half-life of 3.06 and 4.16 days from the treatment at 52.5 and 105 g a.i. ha^{-1}, respectively. Initial residue deposits of imidacloprid from the above treatments did not exceed the MRL value of 0.2 mg kg^{-1} prescribed by Codex. But European Union has fixed MRL of imidacloprid at 0.05 mg kg^{-1} for importing mango from India. Based on this value the pre-harvest interval recommended is 5.0 and 8.0 days, for treatment at the recommended and double the recommended doses, respectively. At harvest i.e. 60 days after the last spray, imidacloprid residues from both the treatments were below the quantifiable limit of 0.01 mg kg^{-1} in mature/ripe mango fruit and pulp (Table 2). The soil samples collected from field at the time of harvest were found to be free from imidacloprid residues.

A study conducted in Philippines showed that when EC formulation of beta cyfluthrin was applied @ 1.6-10 g a.i. h L^{-1}, its residue levels remained in the range of 0.02–0.09 mg kg^{-1}. When beta cyfluthrin was used in combination with imidacloprid @ 18–50 g a.i. ha^{-1} on mango, a pre-harvest interval (PHI) of 14 days was recommended (Anonymous 2007). Mandal et al. (2010) have studied the residue persistence of combination formulation of beta cyfluthrin 9% and imidacloprid 21% (Solomon 300 OD) on brinjal. Residues of beta cyfluthrin and imidacloprid remained on brinjal for 3 and 7 days, respectively. Beta cyfluthrin and imidacloprid dissipated at the half-life of about 2 days when applied to tomato crop @ 18.75 and 20 g a.i. ha^{-1} (Dikshit et al. 2003). When imidacloprid treated mangoes were analyzed at harvest, the residues detected in non-integrated pest management (IPM) samples of mango were found to be below the prescribed limits of maximum residue limit (MRL) while IPM samples were free from pesticide residues (Singh et al. 2008). In the present study, slight longer persistence of both the insecticides on mango may be due to the slow growing nature of mango fruits compared to brinjal and tomato. From the results obtained a safe pre-harvest interval of 8 days is recommended for consumption of mango fruits after treatment of the combination formulation of beta cyfluthrin and imidacloprid (Solomon 300 OD). The mature mango fruits were free from both the insecticides at the time of harvest. So based on this study mango fruits treated with combination formulation of beta cyfluthrin and imidacloprid can be consumed safely after a pre-harvest interval of 8 days.

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