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Persistence behaviour of deltamethrin on tea and its transfer from processed tea to infusion

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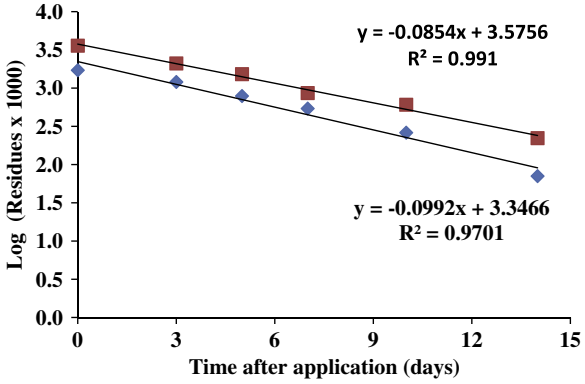
HIGHLIGHTS

- The residues of deltamethrin persisted up to 14 d.
- The $t_{1/2}$ of deltamethrin deposits was between 3.04 and 3.54 d.
- Deltamethrin residues not transferred into the tea infusion.
- The LOD and LOQ were found to be 0.015 and 0.05 mg kg^{-1}, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

The dynamics and residues of deltamethrin in a tea grown in an open field ecosystem were investigated. The quantification was performed using gas chromatography–electron capture detection (GC–ECD) and confirmed by gas chromatograph–mass spectrometry (GC–MS) in selective ion monitoring (SIM) mode. The method was validated using blank samples spiked at three levels and the results showed that recoveries ranged from 87% to 101% with relative standard deviations (RSD) ranging of 0.7–7.1%. The residues of deltamethrin were found to dissipate following first order kinetics with half-life ranging between 3.04 and 3.54 d for two different rates of foliar application. The deltamethrin residues are present in the processed tea are not transferred into the tea infusion during the infusion process, since their water solubility is extremely low. These results can be utilized in formulating the spray schedule and safety evaluation on deltamethrin tea crop.

1. Introduction

Tea (*Camellia sinensis* L.) is an important cash crop in India due to its tremendous export potentialities and known as queen of beverages (Banerjee et al., 2010). It is the healthiest drinks and second most consumed beverage after water (Biswas et al., 2007). India is the largest producer of processed tea and about 20% of its production is exported (Seenivasan and Muraleedharan, 2009). The tea crop is susceptible to a wide range of insects and mite pests, which cause crop loss as well as deterioration in the quality of the processed tea and is often treated with chemical pesticides to manage these problems. Synthetic pyrethroids display a broad spectrum of insecticidal activity coupled with low mammalian toxicity and they have comparatively low application rates, making them environmentally more acceptable than the older, more persistent and toxic organochlorine and organophosphorous insecticides (Seenivasan and Muraleedharan, 2009).

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Deltamethrin, {(S)-α-cyano-3-phenoxybenzyl (1R, 3R)-3-(2-2-dibromovinyl)-2-2-dimethyl cyclopropane carboxylate}, a pyrethroid insecticide, is used for the control of lepidopterous pests on various crops (Hirano, 1989). It kills insects on contact and through ingestion by disrupting their nervous system and is effective against both sucking and chewing insects and has been widely used to control pests of various crops (Mueller-Beilschmidt, 1990). It is stable to light, heat and air, but unstable in alkaline media, and non persistent, highly soluble in organic solvents but almost insoluble in water (Mestres and Mestres, 1992). In recent years, a number of research works have dealt with the behaviour of bifenthrin (Tewary et al., 2005), fenvalerate (Sharma et al., 2008), lambda cyhalothrin (Seenivasan and Muraleedharan, 2009; Chen et al., 2010), spiromesifen (Sharma et al., 2007), fenazaquin (Kumar et al., 2006), abamectin (Pal et al., 2006), imidacloprid (Sanyal et al., 2006; Gupta et al., 2008), acetamiprid (Gupta and Shanker, 2008), imidacloprid and acetamiprid (Gupta and Shanker, 2009), thiacloprid (Dubey et al., 2008; Paramasivam et al., 2012), propineb (Banerjee et al., 2010) clothianidin (Chowdhury et al., 2012), and milbemectin (Pal et al., 2012) pesticides in tea, the influence of various processes on their residues in the processed tea, and their fate from processed tea to infusion. Residue levels of many pesticides in processed tea and its infusion have also been reported (Jaggi et al., 2001; Kumar et al., 2004; Manikandan et al., 2009). To the best of our knowledge, no work has been published on the dissipation of deltamethrin residues in tea, its transfer from processed tea to infusion and its retention in spent tea leaves.

As tea are considerable foreign exchange earners for India, it is essential to assess the impact of use of deltamethrin from the residues point of view, for the safety of consumers and to meet the food regulations of countries importing these products. The present study reports the dissipation behaviour of deltamethrin in tea grown in an open field ecosystem and there by provides an estimate of the application harvesting interval required for the safe use of deltamethrin in tea.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standard of deltamethrin (98.5% purity) and formulation (Decis Forte 10 EC) were obtained from M/s Bayer Crop Science Limited, Mumbai, India. Primary secondary amine (PSA- Bondesil, 40 μm,) was purchased from Agilent Technologies (USA). Ethyl acetate and hexane were of HPLC (high performance liquid chromatography) grade were purchased from Merck (Mumbai, India). Sodium chloride and anhydrous magnesium sulfate were of analytical grade, purchased from Merck. Anhydrous magnesium sulfate was activated by heating at 400 °C in muffle furnace for 6 h before use and kept in desiccators.

2.2. Preparation of standard solutions

The stock solution, 1000 mg L^{-1} was prepared by dissolving 25.4 mg standard in 25 mL hexane. An intermediate standard solution of 100 mg L^{-1} was prepared by diluting 2.5 mL of the stock solution with hexane in a 25 mL volumetric flask. From this intermediate standard solution, working standard solutions were obtained by diluting the stock solution with hexane. All standard solutions were stored at −4 °C before use.

2.3. Determination of deltamethrin residue

The determination of deltamethrin was carried out by gas chromatography (Shimadzu 2010) coupled with an electron capture detector (ECD). The chromatographic separations were performed with a fused silica DB-5 (30 m × 0.25 mm i.d. × 0.25 μm) capillary column (J & W, Agilent Technologies, USA). The detector and injector temperature was maintained at 300, and 250 °C, respectively and oven temperature programmed as follows; 160 °C for 1 min, increased at 15 °C min^{-1} to 200 °C and hold for 2 min and finally increased to 280 °C at 10 °C min^{-1}, hold for 8 min. Ultra high purity nitrogen was used as carrier gas at a constant flow rate of 2 mL min^{-1}. The sample and standards were injected in a split mode with split ratio 1:10 with an auto sampler (Shimadzu AOC 20 s) and an auto injector (Shimadzu AOC 20i). The retention time of deltamethrin was 17.83 min at the above conditions.

The identities of residues in treated samples were confirmed by gas chromatograph-mass spectrometry (Shimadzu GCMS-2010 QP plus) in selective ion monitoring (SIM) mode. The injector, ion source and interface temperature was maintained at 250, 200 and 250 °C, respectively. The GC separations were performed with a fused silica DB-1(30 m × 0.25 mm i.d. × 0.25 μm) capillary column (J & W, Agilent Technologies, USA). The ultra high purity helium was used as carrier gas at a constant flow rate of 1 mL min^{-1}. Samples of 1 μL were injected with an auto sampler/injector (Shimadzu AOC 20 s/AOC 20i) at a split ratio of 1:5. The column temperature was programmed at 160 °C for 1 min, then increased at 8 °C min^{-1} to 250 °C and hold for 2 min, finally increased at 10 °C min^{-1} to 280 °C and hold for 5 min. The mass detector was of quadruple mass analyzer type and used at 70 eV for ionization and the ions m/z 253 and 182 were monitored. The solvent delay was 2 min and retention time of deltamethrin under these conditions was 18.49 min. Data were acquired with the GC–MS software (Lab Solutions, Shimadzu).

2.4. Field experiment and sampling

The open field experiment was conducted at tea garden of the Coonoor Tea Estate, Tamil Nadu, India. Plots measuring 100 sq.m, containing tea plants of TRF-1 cultivars with appropriate guard rows, were used for the study. Tea plants had been planted in double hedge, in triangular planting system at spacing of 1.05 × 0.15 × 0.6 m. The formulation, Decis Forte 10% EC was applied at 10 (recommended dose) and 20 g a.i. ha^{-1} (double the recommended dose) in separate plots at 7 d intervals at active vegetative growth stage. The insecticide was applied with hand operated knapsack sprayer, using a spray volume of 400 L ha^{-1}. Each treatment including the untreated control was replicated three times in randomized block design. Before application of insecticide to the tea garden the fresh green tea leaves were collected and analysed for the presence deltamethrin residue. It was ensured that the insecticide under investigation had not been used earlier on the experimental plots (Table 2). The average minimum and maximum temperature during the experiment were 22.9 and 31.06 °C, with average relative humidity ranging from 65% to 78% and rainfall was 27 mm. The crop was grown by following recommended package of practices.

Table 1
Recoveries and relative standard deviations for deltamethrin in green tea leaves, processed tea, tea infusion, spent tea leaves and soil at various fortification levels.

Substrates	Recovery% (RSD%) (n = 3)		
	0.05 (mg kg^{-1})	0.25 (mg kg^{-1})	0.5 (mg kg^{-1})
Green tea leaves	98.99 ± 5.64	98.86 ± 4.17	99.62 ± 3.32
Processed tea	96.64 ± 3.17	95.26 ± 3.15	97.35 ± 3.61
Tea infusion	100.24 ± 7.09	100.13 ± 4.49	87.72 ± 1.11
Spent tea leaves	89.27 ± 4.07	87.00 ± 3.38	91.24 ± 3.81
Soil	101.43 ± 4.66	98.71 ± 0.67	98.05 ± 4.12

RSD-relative standard deviation.