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Dissipation kinetics of beta-cyfluthrin and imidacloprid in tea and their transfer from processed tea to infusion

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ABSTRACT

Dissipation kinetics of mixed formulation consisting beta-cyfluthrin and imidacloprid in tea crop under an open field ecosystem was investigated. The mixed formulation was applied on tea plant at recommended (27 + 63) and double the recommended (54 + 126 g a.i./ha) dose and residues were determined using gas chromatography-electron capture detector and high performance liquid chromatography-photodiode array detector for beta-cyfluthrin and imidacloprid, respectively. The limit of quantification of analytical method was 0.05 µg/g and the average recoveries were ranged from 88.36% to 103.49% with relative standard deviations of less than 6% at three spiked levels. The experimental results showed that in the green tea leaves imidacloprid dissipated faster than beta-cyfluthrin with the half-life ranging between 1.20–1.39 and 2.89–3.15days, respectively. The beta-cyfluthrin residues present in the processed tea not transferred into the tea infusion during the infusion process and imidacloprid transferred in the range 43.12–49.7%. On the basis of the transfer of residues from processed tea to infusion, a waiting period of 17 days for tea plucking after pesticide application at recommended dose may be suggested.

1. Introduction

Tea plant (*Camellia sinensis* L.) is an economically important plantation crop grown in India due to its high export potentialities and known as a queen of beverages (Biswas et al., 2007). It is the favourite common man's drinks and most popular non-alcoholic beverage consumed globally (Banerjee et al., 2010). The dried leaves of tea are valued for its specific aroma, flavor and health promoting properties of antioxidant, antimicrobial and anticarcinogenic (Yang and Landau, 2000). India is one of the world's second largest producers of tea next to china and also largest consumer of processed tea. Despite the consumption, India is the largest exporter of tea after china to different countries (Seenivasan and Muraleedharan, 2009). The tea plant is prone to attack many insect pests and it is important that different kinds of plant protection chemicals are applied to combat these problems for high yield and economic returns often treated with synthetic pesticides (Paramasivam and Chandrasekaran, 2014). Synthetic pyrethroids are the broad spectrum activity against various agricultural crop insects and mites. It has non-toxic to mammals, low application dosage rates, making them environmentally more acceptable than the more persistent and toxic organochlorine compounds (Seenivasan and Muraleedharan, 2009).

Beta-cyfluthrin (Cyano (4-flouro-3-phenoxyphenyl) methyl 3-(2, 2-dichloroethenyl)-2, 2-dimethylcyclopropane carboxylate) belonging to synthetic pyrethroid class. It is a mixture of four diasteroisomers. The water solubility of beta-cyfluthrin is extremely low (0.002 µg/mL), higher the octanol-water partition coefficient (Log Kow: 5.9) and thermally stable at room temperature. Beta-cyfluthrin is extremely toxic to fish, other aquatic organisms and honeybees, but is moderately toxic to mammals, with LD_{50} ranged from 869 to 1271 mg/kg in rats. It is a nonsystemic synthetic pyrethroid insecticide used to control chewing and sucking insects through contact and stomach poisoning, it attacks the nervous system as well as it combines a rapid knockdown effect with long-lasting efficacy in the field. Beta-cyfluthrin used against tea mosquito bug and red spider mites are the important pests in tea crop and found to reduce the 85.40% infestation (Gurusubramanian et al., 2008). Imidacloprid, N-[1-[(6-chloro-3-pyridyl) methyl]-4, 5-dihydroimidazol-2yl] nitramide, is most frequently used neonicotinoid group of insecticide. The chemical has colourless crystals with weak characteristic odor, melting point of 144 °C, vapour pressure of 0.2 uPa (20 °C) and stability to hydrolysis at pH 5–11. It has high water solubility of 600 µg/mL, which is relatively high and low partition coefficient (3.7). Imidacloprid is an excellent broad spectrum systemic chloronicotinyl nitroquaniline insecticide with low mammalian toxicity. It has an oral LD_{50} in rats of 450 mg/kg. It is used for the management of tea mealy bug and also various sucking pests in the tea plant

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(Ignacimuthu and Jayaraj, 2003; Gupta et al., 2008). It is highly suitable for foliar and soil treatment as it is considered to be very good systemic and translaminar properties (Wamhoff and Schneider, 1999).

The synthetic chemicals applied in the tea plant foliages find their way into the fresh green tea leaves into the processed tea. The dried tea leaf (processed tea) is not consumed directly by the human being as such and it is the tea infusion or liquor which is the form actually consumed. Obliviously, tea infusion is the potential route for human exposure to synthetic pesticide residues present in the processed tea. The residue persistence, dissipation kinetics and leaching behavior of bifenthrin (Tewary et al., 2005), fenvalerate (Sharma et al., 2008), lambda cyhalothrin (Seenivasan and Muraleedharan, 2009), deltamethrin (Paramasivam and Chandrasekaran, 2014), imidacloprid (Gupta et al., 2008), acetamiprid (Gupta and Shanker, 2009) and thiacloprid (Paramasivam et al., 2012) in processed tea to infusion have been studied. Though the persistence and dissipation behavior of mixed formulation of beta-cyfluthrin and imidacloprid has been studied in different food commodities by the scientific researchers, reports on its dissipation kinetics and transfer from processed tea to infusion are lacking among the reported research work. Hence, keeping the above in mind, the present studies were carried out to study the dissipation kinetics of beta-cyfluthrin and imidacloprid on tea leaves and residue transfer from processed tea to tea infusion in real field conditions.

2. Materials and methods

2.1. Chemicals and reagents

High performance liquid chromatography grade solvents of ethyl acetate, hexane, dichloromethane and acetonitrile were purchased from Merck, Mumbai, India. Primary secondary amine (PSA, 40 μm) was obtained from Agilent Technologies, USA. Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), florisil and anhydrous magnesium sulfate ($MgSO_4$) were of analytical grade purchased from Merck, Mumbai, India. A commercial mixed formulation of Solomon 300 OD (9% beta-cyfluthrin + 21% imidacloprid) was obtained from M/s Bayer Crop Science India Limited, Mumbai, India.

2.2. Analytical standard

The technical grade standards of beta-cyfluthrin (99.8% purity) and imidacloprid (99.9% purity) were obtained from M/s Bayer Crop Science India Limited, Mumbai, India. The analytical grade beta-cyfluthrin (25 mg) was dissolved in 25 mL volumetric flask with hexane and shaken well to get a homogenous concentration of 1000 μg/mL standard stock solution. From this 2.5 mL was transferred to 25 mL volumetric flask and volume were made up with hexane to obtain an intermediate stock solution of 100 μg/mL. Working standard solutions ranging from 0.01 to 1 μg/mL were prepared by diluting the intermediate stock solution with hexane. Similarly, the stock solution imidacloprid (1000 μg/mL) was prepared in 25 mL volumetric by dissolving 25 mg of analyte in acetonitrile. The working standard solutions were prepared by diluting the standard stock solution with acetonitrile. All the standard solutions were stored at − 4 °C before and after use.

2.3. Field experiment

An open field experiment was conducted at the tea garden of the Coonoor Tea Estate, Tamil Nadu (India), to determine the residues of beta-cyfluthrin and imidacloprid in fresh green tea leaves, processed tea and their transfer to infusion. The tea plant (Variety, TRF-1) had been planted in a double hedge with a spacing of 1.05 × 0.15 × 0.6 m in a triangular planting system. The fresh green tea leaves were plucked before application of insecticide for the presence of residues of beta-cyfluthrin and imidacloprid and no residue was detected in collected tea leaves which indicate that experimental plot had no previous history of insecticide application. A mixed formulation of beta-cyfluthrin 9% and imidacloprid 21% (Solomon 300 OD) was applied at active vegetative stages of the tea plant. The treatment details as follows recommended dose (27 + 63 g a.i./ha), double the recommended dose (54 + 126 g a.i./ha) along with untreated control and three times replicated each. The insecticide mixed formulation was applied thrice at intervals of seven days with a manually operated knapsack sprayer, using spray fluid of 500 L/ha. The average minimum and maximum temperatures during the trial period were 16 and 31 °C respectively, with an average relative humidity ranged between 54 to 72% and 29 mm rainfall was received.

2.3.1. Sampling

The fresh green tea leaves (2 kg) were plucked (one bud and two leaves) at randomly from treated and untreated each replicate plots separately at an interval on 0 (2hr after the last spraying), 3, 5, 7, 10 and 14 days after spraying of insecticide mixture. The harvested tea leaves were packed in a dry ice and brought to the laboratory from the field and processed immediately for residue analysis. For processed tea residue analysis, green tea leaves (2 kg) were plucked from each plot at 7 and 14 days after the last spraying of insecticide and submitted to Coonoor Tea Estate processing unit in United Planter Association of Southern India (UPASI) to get processed tea.

2.3.2. Sample preparations

The plucked fresh leaves were chopped into small pieces, mixed thoroughly and divided into four sub-samples. The manufacturing process, in brief, the plucked fresh green tea leaves were spread in a withering trough and allowed to wither, blown underneath for 16–18 h with allowing natural air. After the expiry time withered leaves were passed through a rotor vane for crushing, mixing of green tea leaves and juice roller for 30 min with pressure, followed by fermentation at 25–30 °C for an h and relative humidity of 90–95%, finally the leaves were dried at 100 ± 5 °C in a tea dryer with hot air. After completion of manufacturing steps, 150–200 g processed tea was obtained with moisture content of 2–3%. The tea infusion or liquor was prepared by adding 5 g of processed tea in a boiling water of 150 mL. After brewing for five minutes, the infusion was filtered using stainless steel filter and allowed to reach room temperature (Paramasivam and Chandrasekaran, 2014). The spent tea leaves were spread in a folded filter paper after infusion to remove moisture and finally air dried.

2.3.2.1. Beta-cyfluthrin extraction and sample cleanup. The analytical method developed by Paramasivam and Chandrasekaran (2014) was adopted to extract and clean up residues of beta-cyfluthrin in the green tea leaves, processed tea, spent tea leaves and infusion. A representative (10 g) homogenized green tea leaves, processed tea and spent tea leaves were taken separately in a 250 mLconical flask. To this, 50 mL of ethyl acetate was added and soaked for 15 min. Then the sample was shaken for approximately 1 h by using mechanical shaker at 250 rpm. From this 20 mL of the solvent was taken into a 50 mL centrifuge tube by decanting the solution. To this anhydrous $MgSO_4$ (4 g) and NaCl (1 g) was added subsequently and vortexed for 1 min and then the sample was centrifuged (Superspin R-V/FA; Plasto Crafts, Mumbai, India) at 10,000 rpm for 10 min. About 10 mL of the supernatant solution was transferred into a small centrifuge tube and to this 100 mg of PSA and 600 mg of anhydrous $MgSO_4$ was added and mixed well by vortexing 1 min. This solution was again centrifuged at 5000 rpm for 5 min and about 5 mL of the supernatant organic solution was taken from this into a turbovap tube. This solution was evaporated to near dryness using a TurboVap LV (Caliper Life Sciences, Russelsheim, Germany) with the gentle stream of nitrogen with a bath temperature of 40 °C. Then the residue was redissolved in 1 mL of hexane and was analyzed in GC-ECD. From the prepared tea infusion, 10 mL of the aliquot was transferred to a 50 mL centrifuge tube. The residues were extracted with 20 mL of ethyl acetate and 4 g of anhydrous $MgSO_4$ and 1 g of NaCl. The cleanup