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# Persistence of thiacloprid and deltamethrin residues in tea grown at different locations of North-East India

Nitesh Sharma[a], Hemanta Banerjee[a,*], Srikumar Pal[b], K.K. Sharma[c]

[a] AINP on Pesticide Residues, BCKV, West Bengal 741235, India
[b] Department of Agricultural Biochemistry, BCKV, West Bengal 741252, India
[c] AINP on Pesticide Residues, P.C. Cell, I.A.R.I., New Delhi 110012, India

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ABSTRACT

In order to examine the residues of thiacloprid (90 and 180 g a.i./ha) and deltamethrin (10 and 20 g a.i./ha) in fresh tea leaves, made tea and tea infusion, field experiments were conducted at three different locations viz. Kamalpur tea estate, Darjeeling; West Bengal, Teok tea Estate and AAU, Jorhat; Assam in India. Regardless of location and doses, residues of both the insecticides dissipated following first order kinetics. The half-life of Thiacloprid (4.93–5.38 days) was longer than that of deltamethrin (1.78–1.94 days). Processing of green tea leaves reduced the residue level of thiacloprid and deltamethrin in made tea. No residues of both these insecticides could be detected in tea infusion. With respect to the phenolic distribution in tea, a marked increase in total catechin monomers with thiacloprid and greater accumulation of EGCG and ECG (indices of phenol quality) with deltamethrin were observed.

## 1. Introduction

Tea (*Camellia sinensis*), reputed as queen of beverages (Mukhtar & Ahmad, 2000), is consumed worldwide since 3rd century CE (https://en.wikipedia.org/wiki/History of Tea) because of its health promoting effects resulting chiefly from a number of phenolic compounds that vary from catechin monomers in green tea to that of oligomers in black tea (Anesini, Ferraro, & Filip, 2008). These compounds by virtue of their lower one electron reduction potential have been shown to exert antioxidant role both *in vivo* and *in vitro* (Bors, Heller, Michel, & Saran, 1990). India, with its share of 31% of global tea production, has emerged as world leader during the last 150 years and offers a range of tea from original orthodox to CTC (Cut, Tear and Curl) and green tea. The aroma and flavor of Darjeeling tea and strong liquor of Assam tea remain unparallel in the world. Among several biotic and abiotic factors limiting the quality and quantity of tea production (Banerjee et al., 2009; Boriah, 2006), insect pests seem to cause a substantial loss in production. Accordingly, tea, the major commercial crop in India, receives a range of insecticides to guarantee production. Of the several classes of insecticides available in the market, synthetic pyrethroids and neonicotinoids, with their high potency and favorable eco-biological profile, have been recommended for use in modern crop protection schedule (Gupta, Sharma, & Shanker, 2008). Deltamethrin [Cyano-(3-phenoxyphenyl)-methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-1-carboxylate], a synthetic pyrethroid and thiacloprid {(*Z*)-*N*-[3-(6-chloro-pyridin-3-ylmethyl)-thiazolidin-2-ylidene]-cyanamide}, a neonicotinoid, are active against numerous sucking and chewing pests including aphids, whiteflies, beetles and some Lepidoptera species (Kodaka, Kinoshita, Swakita, Kawahara, & Yasui, 1998; Tomizawa & Casida, 2005) are used by the tea growers in India. In recent times, a number of insecticides including quinalphos (Jaggi, Sood, Kumar, Ravindranath, & Shanker, 2001), dimethoate, dicofol, deltamethrin (Sood, Jaggi, Kumar, Ravundranath, & Shankar, 2004), hexaconazole (Kumar, Ravindranath, & Shanker, 2004) and imidacloprid (Gupta et al., 2008) have been examined for their residues in tea and the influence of various manufacturing processes on their residues in made tea. Moreover, as tea being subjected to infusion before consumption, residue levels of many pesticides in tea and its infusion are reported (Bhattacharyya, Chowdhury, Somchowdhury, Pahari, & Roy, 1995; Jaggi et al., 2001). However, in most cases, the residue data are region specific and may be of little relevance to other areas. Reports relating to thiacloprid and deltamethrin residues in tea, grown under North-East agro-climatic regions of India appear to be scanty. Thus, in the present study, the persistence of deltamethrin and thiacloprid in tea grown at three different locations of North-East India with varying agro-climatic situation has been compared. Green tea leaves contain a host of phenolic compounds including catechin, epigallocatechin (EGC), epigallocatechin gallate (EGCG), ethyl gallate (EG) and epicatechin gallate (ECG) and caffeine that contribute to

* Corresponding author.
*E-mail address:* hembckv@rediffmail.com (H. Banerjee).

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quality of tea. The effects of these insecticides in the profile of these phenolic compounds in tea leaves are little understood.

## 2. Materials and methods

### 2.1. Chemicals and reagents

The analytical standards of Thiacloprid and deltamethrin and their formulations Alanto 240SC and Decis 10% respectively were obtained from M/s Bayer Crop Science, Mumbai, India. Analytical standards of catechin, EG, EGC, EGCG and ECG, and caffeine were procured from Sigma Aldrich. Primary secondary amine (40 μm, Bondesil with ethylenediamine – N-propyl) was purchased from Varian (Palo Alto, CA, USA). All the chemicals and reagents used were of analytical grade. Primary stock solutions of thiacloprid and deltamethrin (999 mg/L) were prepared separately in acetonitrile and acetone respectively. The solutions of each of the Tea polyphenols and caffeine were prepared in methanol. The serial dilution techniques were followed to obtain the working standard (individual compounds and their mixture) for fortification and standardization.

### 2.2. Field experiment

To examine the persistence of thiacloprid and deltamethrin in tea, supervised field trials were conducted at three locations viz. Kamalpur Tea Estate, Darjeeling, West Bengal (L1), Teok Tea Estate, Assam (L2) and AAU, Jorhat, Assam (L3). The meteorological data of these three locations during the experimental period is presented in Supplementary Table. Thiacloprid (90 and 180 g a.i./ha i.e. 0.0225 and 0.045% spray concentration) and deltamethrin (10 and 20 g a.i./ha i.e. 0.0025 and 0.005% spray concentration) were applied separately in three replicates as their recommended field doses (RFD) and double the recommended field dose (dRFD) twice at 7 days interval to tea bushes. Water spray constitutes the untreated control. Green tea leaves were collected periodically (0, 3, 5, 7, 10 and 14 days after the second spray) from each treated plots. The fresh green tea leaf samples (500 g) of 7 and 14 days were then processed in the factory of the tea garden following standard manufacturing method to get made tea (CTC, 100 g) since tea leaves are plucked and processed after 7 and 14 days of application. The made tea (3.0 g) obtained for 7 and 14 days was boiled in heater for 2 min in 100 ml distilled water and filtered through a stainless steel filter to get the tea liquor. Green tea leaves, made tea and tea liquor were subjected to residue analysis of each of the insecticides. In order to find out the impact of these insecticides on quality of tea, a similar field experiment was conducted at the University Tea Garden, Gayeshpur, West Bengal (Meteorological data – Supplementary Table) with treatments reported earlier and fresh leaves were collected 0, 7 and 14 days after second spray which were subsequently analysed for tea phenolics and caffeine.

### 2.3. Analysis of residues of insecticides

The extraction and cleanup procedure for the analysis of thiacloprid residues in tea matrices was based on a method reported earlier (Banerjee & Banerjee, 2012) while that of deltamethrin was based on QuEChERS method for cyfluthrin (Banerjee, Banerjee, Roy, Banerjee, & Pal, 2012) with minor modification. The tea liquor was extracted and cleaned up as per method described by Tewary, Kumar, Ravindranath, & Shanker (2005). Thiacloprid residues were analysed by HPLC (Agilent, 1200 coupled with a UV–VIS detector) using a mobile phase consisting of acetonitrile:water (4:6) at a flow rate of 0.5 ml/min and detected at 242 nm with an injection volume of 100 μL. Data analysis were performed with Chemstation software (Agilent Technologies). Analysis of deltamethrin residue was made with GC 2010 (Shimadzu make) equipped with an AOC20i autosampler, split/splitless injector and a J & W Scientific DB-5 column (30 m × 0.25 mm ID × 0.25 μm film thickness) coupled with $Ni^{63}$ ECD and GC solution software was used to control the function of ECD. The operating systems were: nitrogen carrier gas (constant flow) 1.0 ml/min with a total flow of 14 ml/min; injection and detector temperature were 280 °C and 300 °C respectively; temperature programme: 160 °C for 1 min, increase @ 3 °C–280 °C and hold for 10 min; detector current 1 nA and make up flow 30 ml/min.

### 2.4. Analysis of caffeine and tea polyphenols

The tea caffeine and polyphenols were extracted according to methods described by Saito, Froehlich, Gosmann, & Bergold, 2007) with slight modification. Briefly, the green tea leaves subjected to maceration following drying at 40 °C and subsequently grinding material was extracted with 50% aqueous methanol at 80 °C for 20 min with intermittent shaking. After filtration through a Whatman 42 filter, 80 μl acetic acid was added to the extract to stabilize the polyphenol components. A 2 ml of extract was evaporated to dryness using RVE and was made to a 2 ml volume with the mobile phase for analysis by HPLC. The solution was subsequently filtered through 0.45 μm nylon membrane filter (PALL CORPORATION) and ready for injection in HPLC (Model YL 9100) which is coupled with UV–VIS detector of variable wavelength with Autochro 3000 software. The tea constituents were analysed using water, methanol and ethyl acetate (850:130:22.5 v/v) adjusted to pH 2.25 with ortho phosphoric acid as mobile phase at a flow rate of 1.7 ml/min and detected at 280 nm. Chromatographic separation of both thiacloprid and tea constituents were performed on a BDS, Hypersil RP C-18 column (25 cm long, 4 mm i.d and particle size 5 μm).

### 2.5. Risk assessment of thiacloprid and deltamethrin

Risk assessments were calculated by using mean body weight of 50 kg, daily intake (mg/kg bw) based on food consumption data (g/day) for tea and the maximum residue levels recorded on the commodity (mg/kg) from field trials. It was evaluated by comparing the theoretical maximum residue contribution (TMRC = maximum residue level obtained from both the application doses × average daily consumption of tea to the extent of 1.967 g) with the maximum permissible intake (MPI = acceptable daily intake [ADI] × average body weight [50 kg]/[10 kg] of an adult/child). The ADI of thiacloprid and deltamethrin was 0.01 mg/kg bw.

## 3. Results and discussion

### 3.1. Persistence of thiacloprid and deltamethrin in tea

The validity of methods, employed in the present study for the determination of thiacloprid and deltamethrin residues, was examined by fortifying each of the insecticides separately at levels of 0.05, 0.25 and 0.5 mg/kg in the respective extracts of green tea leaves, made tea and tea liquor. The overall mean recovery of thiacloprid and deltamethrin, regardless of matrices, varied from 91–92 and 93–96% respectively which correspond to relative standard deviation (RSD) of 4.63–6.36% and 1.53–3.74% respectively. The percent recovery, RSD along with S/N ratio (> 10) indicated the efficiency, reproducibility and repeatability of methods with limit of quantification of 0.05 mg/kg irrespective of matrices.

The residue data relating to persistence of thiacloprid (Fig. 1) and deltamethrin (Fig. 2), when applied at RFD and dRFD in tea leaves grown under three different locations indicated that initial deposit, although dependent on the type and rates of application of each of the insecticides, did not show any marked differences between locations. The mean initial deposit of thiacloprid in green tea leaf at RFD in location L1, L2 and L3 was found to be 3.81, 3.24 and 3.19 mg/kg respectively while those of at dRFD, the values were 6.31, 5.87 and 5.81 mg/kg respectively. Residues dissipated to the tune of 10.66–32.81% and 37.35–42.59% on three days at RFD and dRFD