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NOTE

Dissipation of Profenofos in/on Tea Leaves

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Dissipation of profenofos 50 EC residue was assessed in tea leaves after application at 500 and 1000 g a.i. ha^{-1} to derive the safe pre-harvest waiting period. Tea leaf samples (250 g) collected from two field trials on 0, 1, 3, 5, 7, 10, 15 and 30 d after the third round of insecticide application gave initial deposits of 3.6271 and 7.1796 µg g^{-1}, respectively in the trial I and 2.8990 and 6.0745 µg g^{-1}, respectively in the trial II. The residues reached below detectable level on the 7^{th} and 10^{th} d at the two doses respectively. Half-life of profenofos ranged from 1.20 to 1.40 d. A safe waiting period of 6.5 d is recommended for harvesting the leaves after spraying profenofos @ 500 g a.i ha^{1}.

Key words: Profenofos, dissipation, residue, tea leaves, half-life, waiting period

Tea, *Camellia sinensis* (L.) O. Kuntze, known as the queen of beverages, is one of the most important cash crops in India due to its tremendous export potential (Banerjee *et al*., 2010). It is reported as the healthiest drink and the second most consumed beverage after water (Biswas *et al.,* 2007) with about one and a half billion cups of tea being consumed daily all over the world (Pal *et al.,* 2006). India is the second largest producer and consumer of tea, and the fourth largest exporter in the world, earning a huge foreign exchange by exporting it (Boriah, 2006)

The tea planters use a wide range of pesticides to combat pest problems (Paramasivam *et al.,* 2012). Though pesticides render powerful control of pests, thereby offering increased yield and high economic returns, they have serious drawbacks such as development of resurgence of pests, outbreak of secondary pests, harmful effects on human health and environment and presence of undesirable residue (Das, 1959; Gurusubramanian *et al.,* 2005; Sarnaik *et al.,* 2006). The developed countries are becoming more health conscious and are gradually lowering the maximum residue limit (MRL) of different pesticides in tea and other food items (Somchoudhury *et al*., 1995).

As tea makes an important contribution to the human diet, data on the fate of chemical residues in tea after application is essential, for the establishment of maximum residue limit in various agro-climatic conditions. Authorization of 450 compounds has already been withdrawn by European Community for use on agricultural products and it has adversely affected the tea exports of many countries including India since the approval for ethion which was extensively used for mite control in tea has been withdrawn (Sarmah *et al.,* 2009).

This has necessitated a search for environmentally and biologically safer pesticide molecules against tea pests. Profenofos is one such broad-spectrum insecticide with contact and stomach poison action against sucking, mining and chewing insects. It is non-systemic but has excellent translaminar action, which provides effective control of boring and mining pests because of the rapid uptake and penetration of the active ingredient into the plant tissue (Buholzer, 1975). This insecticide was widely used in Tamil Nadu by the tea growers for the control of tea mosquito bug, *Helopeltis theivora* Waterhouse. The present investigation was undertaken to study the dissipation pattern of profenofos in tea.

MATERIALS AND METHODS

Test insecticide

The technical standard of the test insecticide profenofos, O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate with 94.4 per cent purity was obtained from Crystal Crop Protection Pvt. Ltd., New Delhi and used for quantification as well as determination of detectable limits.

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Profenofas 50 EC (Kilcron, Crystal Crop Protection Pvt. Ltd.) was also provided by the manufacturer. Its concentrated stock solution (1000 ppm) was prepared in HPLC grade acetone and stored in a refrigerator and the intermediate stock solutions of different concentrations and the working standards were prepared before use.

Field experiments

Two field experiments were carried out in tea estates, one each at Lower Paralai and Iyerpady during 2012 - 2013 in the ruling tea variety Assam. The insecticide spray was given thrice at ten d interval using a hand operated knapsack sprayer at 500 g a.i. ha^{-1} (X dose) and 1000 g a.i. ha^{-1} (2X dose) @ 500 L ha^{-1}. An untreated check was maintained. Each treatment along with the check was replicated thrice.

Sampling

The residue samples (250 g of tea leave) were collected from each plot at different intervals *viz.*, 0, 1, 3, 5, 7, 10, 15 and 30 d after the third round of insecticide application for the determination of residues.

Extraction

The sample preparation was done by adopting QuEChERS method. Twenty-five g of tea leave sample was homogenized using a blender and 10 g of sample taken in 50 mL centrifuge tubes, added with 20 mL of acetonitrile and kept in a mechanical shaker for an h. To this mixture, 4g of magnesium sulphate and 1 g of sodium chloride were added, shaken vigorously for one min and centrifuged at 10,000 rpm for 10 min. Six mL of the upper layer was transferred into a 15 mL centrifuge tube containing 100 mg primary secondary amine and 600 mg of $MgSO_4$. The mixture was shaken vigorously for one min, centrifuged at 5000 rpm for 10 min to separate solids from solution. From the supernatant, 2 mL was transferred to turbovap tube and the solvent removed to dryness in turbovap evaporator. The volume was reconstituted to one mL using acetone for gas chromatography (GC) analysis.

Quantification of residue

The estimation of profenofos residue in tea leaves was done by gas chromatography (Varian Chrompack CP-3800) using electron capture detector (ECD) and Varian CP Sil CB Column with variable temperature (100°C, hold time 1.0 min; 220°C, hold time 3 min @ 40° C min^{-1} and 260°C, hold time 2 min @ 40°C min^{-1}). The temperatures of injector and detector were 250 and 300°C respectively. The flow rate of carrier gas nitrogen was 1 mL min^{-1} and the run time 10 min. The limits of quantification and detection were 0.03 and 0.01 µg g^{-1} respectively. The limit of quantification was determined at the lowest concentration of profenofos giving a response of 10 times the base line noise. The limit of detection was determined at the lowest concentration giving a response of 3 times the base line noise defined from the analysis of control (untreated sample).

In order to assess the reliability of the analytical method adopted, recovery study was conducted by fortifying the tea leaves with the analytical standard of profenofos and processed using the above mentioned procedure. The mean recovery of profenofos from tea leaves was 90.91 per cent.

Computation of half life, waiting period, etc.

The half life ($t_{1/2}$) was determined as DT_{50} = ln 2/k. The pre-harvest interval (PHI) is the maximum time (d) required for the residue to fall below the MRL, and was calculated from the equation: PHI [log intercept – log MRL]/slope of first order equation. The recommended European Union (EU) MRL of 0.1 µg g^{-1} was used for estimation of PHI.

RESULTS AND DISCUSSION

Profenofos deposits and their dissipation

The initial deposits (2 h after treatment) of profenofos at 500 and 1000 g a.i. ha^{-1} were 3.6271 and 7.1796 µg g^{-1}, respectively in the field trial I (Table 1) and 2.8990 and 6.0745 µg g^{-1}, respectively in the field trial II (Table 2). This is in conformity with an earlier study reported by Pramanik *et al.* (2005), in which the initial deposits ranged from 2.63 to 3.44 and 5.53 to 7.07 in profenofos sprays at 500 and 1000 g a.i. ha^{-1}, respectively.

The residues decreased gradually and reached the below detectable level (BDL) on the 7th d at the lower and 10th d at the higher dose of application (Tables 1 and 2). The percentage dissipation was 28.79, 72.07, 94.47 and 100 per cent in the field trial 1 (Table 1) and 24.37, 74.10, 93.96 and 100 per cent in the field trial II (Table 2), respectively at 1, 3, 5 and 7 d of application of profenofos at 500 g a.i. ha^{-1}. At the higher dose (1000 g a.i. ha^{-1}), the corresponding values were 25.15, 59.64, 86.28, 96.51 and

Table 1. Residues of profenofos 50 EC (µg g^{-1}) in tea leaves (Field trial I)

Days after third spraying	Untreated check	500 g a.i. ha^{-1}				Dissipation (%)	1000 g a.i. ha^{-1}				Dissipation (%)
		R1	R2	R3	Mean		R1	R2	R3	Mean	
0(2 HAT)	BDL	3.5171	3.9059	3.4582	3.6271	-	7.4908	6.8775	7.1704	7.1796	-
1	BDL	2.7651	2.7817	2.2019	2.5829	28.79	5.8625	5.5768	4.6832	5.3741	25.15
3	BDL	0.9722	1.0312	1.0303	1.0129	72.07	2.6035	2.7748	3.3157	2.8980	59.64
5	BDL	0.1968	0.2079	0.1975	0.2007	94.47	1.0119	0.9011	1.0425	0.9851	86.28
7	BDL	BDL	BDL	BDL	-	100	0.2194	0.2413	0.2919	0.2509	96.51
10	BDL	BDL	BDL	BDL	-	-	BDL	BDL	BDL	-	100

BDL - Below detectable level; HAT - hours after treatment.

Table 2. Residues of profenofos 50 EC (µg g^{-1}) in tea leaves (Field trial II)

Days after third spraying	Control	500 g a.i. ha^{-1}				Dissipation (%)	1000 g a.i. ha^{-1}				Dissipation (%)
		R1	R2	R3	Mean		R1	R2	R3	Mean	
0(2 HAT)	BDL	2.6257	3.2092	2.8642	2.8997	-	5.7459	5.8306	6.6470	6.0745	-
1	BDL	2.6082	1.9790	1.9918	2.1930	24.37	4.4445	4.6051	4.0082	4.3526	28.35
3	BDL	0.7314	0.7529	0.7684	0.7509	74.10	2.0199	2.2541	2.4863	2.2534	62.60
5	BDL	0.1727	0.1779	0.1745	0.1750	93.96	0.8077	0.7800	0.8364	0.8080	86.70
7	BDL	BDL	BDL	BDL	-	100	0.1378	0.1273	0.1256	0.1303	97.86
10	BDL	BDL	BDL	BDL	-	-	BDL	BDL	BDL	-	100

BDL= Below detectable level; HAT= hours after treatment.

Table 3. Half life and safe waiting period of profenofos on tea

Treatment	Field trial I		Field trial II	
	Half life (d)	Waiting period (d)	Half life (d)	Waiting period (d)
Profenofos 50 EC @ 500 g a.i.ha^{-1}	1.20	6.5	1.22	6.2
Profenofos 50 EC @ 1000 g a.i.ha^{-1}	1.40	9.4	1.31	8.2

Maximum residue limit of profenofos in tea = 0.1 µg g^{-1}

100 per cent in field trial 1 (Table 1) and 28.35, 62.60, 86.70, 97.86 and 100 per cent respectively in the field trial II (Table 2) at 1, 3, 5, 7 and 10 d after treatment respectively. These results are in accordance with the findings of Pramanik *et al.,* (2005) who reported that profenofos at 500 and 1000 g a.i. ha^{-1} reached BDL on the 5^{th} and 10^{th} d, respectively after treatment on tea.

Half life, waiting period

The computed half-life ($T_{1/2}$) was 1.20 and 1.40 d for profenofos 50 EC at 500 and 1000 g a.i. ha^{-1} in trial I, while it was 1.22 and 1.31 d for the corresponding doses in trial II (Table 3). The MRL of profenofos in tea is 0.1 µg g^{-1}. Based on this, safe waiting periods of 6.4 and 9.4 d in field trial I (Table 3) and 6.2 and 8.2 d in field trial II were obtained at X and 2X doses, respectively. A safe waiting period of 6.5 d is recommended for harvesting and using the leaves for processing after spraying of profenofos.

The result is in accordance with Pramanik *et al.* (2005) who reported the half- life of profenofos ranging from 0.77 to 1.01 d for X and 2X doses, respectively.

CONCLUSION

It is concluded that the profenofos residues were not detected in tea leaves after 7 DAT at the recommended dose of 500 g a.i. ha^{-1} and the half-life ranged from 1.20 to 1.40 d. A safe waiting period of 6.5 d is recommended for harvesting tea after application of profenofos 50 EC.

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REFERENCES

Banerjee H, Ganguly P, Roy S, Banerjee D, Paramasivam M, Banerjee T and Sharma KK (2010) Persistence and safety risk assessment of propineb in Indian tea. *Environmental Monitoring and Assessment* **170**: 311-314.

Biswas PK, Pramanik SK, Mitra SR and Bhattacharyya A (2007) Persistence of napropamide in/on tea under North-East Indian climatic condition. *Bulletin of Environmental Contamination and Toxicology* **79**: 566-569.

Boriah G (2006) Tea production: Substantial Forex Earnings. In: *The Hindu Survey of Indian Agriculture*, N Ram (Ed.). National Press, Chennai, pp 213-215.

Buholzer F (1975) Profenofos - a new insecticide for the control of cotton and vegetable pests. In: *Proceedings of the Eighth British Insecticide Fungicide Conference*, 17-20 November, 1975, Hotel Metropole, Brighton, England, pp 659-665.

Das GM (1959) Bionomics of the tea red spider, *Oligonychus coffeae* (Nietner). *Bulletin of Entomological Research* **50**: 265-274.

Gurusubramanian G, Borthakur M, Sarmah M and Rahman A (2005) Pesticide selection, precautions, regulatory measures and usage. In: *Plant Protection in Tea*. AK Dutta, G Gurusubrmanian and BK Barthakur (Eds.). Assam Printing Works Private Limited, Tocklai Experimental Station, TRA, Jorhat, Assam, India. Pp 81-91.

Hou RY, Hu JF, Qian X, Su T, Wang XH, Zhao XX and Wan XC (2013) Comparison of the dissipation behaviour of three neonicotinoid insecticides in tea. *Food Additives Contaminants* **30**: 1761-1769.

Pal R, Sanyal N, Das P, Pramanik SK, Das C, Bhattacharyya A and Chowdhury A (2006) Abamectin in tea and tea liquor under northeastern Indian climatic conditions. *Bulletin of Environmental Contamination and Toxicology* **76**: 126-131.

Paramasivam M, Kavitha J and Chandrasekaran S (2012) Persistence behaviour of thiacloprid residues in/on green tea leaves, processed tea and tea infusion. *Bulletin of Environmental Contamination and Toxicology* **89**: 602-605.

Pramanik SK, Dutta S, Bhattacharyya J, Saha T, Dey, PK, Das S and Bhattacharyya A (2005) Persistence of profenofos residue on tea under northeast Indian climatic conditions. *Bulletin of Environmental Contamination and Toxicology* **74**: 645-651.

Romeh AA, Mekky TM, Ramadan RA and Hendawi MY (2009) Dissipation of profenofos, imidacloprid and penconazole in tomato fruits and products. *Bulletin of Environmental Contamination and Toxicology* **83**: 812-817.

Sarmah M, Rahman A, Phukan AK and Gurusubramanian G (2009) Effect of aqueous plant extracts on tea red spider mite, *Oligonychus coffeae*, Nietner (Tetranychidae: Acarina) and *Stethorus gilvifrons* Mulsant. *African Journal of Biotechnology* **8**: 417-423.

Sarnaik SS, Kanekar PP, Raut VM, Taware SP, Chavan KS and Bhadbhade BJ (2006) Effect of application of different pesticides to soybean on the soil microflora. *Journal of Environmental Biology* **27**: 423-426.

Somchoudhury AK, Saha K, Sarkar PK, Choudhury A and Bhattacharya A (1995) Approaches to integrated control of red spider mite, *Oligonychus coffeae* (Nietner) on tea. In: *Proceedings 1995 International Tea-Quality-Human-Health Symposium*, Shanghai, China, pp 263-268.

Suganyakanna S, Karuppusamy P, Kuttalam S, Chandrasekaran S and Sharma KK (2006) Determination of residues of spiromesifen 240 SC (Oberon®) in tea. *Pestology* **30**(8): 20-21.

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