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Persistence of Napropamide in/on Tea under North-East Indian Climatic Condition

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Abstract Napropamide is an amide group of herbicide, used as pre-emergence herbicide controlling in broad leaved weeds of tea, ground nut, citrus, etc. Napropamide 45 SC (Devrinol) was applied on tea bushes twice @ 1.125 and 2.250 g a.i./ha along with untreated control. After following the standard extraction process, the residue of napropamide in made tea and soil cropped with tea was analyzed by HPLC. Napropamide was rapidly dissipated in soil following the first-order kinetics with half-lives in the range of 12.54–27.87 days. The residue in made tea found to be below detectable limit on 7th day samples.

Keywords Napropamide · Made tea · Soil · Residue

Tea (*Camellia sinensis*) is a perennial crop grown on wide variety of soil types and climatic conditions. It is the healthiest drinks and second most consumed beverage after water. The north-east India accounts for the 75% of total productions and earns good amount of foreign exchange by exporting tea. India is the highest producer of tea in the world. In India tea is being cultivated mainly in north-east and south India. In north-east region of India, presence of different weeds in the tea fields causes serious problems in tea plantation mainly in Dooar's and Darjeeling region of West Bengal. It has already been established that the slashing of weeds four times a year resulted in a 12% crop loss compared to standard chemical weed control. There are many herbicides are introduced in the hill region to control the weeds. Napropamide [RS-*N*, *N*-diethyl-2-(1-Naphthyl-oxy) propinamide], is an amide herbicide to be introduced first time in India subcontinent by M/s United Phosphorus Limited, Mumbai. It is used to control the weed flora in the tea fields. The herbicide has no adverse effect on biological activity in the soil and has excellent residual activity. Napropamide (Fig. 1) is quite polar and slightly soluble in water and widely used as pre-emergence herbicide controlling in broad leaved weeds of tea, ground nut, citrus, grape vines, oil seeds, tobacco, tomatoes, and brinjal etc. (Agav and Voevodin 1985; Chang et al. 1991; Kalinova and Rastenievdni 1991; Murillo Pulgariän and Garciäa Bermejo 2002). It is non-phytotoxic and gives full coverage of treated leaves but it is moderately toxic to fresh water fish (Anonymous 1984). Although some information is available on the residual fate of napropamide in brinjal, copped soil (Agav and Voevodin 1985), but no systematic study has been done on the persistence of napropamide in made tea. Therefore a long-term systematic study was undertaken to find out the persistence pattern as well as the residual level of napropamide present in the tea cropped soil and made tea.

Materials and Methods

The field experiment was conducted in a randomized block design (RBD) replicated thrice at Kamalpur Tea Estate,

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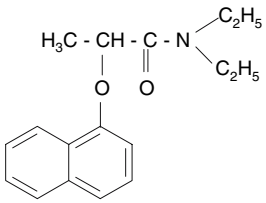
Fig. 1 Structure of napropamide



Darjeeling, West Bengal, India during 2001–2002 [first season; May–August (Pre monsoon) 2001, second season; September–November (Post monsoon) 2001, third season; May–August (Pre monsoon) 2002] on tea (variety TV-23 and TV-29). A plot of 100 sq m was taken for individual treatment.

The commercial formulation of napropamide 45 SC (Devrinol) was applied to tea bushes twice @ 1.125 g a.i./ha (recommended dose, i.e., T_1) and 2.250 g a.i./ha (double the recommended dose, i.e., T_2) by a Knapsack sprayer and untreated control (T_3) was simultaneously maintained. The volume of water was used 400 L/ha. The number of bushes per treatment was 100 and spacing between the bushes was double hedge type. Green tea leaves (Two leaf and a bud, 1 kg) were plucked randomly from each treatment replication-wise at different time interval [0 (4 h after spraying) and 7 days] after application of napropamide and the green tea leaf samples processes to made tea (CTC, 100 g) at Kamalpur Tea Estate factory following standard manufacturing methods. Soil samples (100 g) cropped with tea was collected in a similar way at 0, 7, 10, 30, 60 and 90 days after the application of herbicide.

Cropped soil samples (100 g) were suspended with 100 mL mixture of methanol and water (6:4; v/v) for overnight. Then it was shaken for 1 h in a mechanical shaker and laid aside for floculation of soil particles. The supernatant was filtered through a buchner funnel using 100 mL same solvent mixture as washing solvent. The combined filtrate was then concentrated by rotary vacuum evaporator at 40°C. The concentrated extract was transferred to a separatory funnel with 50 mL water followed by addition of HCl. Then it was partitioned thrice with (100 + 50 + 50) mL benzene and the organic phase was collected over anhydrous sodium sulphate. The combined organic fraction was evaporated to dryness and subsequently reconstituted with acetonitrile for HPLC analysis.

Made tea samples (20 g) were homogenized with 150 mL mixture of methanol and water (6:4; v/v) in a Remi automix blender (3 min). The homogenate was filtered through buchner funnel and residue was re-extracted twice (2 × 25 mL) with same solvent mixture and filtered. The combined filtrate was concentrated (50 mL) by a rotary vacuum evaporator at 40°C. The concentrated extract was then transferred into a 500 mL separatory funnel with addition of 100 mL water and 10 mL dilute hydrochloric acid and then it was partitioned thrice with (100 + 50 + 50) mL benzene and allowed to separate the phases. The benzene layer was passed through anhydrous sodium sulphate and the entire benzene fraction was combined. The combined fraction was evaporated to near dryness at 40°C and subsequently reconstituted with acetonitrile to suitable volume for HPLC analysis.

Final analysis of napropamide residue in made tea and cropped soil were done by HPLC (Model 1050, Hewlett Packard, USA) with UV/vis variable detector coupled with 3392A integrator. The Reversed phase Thermo Hypersil (250 × 4.6 mm) 5 μ Hypersil® ODS shandon HPLC, UK (μ Bondapack C_{18}) column was used. Acetonitrile (100%) was used as mobile phase for the detection of napropamide residue. The other parameters like flow, wave length (λ_{max}), retention time, limit of quantification (LOQ) and limit of detection (LOD) were 0.5 mL/min, 240 nm, 3.12 ± 0.2 min, 0.01 μg/g and 0.005 μg/g, respectively.

In order to evaluate the efficiency and reliability of the analytical method adopted, recovery study was carried out by fortifying made tea and soil samples with 0.5, 1 and 5 μg/g of analytical grade napropamide. The average recovery was found in the range of 85.5%–89%. Dissipation data was subjected to regression equation (Hoskins 1961) for computing residual half-life and waiting period (Gunther and Blinn 1955).

Results and Discussion

The residue data of napropamide in field soil cropped with tea at different day's interval was presented in the following table (Tables 1, 2, 3). The corresponding dissipation rate, half-lives and regression equation has also been calculated on the basis of residue data (Table 4). It has been found from the result that the napropamide residue in tea cropped soil declined progressively with time irrespective of any dose and season taking residues at 0 day as initial residues. The initial deposit of napropamide in tea cropped soil was found in the range of 1.18–1.49 and 2.08–2.90 μg/g for recommended dose (T_1) and double the recommended dose (T_2) respectively irrespective of any season and doses. At 30 days after application of the herbicide, more than 50% of the residue was dissipated. The residue declined below detectable limit in tea cropped soil on day 60 for T_1 and day 90 for T_2 irrespective of season. The dissipation of Napropamide in tea cropped soil followed the first-order kinetics with the half-life values varying from 12.54 to 27.87 days irrespective of doses and seasons.

In made tea (Table 5), the initial concentration of napropamide was found in the range of 0.14–0.20 μg/g in recommended dose (T_1) and 0.35–0.44 μg/g in double the

Table 1 Residues of napropamide in tea cropped soil (first season)

Season	DAT	Treatment	Residue in μg/g (M* ± SD)	Dissipation (%)
Pre monsoon (2001)	0	T_1 (1.125 g a.i./ha)	1.18 ± 0.19	–
	10		0.73 ± 0.12	38.14
	30		0.50 ± 0.14	57.63
	60		BDL	–
	90		BDL	–
	0	T_2 (2.250 g a.i./ha)	2.08 ± 0.27	–
	10		1.13 ± 0.17	45.67
	30		0.75 ± 0.11	63.94
	60		0.40 ± 0.09	80.77
	60		BDL	–

DAT Day's after treatment, *M** average of three replication, *BDL* Below detectable level

Table 2 Residues of napropamide in tea cropped soil (second season)

Season	DAT	Treatment	Residue in μg/g (M* ± SD)	Dissipation (%)
Post Monsoon (2001)	0	T_1 (1.125 g a.i./ha)	1.49 ± 0.33	–
	10		1.03 ± 0.17	30.87
	30		0.56 ± 0.11	62.42
	60		BDL	–
	90		BDL	–
	0	T_2 (2.250 g a.i./ha)	2.90 ± 0.33	–
	10		1.87 ± 0.26	35.52
	30		1.12 ± 0.17	61.38
	60		0.52 ± 0.14	82.07
	60		BDL	–

DAT Day's after treatment, *M** average of three replication, *BDL* Below detectable level

Table 3 Residues of napropamide in tea cropped soil (third season)

Season	DAT	Treatment	Residue in μg/g (M* ± SD)	Dissipation (%)
Pre Monsoon (2002)	0	T_1 (1.125 g a.i./ha)	1.30 ± 0.29	–
	10		0.64 ± 0.08	50.77
	30		0.24 ± 0.07	81.54
	60		BDL	–
	90		BDL	–
	0	T_2 (2.250 g a.i./ha)	2.43 ± 0.30	–
	10		1.45 ± 0.10	40.33
	30		0.70 ± 0.78	71.19
	60		0.33 ± 0.70	86.42
	60		BDL	–

DAT Day's after treatment, *M** average of three replication, *BDL* Below detectable level

recommended dose (T_2) in three seasons. On 7th day after application the residue was found to be below detectable limit in both the treatments irrespective of seasons. No residue was detected in the untreated control samples through out the study.

From this result, it revealed that the no residue of napropamide was detected in made tea 7 days after application which is befitting with the plucking schedule of the north-east region of India. Therefore, napropamide may be safely used in tea crop for weed control purpose at the recommended or double the recommended dose as pre emergence and it may not pose any residual toxicity in made tea.

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Table 4 Statistical interpretation of the residual data

Treatment	Season	Residual half-life (RL_{50} or $t_{1/2}$) (days)	Regression equation
T_1 (1.125 g a.i./ha)	Season-I	25.51	$Y = 3.036 - 0.0118X$
	Season-II	21.50	$Y = 3.166 - 0.0140X$
	Season-III	12.54	$Y = 3.087 - 0.0240X$
T_2 (2.250 g a.i./ha)	Season-I	27.87	$Y = 3.237 - 0.0108X$
	Season-II	24.88	$Y = 3.426 - 0.0121X$
	Season-III	21.35	$Y = 3.330 - 0.0141X$

DAT Day's after treatment, *M** average of three replication, *BDL* Below detectable level

Table 5 Residues of Napropamide in made tea

Treatment	Season	Residue in μg/g (M* ± SD)	
		0 days	7 days
T_1 (1.125 g a.i./ha)	Season-I	0.20 ± 0.05	BDL
	Season-II	0.16 ± 0.03	BDL
	Season-III	0.14 ± 0.07	BDL
T_2 (2.250 g a.i./ha)	Season-I	0.39 ± 0.09	BDL
	Season-II	0.44 ± 0.10	BDL
	Season-III	0.35 ± 0.11	BDL

DAT Day's after treatment, *M** average of three replication, *BDL* Below detectable level

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