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Carbofuran Residue in Water, Soil, and Trapa Fruits, after Field Application

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Carbofuran (2,3-dihydroxy-2,2-dimethyl-7-benzofuranyl methyl carbamate) used for insect as well as nematode problem is one of the carbamate pesticide widely used by Trapa growers to control various pests of the crop (Agarwal and Agarwal 1960; Bindra and Saxena, 1964). The relative efficacy of various insecticides on Singhara beetle, *Galerucella birmanica* has been studied by Pradhan et al (1964). Several studies on their environmental impact have been conducted on various crops (Rajukkannu et al. 1976, 1978; Misra and Agarwal, 1989; Patnaik et al. 1989).

Trapa natans L. var. *bispinosa* (Roxb) Makino (Trapaceae) is cultivated extensively for its fruits in tanks, lakes, ponds etc. throughout India, particularly Uttar Pradesh, Madhya Pradesh, Bihar and Orissa. The fruits are eaten raw when tender and sometimes after boiling and roasting (Anonymous 1976). The meal prepared by grinding the dried kernels is used as substitute for cereal flour (Anonymous 1976).

There is much information of carbofuran application on various crop but lacks residue data in *T. natans*. However in this paper we report the results of a survey of carbofuran residue in fruits of Trapa procurred from market and also in water and soil samples of the ponds where the crop is grown. Owing to the high level of carbofuran residue observed in Trapa fruits it is prudent to lay a field experiment and to study the residue level of carbofuran in the plant, fruits, water and soil samples of the pond.

MATERIALS AND METHODS

The fruits of *T. natans* were procurred from the market at various localities of 5 districts of Uttar Pradesh,

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India. The fruits were separated into kernel and peels prior to analysis. 5Ø g each of kernel, peel as well as flour prepared from dried kernels were taken up for analysis. The water and soil samples were collected from various ponds where the crop was grown. The water samples were taken from four different positions in the pond, combined and filtered through Whatman No.1 filter paper before analysis. An aliquot (5ØØ ml) was processed for the carbofuran residue. The soil samples were picked up from 6 sampling sites in the pond, air dried, ground and sieved through a 2 mm mesh screen before use. Finally these specimens were combined and an aliquot (5Ø g) was processed.

A pond (area 1 acre depth 1 m) located at District Unnao, Uttar Pradesh, was selected for the experiment. The experiment was carried out in July 1991. The crop experienced rainy season from July to mid-October and early winter from October to mid-December. The mean maximum temperature ranged between 28.5^{o}-34.5^{o} while the mean minimum between 12.5^{o}-$28.Ø^{o}$. The pH of the water and soil was found to be 7.2 and 7.8. Three treatments of carbofuran at 75 g (a.i.) ha^{-1} were broadcast by hand uniformly over the water at biweekly intervals. The plant samples were collected immediatley before and after 24 hr of each of the three applications of the pesticide to check the presence of carbofuran residue. The fruit samples were collected on weekly basis right from the tender age to maturity. It is interesting to note that in the control pond no plant survived till the stage of fruiting. The samples were immediately transported back to the laboratory for extraction of the carbofuran residue. The fruits were separated into kernel and peel prior to analysis. The residue in kernel was also estimated on outer and inner kernel basis. Some of the fruit samples were analysed after boiling them in distilled water. 5Ø g each of the samples were processed for analysis. Water and soil samples were collected before the first application of the insecticide and were taken as control water and soils samples were also collected 24 hr after each application of carbofuran which was given at biweekly intervals upto 3Ø days. After this period sampling continued at 45, 75 and 1Ø5 days after the first application of the pesticide. The water and soil sample were analysed as described above.

All the samples were analysed in triplicate according to the procedure described by Lee and Westcott (198Ø) without any major change. The extraction and clean-up procedures differed slightly according to the type of the samples. For clean-up of the residue in case of fruits, boiled fruits and flour it was dissolved in

methanol (25 ml), treated with activated charcoal (500 mg), extracted from the charcoal by boiling methanol and finally filtered.

The soil samples were also analysed following the above mentioned analytical procedure. The water samples, after preliminary filtration did not require additional clean-up.

The carbofuran residue finally obtained was taken up in methanol (Merck, HPLC grade, 5 ml) in each case whereas in case of water it was dissolved in methanol (1 ml). The HPLC system was a Gynkotek model 300 C and Shimadzu SPD-6A UV detector which was connected to a Chromatopac C-R3A data processor. The column packed with Nueleosil C-18 (4.5 x 250 mm) at λmax 254 nm was used. For analysis a 20 µl aliquot of each of the samples was injected into the HPLC system via Hamilton syringe to the auto sample injector (loop, 20 µl).

Before an unknown sample was analysed the response factor of carbofuran standard was determined from the chromatogram 1,2,5,10,15 and 20 ppm solution. The calibration curve was plotted obtaining good linearity. The carbofuran standard was obtained by crystallising technical grade carbofuran (75% purity) from Rallis India Limited, Bangalore, which melted at 150-52°, molecular weight 221 and was sparingly soluble in water.

The recovery tests were performed independently for the plant materials, water and soil samples and the mean recoveries were 82, 95 and 85% respectively.

RESULTS AND DISCUSSION

The survey of the market samples from five districts of Uttar Pradesh during the period October and December 1991 showed carbofuran residue in the kernel of *T. natans* ranging from 0.56-2.82 µg/g whereas the corresponding values for peels ranged from 0.34-1.71 µg/g. The flour prepared from kernel showed 0.28 µg/g residue of carbofuran (Table 1). The samples from Lucknow and Unnao region showed significantly high levels of carbofuran residue as compared to others. However, with very few exceptions the fruit samples were above the tolerance limit of 0.5 ppm (Annonymous 1985).

Since Trapa fruits are also eaten boiled, the residue levels in the boiled fruits was also determined and reported in Table 2. There is a report that carbofuran

residue in potatoes is reduced below tolerance limit by boiling (Misra and Agarwal 1989). The boiling of the fruits in case of *T. natans* also reduced the level of carbofuran about ten times which was well below the tolerance limit.

The carbofuran concentrations in water and soil samples from various ponds are presented in Table 3. The residue of carbofuran in water as well as in soil samples from Unnao region was significantly high as compared to other places. It may not be out of place to mention here that the biodegradation of carbofuran in flooded soils and by soil micro-organism have already been reported (Venkateswarlu et al. 1977; Kandasamy et al. 1977).

Table 1. Carbofuran residue in fruits of *T. natans* procured from market.

Location	No. of analyses	Parts used	Range µg/g	Mean value
Barabanki	9	Kernel	Ø.8Ø-Ø.93	Ø.Ø7
		Peel	Ø.62-Ø.7Ø	Ø.66
Lucknow	18	Kernel	Ø.83-2.82	1.97
		Peel	Ø.51-1.71	1.2Ø
Rai Bareilly	15	Kernel	Ø.56-1.58	1.16
		Peel	Ø.34-Ø.91	Ø.71
Sitapur	9	Kernel	Ø.64-Ø.71	Ø.67
		Peel	Ø.48-Ø.54	Ø.51
Unnao	24	Kernel	Ø.68-2.64	1.24
		Peel	Ø.42-1.65	Ø.76
Lucknow	9	Flour	Ø.21-Ø.35	Ø.28

Table 2. Carbofuran residue in boiled kernel.

Locality	No. of analysis	Range µg/g	
		before boiling	after boiling
Lucknow	9	1.68 (Ø.83-2.82)	Ø.17 (Ø.Ø8-Ø.28)
Rai Bareilly	9	1.Ø3 (Ø.56-1.58)	Ø.1Ø (Ø.Ø5-Ø.16)
Unnao	9	1.6Ø (Ø.82-2.64)	Ø.16 (Ø.Ø8-Ø.26)

Table 3. Carbofuran concentrations in water and soil samples.

Location	No. of analysis	Range	Mean value
Water samples			
Lucknow	9	Ø.Ø5-Ø.1Ø	Ø.Ø7
Rai Bareilly	9	Ø.Ø1-Ø.41	Ø.19
Unnao	9	Ø.65-1.31	Ø.96
Soil samples			
Lucknow	9	1.Ø5-2.Ø8	1.57
Rai Bareilly	9	Ø.32-3.76	2.22
Unnao	9	3.87-12.55	7.48

Table 4. Residue levels of carbofuran in *Trapa natans* whole plant, pond water and soil.

Time (Days)		Residue*		
		Whole Plant (µg/g)	Pond Water (µg/L)	Soil (µg/g)
0	Control	Ø.Ø5	Ø.Ø2	Ø.Ø8
1	1st Application (Ø3-Ø9-91)	2.23 (2.21-2.25)	Ø.83 (Ø.82-Ø.84)	3.59 (3.56-3.62)
14		1.78 (1.77-1.8Ø)	-	-
15	2nd Application (17-Ø9-91)	4.Ø5 (4.Ø3-4.Ø8)	1.45 (1.44-1.46)	6.74 (6.72-6.75)
29		3.12 (3.1Ø-3.13)	-	-
3Ø	3rd Application (Ø1-1Ø-91)	5.32 (5.29-5.35)	2.Ø5 (2.Ø4-2.Ø7)	9.92 (9.89-9.96)
45			1.25 (1.24-1.26)	6.Ø5 (6.Ø3-6.Ø9)
75			Ø.42 (Ø.44-Ø.46)	2.Ø8 (2.Ø7-2.Ø9)
1Ø5			Ø.1Ø (Ø.Ø8-Ø.12)	Ø.48 (Ø.47-Ø.5Ø)

* Mean value of three replicate samples.

The analytical findings of the levels of carbofuran residue in plant, water and soil samples after field application were recorded in Table 4 and that of fruits in Table 5.

Table 5. Estimate of carbofuran in Trapa fruits.

Time (Days) after final application	Residue* µg/g				Ratio of outer/inner kernel
	Peel	Kernel	Outer kernel	Inner kernel	
10	2.08 (2.06-2.10)	4.30 (4.26-4.33)	2.53 (2.52-2.54)	1.63 (1.62-1.65)	1.5
17	1.52 (1.52-1.54)	3.14 (3.11-3.17)	1.85 (1.83-1.87)	1.19 (1.18-1.20)	1.5
24	0.94 (0.93-0.95)	1.94 (1.93-1.96)	1.12 (1.10-1.13)	0.93 (0.91-0.94)	1.5
31	0.57 (0.54-0.59)	1.16 (1.15-1.17)	0.63 (0.61-0.64)	0.42 (0.40-0.43)	1.5

*Mean value of three replicate samples.

Our experimental results in the field agree with the high values of carbofuran residue observed in market samples. The extent of residue left over exceeded the tolerance limit of 0.5 ppm fixed by FAO/WHO (Anonymous 1985). Thus it could be concluded that although carbofuran provided an effective control of pests on Trapa their accumulation and persistence in the fruits posed a residue hazard. The study calls for either reduction in the application of carbofuran or any other remedial measures to control the pests on Trapa.

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REFERENCES

Anonymous (1976) Wealth of India, Raw Materials, CSIR Publications. New Delhi, 10: 274-277.

Anonymous (1985) FAO/WHO (1985) Guide to Codex recommendation concerning pesticide residue Part II FAO/WHO Food Standards Programme, Codex Alimentarious Commission, Second Preliminary Issue, CAC/PR2-1985, FAO/WHO, Rome.

Agarwal NS and Agarwal HS (1960) *Chironomis* spp as a pest of Singhara (*Trapa bispinosa*) at Kanpur. Science and Culture 26: 278-279.

Bindra OS and Saxena DK (1964) Studies on insect pests of water-nut with special reference to biology of the Singhara beetle, *Galerucella birmanica* (Jacoby) (Coleoptera; Chrysomelidae). Indian J Hort 21: 85-95.

Kandasamy D, Chendrayan K, Rajukkannu K and Balasubramaniam M (1977) On the variation in the degradation of carbofuran by three soil fungi. Current Science 46: 280-281.

Lee YM and Westcott ND (1980) Direct analysis of carbofuran and 3-hyroxycarbofuran in rape plants by reversed-phase high performance liquid Chromatography. J Agr Fd Chem 28: 719-722.

Misra SS and Agarwal HO (1989) Persistence of aldicarb and carbofuran residues in potatoes grown in Western Plains of India. Trop Pest Management 35: 370-373.

Patnaik MR, Senapati HK, Pal AK and Acharya A (1989) Persistence of carbofuran in betelvine. Indian J Hort 46: 119-121.

Pradhan H, Jotwani MJ and Swaroop P (1964) Relative efficacy of different insecticides to the grub of Singhara beetle, *Galerucella birmanica* Jacoby (Chrysomelidae; Coleoptera). Indian J Ent 26: 92-96.

Rajukkannu K, Raguraj R, Muthuswamy P and Krishnamurthy KK (1976) Residues of certain systematic insecticide in sweet potato tubers. Current Science 45: 35.

Rajukkannu K, Saivaraj K, Vasudevan P and Balasubramanian M (1978) Carbofuran and aldicarb residues in green chillies. Current Science 47: 784.

Rajukkannu K, Venugopal MS, Vasudevan P and Balasubramanian M (1978) Carbofuran residue in banana. Current Science 47: 809-810.

Venkateswarlu K, Gowda TKS and Sethunathan N (1977) Persistence and biodegradation of carbofuran in flooded soils. J Agr Fd Chem 25: 535-536.