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Field appraisal of controlled release formulations of cartap hydrochloride against rice leaf folder (*Cnaphalocrocis medinalis*)

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ABSTRACT

An experiment was conducted during 2005 to study the bioefficacy of controlled release formulations of cartap hydrochloride (2-dimethylaminopropane-1, 3-diol) against the rice leaf folder [*Cnaphalocrocis medinalis* (Guenee)]. Controlled release formulations of insecticide cartap hydrochloride were prepared using commercially available polyvinyl chloride (emulsion and suspension), carboxy methyl cellulose and carboxy methyl cellulose with clay (bentonite, kaolinite and Fullers' earth). These released cartap hydrochloride beyond 45 days as compared to 14 days from its commercial 4G. sodium carboxy Methyl cellulose-Kaolinite-based formulation provided a superior control (3.33%) of rice leaf folder in field grown rice (*Oryza sativa* L.) at half the dose (375 g a i/ha) in comparison to cartap hydrochloride 4 G (5.44%) at 72 days after treatment. The residue of cartap hydrochloride was detected below maximum residue limit of 0.1 mg/kg in grain 72 days after its application.

Key words: Cartap hydrochloride, Controlled release formulation, Polymeric matrices, Rice, Rice leaf folder

Cartap hydrochloride (2-dimethylaminopropane-1, 3-diol) is a systemic insecticide for soil. To achieve control of insects, it is necessary to maintain regulated supply of an appropriate concentration of chemical in the plant rhizosphere. To counter environmental losses and maintain the concentration above the minimum threshold of activity, application of excessive amount of conventional formulation of cartap hydrochloride is required. Increase in application rate, however, results in an increase in the potential adverse impact on the environment. Controlled release formulations can ameliorate pesticide losses due to leaching, evaporation, degradation etc (Fernandez-Perez *et al*. 2000) and thus maintain toxicant levels above the minimum threshold for long. Due to the various advantages, numerous examples are available in literature wherein such products have been effectively employed to combat the pests (Mulqueen 1998, Kumar *et al*. 2003a). Field appraisal of controlled release formulation of phorate and carbofuran against the rice leaf folder [*Cnaphalocrocis medinalis* (Guenee)]. is also reported (Kumar *et al*. 2003).

Rice leaf folder [*C. medinalis* (Guence)] is an important pest of rice and causes severe damage (60–70%) to the crop. It is currently controlled by spraying the crop with thiamethoxam, monocrotophos, aldicarb, carbofuran, profenphos, lambda cyhalothrin, phorate etc. In view of the large area under rice crop in India, its pest problems and insecticide consumption, the controlled release formulations of cartap hydrochloride were developed and evaluated for its efficacy for the management of rice leaf folder along with its commercial formulation 4G (4% ai) in rice (*Oryza sativa* L.) field during the rainy season of 2006 at Indian Agricultural Research Institute, New Delhi.

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MATERIALS AND METHODS

Commercial grade bentonite, kaolinite and Fullers' earth (MCA Industries, New Delhi, India), carboxy methyl cellulose-Na (Merck India Ltd, Mumbai), polyvinyl chloride emulsion and polyvinyl chloride suspension (Choudhary Polycoats, Bahadurgarh, Haryana) were used. Cartap hydrochloride (Technical Grade) with purity of 85% w/w and commercial granules (4% a i) were obtained from its manufacturer M/S Northern Minerals Ltd, Gurgaon. For routine laboratory work, laboratory grade, and for HPLC analysis, analytical grade, chemicals and solvents were employed.

Polyvinyl chloride suspension (PVC-suspension) and polyvinyl chloride emulsion (PVC-emulsion) were prepared as follows:

The polymer (9.529 g), and cartap hydrochloride (0.471 g, 85% purity) were dissolved in dichloromethane. The solution was thoroughly mixed with a metal spatula. The slurry so formed was dried in a Petri-dish to yield a hard mass which after drying was ground in a laboratory Wiley mill and then sieved to obtain granule of size 30/60-mesh size.

A mixture (104.71 g) of sodium carboxy methyl cellulose, clay and cartap hydrochloride technical (85% purity) was prepared in the ratio of 50:50: 4.71 by weight to obtain 4% a i products and was mixed well in a mixer grinder. Water (250.0 ml) was added to it for making dough. For overcoming stickiness, 51.0 ml of aluminium sulphate (0.5 M) was added as a gelling agent. The resultant mass (120.82 g) was dried at 40°C in an oven. The dried mass was ground in a laboratory Wiley mill and sieved to obtain particle of 30/60-mesh size.

To Prepare sodium carboxy methyl cellulose-based formulations one mixture of sodium carboxy methyl cellulose and cartap hydrochloride technical (85% purity) was prepared in the ratio of 100: 4.71 by weight to obtain 4% a i products and was mixed well in a mixer grinder. The mixture was processed as in sodium carboxy methyl cellulose clay-based formulations.

The content of cartap hydrochloride in developed products was estimated. Granules (250 mg) of CMC and CMC-clay-based formulations were treated with acetonitrile (15 ml) in an ultrasound bath for 10 min. This led to the complete disintegration of the granules. After an interval of 2 hr at room temperature, the mixture was sonicated again for 10 min (2 times) and was then filtered quantitatively through a syringe filter (0.2 µm). The volume was made up to 10.0 ml.

A 250 mg sample of PVC-Suspension and PVC –Emulsion was refluxed for 6 h in acetone and filtered. Acetone was removed from the filtrate at 30°C in a rotavapor under reduced pressure. The residue was taken in acetonitrile and was then filtered quantitatively through a syringe filter (0.2 µm). Recovery of cartap hydrochloride from different CR formulations varied from 90.4 to 98.6%.

Cartap hydrochloride was estimated using a Shimadzu high performance liquid chromatograph (HPLC) fitted with SPDM6A Photodiode array detector. Samples were resolved isocratically on a 15 cm × 3.9 mm id RP 18 column using acetonitrile-water (70:30) at 1 ml/min as mobile phase. The absorbance was recorded at 276 nm at sensitivity of 0.05 AUFS by injecting a volume of 20 µl.

It was studied as per Fernandez-Perez *et al*. (2000) and Choudhary *et al.* (2006). For comparison, the term ai release was considered as the amount of active ingredient recorded at a given time. The release was studied in comparison with the commercial granular formulation.

The nursery of 'Pusa Sugandh 3' rice susceptible to rice leaf folder was raised and transplanted during the rainy season of 2005 following a simple randomized block design with 3 replicates. The plot size was 2 m × 2 m. The rows and plants were spaced 20 and 15 cm apart, respectively. All the formulations were broadcast in standing crop 20 days after transplanting. The release of cartap hydrochloride from PVC-Suspension and PVC-emulsion was relatively slower therefore was not included for bioefficacy study. The controlled release formulations (CMC, CMC-Kaolinite, CMC-Bentonite and CMC-Fullers'earth) were evaluated at 10, 5 and 2.5 g/4 m^2; equivalent 750, 375 and 187.5 g a i/ha, respectively and the commercial 4G at 10 g/4 m^2; equivalent 750 a i g/ha only. Per cent leaf folder damage, 27 days after treatment, was recorded by counting the number of damaged leaves/hill, before and after treatment, from 10 randomly selected hills in each plot. Observations were similarly recorded at 27, 42, 57 and 72 days after treatment. The leaf folder damage (%) was calculated as follows:

$$\text{Leaf-folder damage (\%)} = \frac{\text{Damaged leaves/10 hills}}{\text{Total leaves/10 hills}} \times 100$$

Cartap hydrochloride (25 mg) of analytical grade was weighed and dissolved in 50 ml of distilled water in a volumetric flask to make 500 ppm solution. To this solution 5 ml of nickelous chloride solution and 5 ml of concentrated ammonium hydroxide were added and shaken for 30 min. The nereistoxin was extracted twice with 25 ml of n-hexane by the separating funnel, hexane was removed and residue was dissolved in acetonitrile. Convergence of cartap hydrochloride into nereistoxin was confirmed based on their respective retention time 3.86 min. and 4.26 min. by HPLC analysis (Shimadzu). The nereistoxin thus formed was used as standard.

The straw and grain samples at harvest were air-dried at room temperature and stored at –20°C before analysis. The cartap hydrochloride residues in straw and grain were estimated separately. A representative chopped sample (25 g) of straw/ground rice grain (25 g) was homogenized with 200 ml (0.02 M HCl) in a mixer grinder for 15 min. at a high speed. It was filtered through Bückner funnel under suction. The residue was taken back in mixer grinder and extraction repeated with a fresh lot of 200 ml (0.02 M HCl). Each mixture was shaken with 5 ml of 2% nickel chloride solution and 5 ml of concentrated ammonium hydroxide for 15 min. The extracts were combined and the aqueous phase was extracted twice with 100 ml n-hexane. The aqueous layer (lower) was discarded. The organic layer (upper) was filtered dried by passing through 2 cm layer of anhydrous sodium sulphate, concentrated and subjected to GLC analysis.

RESULTS AND DISCUSSION

Release of cartap hydrochloride in soil

Periodic release of cartap hydrochloride from the test polymeric products along with its commercial formulation 4G in soil is presented in Fig 1. The rate of release from controlled release formulations were much slower than commercial formulation 4G, which achieved its maximum

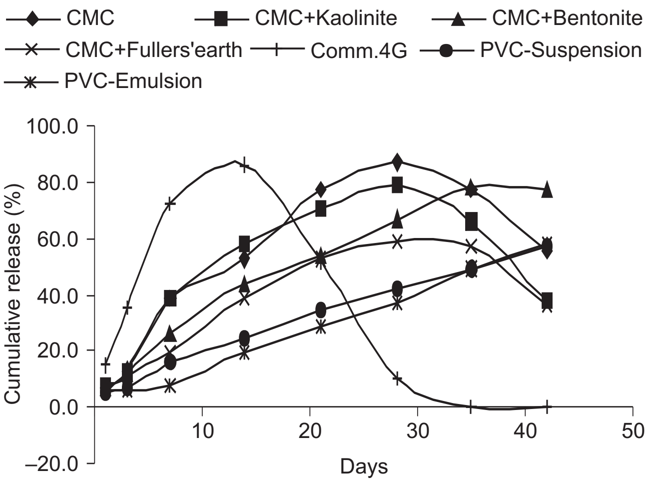

Fig 1 Rate of release of cartap hydrochloride in soil from controlled release and commercial formulations

release of active ingredient by day 12 and 18 in water and soil, respectively after which the ai content decreased, probably because of its degradation. In contrast cartap hydrochloride content increased gradually in all the polymeric formulations. The release followed the order:

Commercial formulation 4G > CMC > CMC-Kaolinite > CMC-Bentonite > CMC-Fullers'earth > PVC emulsion> PVC suspension.

It is apparent that so long as cartap hydrochloride is retained in a stable polymeric structure, it is protected from various biotic and abiotic losses. In case of commercial formulation 4G, the cartap hydrochloride was detectable up to 30 days, whereas in the polymeric formulations, it was available beyond 42 days. Carboxy methyl cellulose released cartap hydrochloride faster than the other polymers, polyvinyl chloride emulsion and polyvinyl chloride suspension being the slowest. Linear release was evident during the first 30 days (CMC and CMC-clay), and 42 days in other polymers. After this, the rate decreased sharply in carboxy methyl cellulose and other carboxy methyl cellulose-clay-based formulations. It appears that on complete release of cartap hydrochloride from the controlled release formulations, its degradation occurred fast in soil (30–42 days) in carboxymethyl cellulose formulations. Carboxy methyl cellulose showing faster release is hydrophilic in nature and is easily biodegradable (Cotterill *et al*. 1996). The hydrophobic polymers with cross-linked matrices such as PVC emulsion and PVC suspension showed slower release. Similar results have been reported with diuron granules based on lignin (Cotterill *et al*. 1996), phorate on polyvinyl, polystyrene, cellulose acetate and polyethylene glycol 6000 (Rao 1992) and butachlor on ethyl cellulose and polyvinyl matrices (Kumar *et al*. 2003a). All CMC-clay formulations showed slower release in comparison to CMC alone up to 28 days. It is evident that the incorporation of clay in CMC slowdowns the release of cartap hydrochloride.

Field evaluation

All the treatments gave a significantly superior control of the pest over the untreated control at 27, 42, 57 and 72 days after transplanting (Table 1). The CMC-Kaolinite @ 10 g (T_5) was significantly superior to all the treatments throughout the observations. The treatments cartap hydrochloride 4G (@ 10 g (T_1), CMC @ 10 g (T_2) and CMC-

Table 1 Bioefficacy of controlled release and commercial cartap hydrochloride 4G formulations against rice folder [*Cnaphalocrocis medinalis* (Guenee)]

Treatment	Pre-treatment count	Folded leaves/10 hills (%)			
		27DAT	42DAT	57 DAT	72DAT
Control	^{a}3.89 (0.47)	^{a}16.89 (8.46)	^{a}23.17(15.50)	^{a} 25.55(18.62)	^{a}26.21(19.52)
T_1 Cartap hydrochloride 4G (10g)	^{a} 3.37(0.27)	^{fg}2.99 (0.27)	^{f}6.16 (1.15)	^{fgh}10.52 (3.34)	^{def}13.47 (5.44)
T_2 CMC(10g)	^{a} 2.49(0.22)	^{fg} 3.15 (0.31)	^{cd}7.75(1.82)	^{fgh} 10.30 (3.20)	^{def} 13.39 (5.38)
T_3 CMC(5g)	^{a} 2.99 (0.24)	^{ef} 3.89 (0.47)	^{c}8.92 (2.41)	^{d}12.19 (4.47)	^{c}15.30(6.97)
T_4 CMC(2.5 g)	^{a} 3.04 (0.28)	$^{d\ e}$4.31(0.57)	^{b}11.03 (3.67)	^{b}15.12 (6.82)	^{b}18.82(10.42)
T_5 CMC-Kaolinite (10g)	^{a} 2.92 (0.26)	^{g}2.21 (0.15)	^{g}5.06 (0.78)	^{i}8.88 (2.39)	^{h}10.51(3.33)
T_6 CMC-Kaolinite (5g)	^{a}3.74(0.447)	^{ef}4.11(0.51)	^{f}6.29 (1.20)	^{gh} 10.13 (3.10)	^{fg}12.22(4.49)
T_7 CMC-Kaolinite (2.5g)	^{a} 3.13 (0.33)	^{d}5.28(0.85)	^{cde}7.99 (1.94)	^{ef}11.14 (3.74)	^{cde}14.13(5.96)
T_8 CMC-Bentonite (10g)	^{a} 2.95 (0.31)	^{fg}3.10(0.29)	^{ef}6.96(1.47)	^{hi}9.68 (2.83)	^{gh}11.10 (3.71)
T_9 CMC-Bentonite (5.0g)	^{a} 3.54(0.38)	$^{d\ e}$4.70(0.67)	^{cd}8.54(2.21)	^{fgh}10.29 (3.19)	^{ef}13.15(5.19)
T_{10} CMC-Bentonite (2.5g)	^{a} 3.57 (0.41)	^{c}6.69(1.36)	^{b}10.52 (3.35)	^{cd}11.94 (4.29)	^{cd}14.59 (6.35)
T_{11} CMC-Fullers'earth (10g)	^{a} 3.02 (0.30)	$^{d\ e}$4.76(0.69)	^{de}7.65(1.77)	^{fg} 10.01 (3.03)	^{f}12.61 (4.77)
T_{12} CMC-Fullers'earth (5.0g)	^{a} 3.35(0.35)	^{c}6.75(1.38)	^{cd}8.65(2.26)	^{fg}10.68(3.44)	^{cd}14.628(6.39)
T_{13} CMC-Fullers'earth (2.5g)	^{a} 3.69(0.42)	^{b}7.97(1.93)	^{b}10.77(3.50)	^{c}13.49 (5.45)	^{b}17.41 (8.97)
Tukey's HSD	2.62	1.11	1.07	0.94	1.41
Prob.>F(trt)	0.83	<.0001	<.0001	<.0001	<.0001

DAT, Days after transplanting; Values in parentheses are mean values

Bentonite @ 10 g (T_8) were statistically at par at 27 days after transplanting and were most effective than other treatments except T_5 which was the best. At 42 days after transplanting, cartap hydrochloride 4G (@ 10 g (T_1) and CMC-Kaolinite @ 5 g (T_6) were at par, followed by CMC-Bentonite @ 10 g (T_8). The treatments CMC @ 2.5 g (T_4), CMC-Bentonite @ 2.5 g (T_{10}) and CMC-Fullers' earth @ 2.5 g (T_{13}) were least effective but significantly superior to control. The treatments CMC-Kaolinite @ 5 g (T_6) and CMC-Bentonite @ 10 g (T_8) provided a superior control than cartap hydrochloride 4G (@ 10 g (T_1) at 52 days after transplanting whereas CMC @ 10 g (T_2), CMC-Bentonite @ 5 g (T_9), CMC-Fullers'earth @ 10 g (T_{11}) and CMC-Fullers'earth @ 5 g (T_{12}) were at par. At 72 days after transplanting, T_5 followed by T_6 and T_{11} were the best treatments. The treatments $T_{1,}$ $T_{2,}$ T_7 and T_9 were statistically at par and better than other treatments (T_3, T_4 and T_{13}). The CMC-Kaolinite @ 2.5 g (T_7) also provided at par control than cartap hydrochloride 4G (@ 10 g (T_1).

Residue of cartap hydrochloride in rice husk and seeds

The cartap hydrochloride residue in rice husk and seeds at harvest are reported in Table 2.The extracts of untreated samples revealed no interference in analysis by GLC under the test conditions. The maximum residue (0.051 mg/kg) of cartap hydrochloride (@ 10 g/4 m^2) in straw was observed in its commercial 4G granules (T_1), followed by CMC (T_2) and CMC-Kaolinite (T_5)which were 0.032 and 0.027 mg/kg, respectively. Amongst the treatments @ 5.0 g/4 m^2, CMC-Fullers'earth (T_{12}) showed the least residue. No residue was recorded in any treatment of 2. 5 g/4 m^2.

At 10 g/4 m^2 rate of application, commercial 4G granules, CMC, CMC-Kaolinite, CMC-Bentonite and CMC-Fullers'earth revealed residues of 0.031, 0.018, 0.015 and 0.011 mg/kg, respectively in the grains. No residue of cartap hydrochloride was detected in seed at harvest at the application rate of 5 g and 2.5 g/4 m^2 plot.

Higher residues at higher rates of application are expected. In case of phorate and imidacloprid, similar observations have been reported by Kumar *et al*. (2003b) and Ramparasad *et al.* (2007), respectively. The estimated residue, both in husk and seed, followed the same pattern. The average residues of cartap hydrochloride were higher in straw than seed in all the treatments. After harvest residue were significantly low in all the treatments. These were lower than maximum residue limit (0.1 mg/kg) assigned in grains. Hence, application of controlled release formulations of cartap hydrochloride can be safely recommended on rice crop for the control of rice leaf-folder *C. medinalis* to minimize the number of applications of pesticide, thus reducing the application cost and load in the environment.

Table 2 Cartap hydrochloride residues in rice straw and seed after harvesting

Treatment	Average residues (mg/kg)	
	Straw	Grain
Control	0.00	0.00
T_1; Cartap hydrochloride 4G (10 g)	0.051	0.031
T_2; CMC (10 g)	0.032	0.020
T_3; CMC (5 g)	0.012	ND
T_4; CMC (2.5 g)	ND	ND
T_5; CMC-Kaolinite (10 g)	0.027	0.018
T_6; CMC-Kaolinite (5 g)	0.011	ND
T_7; CMC-Kaolinite (2.5 g)	ND	ND
T_8; CMC-Bentonite (10 g)	0.024	0.015
T_9; CMC-Bentonite (5.0 g)	0.010	ND
T_{10}; CMC-Bentonite (2.5 g)	ND	ND
T_{11}; CMC-Fullers' earth (10 g)	0.020	0.011
T_{12}; CMC-Fullers' earth (5.0 g)	ND	ND
T_{13}; CMC-Fullers' earth (2.5 g)	ND	ND

ND, Not detectable; CMC, sodium carboxy methyl cellulose

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