Indian Journal of Agricultural Sciences **80** (7): 636–9, July 2010

Field appraisal of slow release formulations of acephate against mustard aphid (*Lipaphis erysimi*)

JITENDRA KUMAR[1], K NISAR[2], DEBJANI DEY[3], N A SHAKIL[4], PANKAJ[5] and SURESH WALIA[6]

Indian Agricultural Research Institute, New Delhi 110 012

Received: 25 September 2009; Accepted: 30 April 2010

ABSTRACT

An experiment was conducted during 2007 to study the bioefficacy of slow release formulations of acephate against mustard aphid (*Lipaphis erysimi* Kalt.). Slow release formulations of insecticide acephate have been prepared using commercially available polyvinyl chloride, carboxy methyl cellulose and carboxy methyl cellulose with kaolinite. These released Acephate beyond 63 days as compared to 28 days from its commercial 75 DF CMC-Kaolinite-based formulation provided a superior control (3.63%) of mustard aphid in field grown mustard (*Brassica campestris* L.) in comparison to acephate 75 DF (4.86%) at the dose (584 g a i/ha) after 72 days of treatment. The residue of acephate was not detected in any treatment.

Key words: Acephate, *Lipaphis erysimi*,Mustard, Polymeric matrices, Slow release formulation

Acephate (O, S-dimethyl acetylphosphoramidothioate), is a broad-spectrum 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 acephate 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 and degradation etc. (Fernandez-Perez *et al.* 2000) and thus maintain toxicant levels above the minimum threshold for long. Due to various advantages, numerous examples are available in literature wherein such products have been effectively employed to combat the pests (Kumar *et al*. 2003a, Kumar *et al*. 2003b, 2006).

Mustard is an important oilseed crop of India and mustard aphid [*Lipaphis erysimi* (Kalt.)] is one of the serious pests of mustard (*Brassica campestris* L.), turnip (*B. rapa* L.) and radish (*Raphanus sativus* L.) inflicting as high as 97.6% yield loss in different varieties of mustard (Patel *et al*. 2004).

In view of the yield losses due to aphids in mustard crop in India and insecticide consumption, the controlled release formulations of acephate were developed and evaluated for its efficacy in controlling the mustard aphids.

MATERIALS AND METHODS

Commercial grade kaolinite (MCA Industries, New Delhi, India), carboxy methyl cellulose-Na (Merck India Ltd., Mumbai), polyvinyl chloride (Choudhary Polycoats, Bahadurgarh, Haryana) were used. Acephate (purity; 97% w/w) and commercial formulation 75 DF were obtained from its manufacturer M/s Rallis India Ltd, Agrochemical Division, Ratnagiri. For routine laboratory work, laboratory grade, and for HPLC analysis, analytical grade, chemicals and solvents were employed.

To prepare polyvinyl chloride (AC-PVC-3) polymer (200 g) and acephate (6.19 g, 97% purity) were dissolved in a compatible organic solvent. 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.

Sodium carboxy methyl cellulose – kaolinite formulations (AC-CMC-KAO-3) was prepared by a mixture (103.71 g) of sodium carboxy methyl cellulose, kaolinite and acephate technical (purity; 97% w/w) in the ratio of 50: 50: 3.71 by weight to obtain 3% ai products and was mixed well in a

[1]Senior Scientist (e mail: jitendrakumar7@yahoo.com), [2]SRF (e mail: hellonisar@yahoo.com), [4]Senior Scientist (e mail: iamshakil@gmail.com), [6]Principal Scientist (e mail: suresh_walia@yahoo.com), Division of Agricultural Chemicals;

[3]Principal Scientist (e mail: ddeyiari@hotmail.com), Division of Entomology;

[5]Senior Scientist (e mail: pankaj_nema@yahoo.com), Division of Nematology

mixer grinder. Water (250 ml) was added to it for making dough. For removing stickiness, 51.0 ml of aluminum phosphate (0.5 M) was added to it as gelling agent. The resultant mass was dried at 40°C in an oven for 2 hr. After drying, the mass (119.80 g) was ground in a laboratory Wiley mill and then sieved to obtain particle of size of 30/60.

A mixture of sodium carboxy methyl cellulose and acephate technical (3.71 g, 97% purity) was prepared in the ratio of 100: 3.71 by weight to obtain sodium carboxy methyl cellulose (CMC) formulations (AC-CMC-3) containing 3% active ingredient in final product and was mixed well in a mixer grinder. The mixture was further processed as in sodium carboxy methyl cellulose – kaolinite-based formulations.

To analyze acephate in test formulations, the granules (250.0 mg) of CMC and CMC–kaolinite-based formulations were mixed with acetonitrile (15.0 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 was refluxed for 6 hr 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).

Acephate was estimated using a Shimadzu high performance liquid chromatograph (HPLC) fitted with SPDM6A photodiode array detector was used. Samples were resolved isocratically on a 15 cm × 3.9 mm id RP 18 column (Merck) using acetonitrile-water (70: 30) at 0.5 mL/min as mobile phase. The absorbance was recorded at 217 nm at sensitivity of 0.05 AUFS by injecting a volume of 20 µl.

Release of acephate in soil was studied as per Fernandez-Perez *et al*. (2000) and Choudhary *et al*. (2006). For comparison, the term active ingredient 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 release data was subjected to the empirical equation (Ritger and Peppas 1987) for calculating the diffusion exponents.

$$M_t/M_o = Kt^n \quad \ldots (1)$$

Where M_t/M_o is the fraction of active ingredient released at time t, K is a constant that incorporates characteristics (porosity, tortuosity) of the macro molecular network system and the active ingredients, and n, a diffusional parameter which is indicative of the transport mechanism. The model was fitted by taking logarithm on both sides of equation (I)

$$\log_e M_t/M_o = \log_e K + n \log_e t + e \quad \ldots (2)$$

The values of K and n were determined from acephate release. From the constants, $T_{1/2}$ (time taken for release of 50% of initial acephate) was calculated as per the equation.

$$T_{1/2} = (50/K)^{1/n} \quad \ldots (3)$$

The seeds of mustard variety 'Pusa Bold', moderately susceptible to mustard aphid (*L. erysimi*), was obtained from the Division of Entomology, IARI and sown during winter (*rabi*) season (2007) in a simple randomized block design, in plot size of 9 m × 9 m replicated thrice. In each plot the row-to-row distance was 30 cm and plant-to-plant 10 cm, which were maintained by thinning.

All the formulations were applied in furrows along with seeds at the time of sowing. The controlled release formulations- AC-PVC-3 [146 (T_1), 292 (T_2), 584 (T_3) g ai/ ha] CMC-3 [146 (T_4), 292 (T_5), 584 (T_6) g ai/ ha] and AC-CMC-KAO-3 [146 (T_7), 292 (T_8), 584 (T_9) g ai/ha] were evaluated at (4.4, 8.8 and 17.6 g 9/m^2) respectively and the commercial 75 DF (T_{10}) at (17.6 g 9/m^2; equivalent 584 g ai/ha) only. The bioefficacy of controlled release formulations and commercial formulation (75% DF) were recorded at 60, 70, 80, 90, 100 and 110 days after sowing. The number of aphids *(L. erysimi)* present on 10 randomly selected 10 cm long inflorescence shoot/plot was counted. The data on population counts of *L. erysimi* was recorded regularly for the control and was used for calculation of per cent reduction of pest population over control using modified Abbott's formula. The reduction percentage was transformed into Arcsine values and subjected to analysis of variance.

To estimate the acephate residue, the mustard seed samples at harvest were air-dried at room temperature and stored at –20°C before analysis for acephate residues. A representative sample of the seed (25 g) was homogenized in a mixer grinder for 5 min. at a high speed. It was transferred into a Soxhlet extraction thimble. The thimble was placed in an extractor fitted to a 500 ml, round-bottomed flask containing hexane and acetonitrile. Some boiling chips were added to prevent the bumping and the extraction was continued for 6 hr. The hexane fraction (upper layer) was separated out. The acetonitrile fraction (lower layer) was again partitioned with hexane for removing the fatty materials, filtered, decolourised with activated charcoal (to remove the yellow colouration) dried by passing through 2 cm layer of anhydrous sodium sulphate, concentrated and subjected to GLC analysis.

RESULTS AND DISCUSSION

Release of acephate in soil: The rate of release of acephate in soil from the polymer/ polymer-kaolinite based controlled released and commercial 75 DF formulations is shown in Fig 1. The commercial 75 DF showed its maximum release on day 14 after which the active ingredient content started decreasing. It became non-detectable after day 42 of soil release analysis. In contrast, the amount of release of acephate increased gradually in case of polymeric/ polymeric-clay formulations between 28 and 35 days. The AC-CMC-3 formulation showed its maximum release on day 28, whereas AC-CMC-KAO-3 and AC-PVC-3 and CMC-Fuller's earth showed its maximum release on day 35 and day 56,

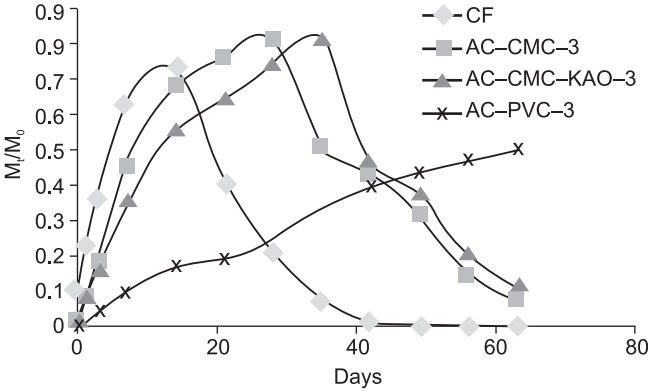

Fig 1 Rate of release of acephate in soil from controlled release and commercial formulations

respectively. In case of AC-CMC-3, the concentration of acephate was lesser than AC-CMC-KAO-3.The soil release pattern of acephate reveals that the polymer/clay polymers protected acephate from its degradation in soil. As long as acephate is entrapped in a stable polymeric structure, it is protected from, microbes attack and other atmospheric and climatic degradation agents such as sunlight, water, oxygen, hydrolysis, oxidation and reduction.

The $t_{1/2}$ of acephate in commercial 75 DF formulations was found 2.98 days (Table 1). The release of acephate followed first order kinetics. The $t_{1/2}$ value of different controlled release formulations ranged from 2.98 to 76.38 days in soil. In order of increasing $t_{1/2}$ values, the various formulations revealed the following order:

Commercial granule 75 DF > AC-CMC-3 > AC-CMC-KAO-3 > AC-PVC-3

The value of $t_{1/2}$ of acephate in biodegradable polymers such as CMC, CMC-Kaolinite, 9.21 and 12.98 days and for PVC, non-biodegradable polymer, was more than 76.38 days in water, implying very slow release.

It appears that on complete release of acephate from the controlled release formulations, its degradation occurred fast in soil (30–42 days) in carboxymethyl cellulose formulations.

Table 1 Constants derived from fitting of empirical equation $M_t/M_o = Kt^n$ to release data of acephate in soil from controlled release and commercial formulations

Formulation	Log k	n	R-square	Prob. >F	1/n	k	$t_{1/2}$ (days)
AC-PVC-3	2.091(0.638)	0.420(0.21)	0.286	0.073	2.380952	8.093004	76.38
AC-CMC-3	1.998 (0.031)	0.532 (0.013)	0.675	0.001	1.886	89.29	9.21
AC-CMC-KAO-3	2.424(0.749)	0.515(0.236)	0.736	0.318	1.960	52.56235	12.98
Commercial 75DF	4.51(1.077)	–0.547(0.387)	0.250	0.207	–1.82815	90.92182	2.98

Table 2 Bioefficacy of controlled release and commercial 75 DF formulations of acephate against mustard aphid

Treatment	60 DAS	70 DAS	80 DAS	90 DAS	100 DAS	110 DAS
AC-PVC-3 @146 g ai/ha (T_1)	19.23^{ab}(4.38)	31.90^{bc}(5.63)	200.00^{bc}(14.13)	319.37^{bc}(17.87)	115.77^{ab}(10.76)	41.07^{abc}(6.41)
AC-PVC-3 @292 g ai/ha (T_2)	16.53^{bc}(4.06)	28.49^{cd}(5.33)	184.10^{bcd}(13.56)	306.57^{cd}(17.51)	111.13^{abc}(10.54)	40.87^{abc}(6.39)
AC-PVC-3 @584 g ai/ha (T_3)	9.60^{ef}(3.08)	18.08 g^{h}(4.25)	151.90^{de}(12.32)	179.57 g^{h}(13.40)	89.67^{ef}(9.47)	37.49^{c}(6.12)
AC-CMC-3 @146 g ai/ha (T_4)	19.13^{ab}(4.37)	34.01^{b}(5.83)	225.00^{b}(14.99)	348.27^{ab}(18.66)	119.60^{ab}(10.93)	42.10^{ab}(6.49)
AC-CMC-3 @292 g ai/ha (T_5)	11.07^{de}(3.32)	23.02^{ef}(4.80)	165.70^{cde}(12.87)	216.83^{f}(14.72)	104.80^{bcd}(10.24)	39.03^{bc}(6.25)
AC-CMC-3 @584 g ai/ha (T_6)	7.87^{fg}(2.80)	15.94^{hi}(3.99)	160.80^{cde}(12.68)	200.97^{fg}(14.17)	99.40^{cde}(9.96)	38.50^{bc}(6.20)
AC-CMC-KAO-3 @146 g ai/ha (T_7)	13.63^{cd}(3.69)	24.81^{de}(4.98)	181.83^{cde}(13.48)	289.83^{d}(17.02)	109.47^{abcd}(10.46)	40.57^{abc}(6.37)
AC-CMC-KAO-3 @292 g ai/ha (T_8)	9.30^{ef}(3.03)	20.30^{fg}(4.50	159.23^{de}(12.62)	186.27 g^{h}(13.65)	95.00^{def}(9.74)	37.87^{c}(6.15)
AC-CMC-KAO-3 @584 g ai/ha (T_9)	6.00 g(2.44)	13.22^{i}(3.63)	138.00^{e}(11.75)	169.77^{h}(13.03)	82.80^{f}(9.10)	33.65^{d}(5.79)
Commercial 75% DF @584 g ai/ha (T_{10})	13.37^{cd}(3.65)	23.62^{ef}(4.86)	173.50^{cde}(13.17)	238.30^{e}(15.44)	109.37^{abcd}(10.46)	40.47^{abc}(6.37)
Control (T_{11})	22.10^{a}(4.70)	42.27^{a}(6.50)	275.07^{a}(16.56)	363.43^{a}(19.06)	124.83^{a}(11.17)	44.12^{a}(6.64)

Means with the same letter are not significantly different
Values in parentheses are transformed values

Carboxy methyl cellulose showing faster release is hydrophilic in nature and is easily biodegradable (Cotterill *et al*. 1996). The hydrophobic cross-linked polymers, 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 chloride (Kumar *et al*. 2003a). The CMC–kaolinite 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 acephate.

As infestation of mustard aphid is maximum from January to February in India. The bioefficacy data of all test formulations is reported in Table 2. Most of the insecticidal treatments except T_1 and T_4 caused a significant reduction in aphid population as compared to control. T_9 (AC-CMC-KAO-3 @ 584 g ai/ha) was the most effective treatment at both 60 and 110 days after sowing, followed by T_3, T_8, T_5, T_6 and others. T_1 and T_4 at 60 days after sowing were at par with control. The remaining treatments were in between in performance. The aphid population was invariably lower at 100 and 110 days after sowing, as compared with the corresponding value at 80 and 90 days after sowing. All treatments of controlled release formulations employing 584 g ai/ha were at par at 70–90 days after sowing and were significantly superior over control. T_9 was the most effective formulation at 110 days after sowing, followed by T_3 and T_8. Amongst the 292 g ai/ha treatments, T_8 was the most effective, followed by T_5 at 60 days after sowing and 110 days after sowing but T_2 and T_5 were at par at 110 days after sowing. The controlled release formulation @ 146 g ai/ha treatments, T_7 was the most effective though at par with T_1 and T_5 at 60 and 70 days after sowing. All the treatments employing 146 g ai/ha were at par 100 and 110 days after sowing. The effect in all treatments improved with increase in dose of ai.

The acephate residue in seeds at harvest was carried out. The extracts of untreated samples revealed no interference in analysis by GLC under the test conditions. No residue was recorded in any treatment. Therefore, application of controlled release formulations of acephate can be safely recommended on mustard crop for the control of *L. erysimi* to minimize the number of applications of pesticide, thus reducing the application cost and load in the environment.

REFERENCES

Choudhary G, Kumar J, Walia S, Parsad R and Parmar B S. 2006. Development of controlled release formulations of carbofuran and evaluation of their efficacy against *Meloidogyne incognita*. *Journal of Agricultural and Food Chemistry* (USA) **54**: 4727–33.

Cotterill J V, Wilkins R M and Dasilva F T 1996. Controlled release of diuron from granules based on a lignin matrix system. *Journal of Controlled Release* **40**: 133–42.

Fernandez-Perez M, Villafranca-Sanchez M, Gonzalez-Pradas E, Martinez-Lopez and Flores-Cespedes F. 2000. Controlled release of carbofuran from an alginate bentonite formulation water release kinetics and soil mobility. *Journal of Agricultural and Food Chemistry* (USA), **48** (3): 938– 43.

Kumar J, Singh G, Walia S, Prasad R and Parmar B S. 2003 (a). Controlled release formulations of butachlor: soil release and bioefficacy against *Ecinochloa colonum*. *Indian Journal of Agricultural Sciences* **73** (8): 441–5.

Kumar J, Chalapathi Rao, N B V, Singh V S and Parmar B S. 2003 (b). Field appraisal of controlled release formulation of phorate against the mustard leaf folder, *Cnaphalocrocis medinalis* (Guenee). *Annals of Plant Protection Sci*ences **11** (1): 129–33.

Kumar J, Singh G, Walia S, Jain S and Parmar B S. 2004. Controlled release formulations of imidacloprid: water and soil release kinetics. *Pesticide Research Journal* **16** (1): 19–23.

Kumar J, Singh G, Walia S, Jain S and Parmar B S. 2006. Field appraisal of controlled release formulation of carbofuran against the mustard leaf folder, *Cnaphalocrocis medinalis* (Guenee) *Indian Journal of Agricultural Sciences* **76** (12): 732–5.

Patel S R, Awasthi A K and Tomar R K S. 2004. Assessment of yield losses in mustard (*Brassica juncea* L.) due to mustard aphid *Lipaphis erysimi* (Kalt.) under different thermal environment in Eastern Central India. *Applied Ecology and Environmental Research* **2**: 1–5.

Rao K N 1992 'Development and appraisal of controlled release formulation of phorate'. Ph D thesis, Indian Agricultural Research Institute, New Delhi.