Pakistan J. Sci. Ind. Res., Vol. 30, No. 2, February 1987

# THE PERSISTENCE OF SOME ORGANOPHOSPHATE, CARBAMATE AND PYRETHROID INSECTICIDES ON ALFALFA (*MEDICAGO SATIVA*)

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(Received March 24, 1986; revised October 5, 1986)

The persistence of dichlorvos, carbaryl, pirimicarb and cypermethrin insecticides was studied on the alfalfa crop. Dichlorvos, carbaryl and cypermethrin, each at 0.2% and pirimicarb at 0.1% concentration were applied to the leaves of the crop. Samples for residue analysis were collected at 0, 1, 2, 4, 8, 10, 14 and 17 days post-treatment. The samples were extracted for residues and analysed on gas liquid chromatograph.

The degree of persistence, in terms of residual life, amongst the insecticides tested was on cypermethrin > carbaryl > pirimicarb > dichlorvos. Residues of carbaryl subsided well below the tolerance limit (100 ppm) one day after application while that of dichlorvos reached the tolerance limit (0.5 ppm) 2 days after application to the alfalfa crop.

Key words: Insecticies; Residues; Medicago sativa.

## INTRODUCTION

Alfalfa (Medicago sativa)<sub>1</sub> like other agricultural crops, is liable to insect-pest infestation. A large number of pesticides are being used for controlling the onslaught of crops by insectpests [8, 14]. However, the increasing trend of pesticides application to crops has been noticed with a rising concern over the possible deleterious effect of pesticides on consumers and the environment as a whole [15].

Recent advances in the area of pesticides have resulted in the development of less persistent and more selective pesticides. Chemicals which have attracted particular attention in this respect are the organophosphate, carbamate and pyrethroid insecticides. The persistence and toxicities of organophosphate and carbamate insecticides have been stuided and compared on different agricultural crops [6, 12, 14]. Synthetic pyrethroids are effective insect-pests control agents but the scope of their use is limited by high cost [9, 10]. The excellent potential of pyrethriods for insect-pests control in crops has been demonstrated by a number of researchers [3, 4, 7, 13].

The type of studies mentioned above have not been conducted on alfalfa, the main forage crop in the Kingdom of Saudi Arabia, where these insecticides are being used frequently. The main purpose of the present investigations was to study the persistence of three kinds of pesticides: organophosphates (dichlorvos); carbamates (Carbary, Pirimicarb); and pyrethriods (Cypermethrin) on alfalfa at different intervals after application. It is anticipated that these studies will help in the selection of the right kind of insecticide for alfalfa pest control and identify the safe period for harvesting the crop after treatment with the above mentioned insecticides.

#### MATERIALS AND METHODS

A field experiment was conducted on the persistnece of some organophosphate, carbamate and pyrethriod insecticides on alfalfa crop at Al-Kharj Agricultural Research Station during the year 1984-85.

- Pesticides used
- Dichlorvos (NOGOS 50% EC):

2, 2, dichlorovinyl dimethyl phosphate

R Carbaryl (Sevin 85% WP):

1-Napthyl N-methyl carbamate

Pirimicarb (Pirimor 50% WP):

2-dimetyl amino-5, 6-dimethyl pyrimidine-4-yl dimethyl carbamate

Cypermethrin (Cymbush 5% EC):

(RS)  $\alpha$  cyano-3-phenoxy benzyl (IRS)-cis-trans-3-(2, 2dichlorovinyl)-, 1, 1-dimethylcyclopropanecarboxylate

Treatment and sampling. Dichlorvos, carbaryl, and cypermethrin insecticides were foliarly applied to alfalfa (15-20 cm high) each at 0.2% concentration while pirimicarb was sprayed on the crop at 0.1% concentration. Each

treatment plot  $(5 \times 4.5 \text{ m})$  was repeated and left in between two rows unprayed. In addition, two plots were left unsprayed to serve as control. All insecticides were applied with a knapsack sprayer.

One kg sample of fresh alfalfa above the soil surface was taken randomly from the middle, length-wise strip of each treated and control plots at 0, 1, 2, 8, 10, 14 and 17 days post treatment for residue analysis. The samples were stored at  $-40^{\circ}$  for residue analysis, immediately after collecting from the field.

Residue analysis. Extraction: After a short period of thawing, 25.0 g. of the chopped alfalfa sample was blended with 150 ml of aqueous acetone (1:1) in a Waring blender at high speed for 3 min. The liquid extract was decanted and suction-filtered through a Buchner funnel with a 7 cm. whatman (No. 4) filter paper. The blending process was repeated for the alfalfa residue in the jar. After the second blending, the liquid extract and alfalfa residue was transferred to the Buchner funnel and washed down with additional 50 ml aqueous acetone (1:1). The combined liquid extracts were transferred to a separatory funnel and further extracted three times with 30 ml each of chloroform. The chloroform extracts were received through anhydrous Na<sub>2</sub>SO<sub>4</sub> and rotarily evaported to dryness at 40<sup>0</sup>.

*Clean-up.* The sample extract was cooled in the refrigerator and transferred to separatory funnel by washing ten times with 5 ml each of cold agueous acetone (1:1) on filter paper and allowed to reach room temperature. The aqueous acetone washings were extracted with chloroform and collected through anhydrous sodium sulphate and evaporated to dryness under vacuum [2].

Gas chromatography. A Hewlett-Packard Model 5830A gas chromatograph equipped with ECD ( $Ni^{63}$ ) and alkali flame ionization detector (AFID) were used for

residue analysis. A glass column (1.8 m x 4.0 mm id), packed with 3% OV-101 on 100-120 mesh WHP was used for dichlorvos, pirimicarb and carbaryl analysis on alkali flame ionization detector. The GC was operated at an injector temperature  $210^{\circ}$ , column temperature of  $150^{\circ}$ (dichlorvos) and  $200^{\circ}$  for pirimicarb and carbaryl, at detector temperature  $300^{\circ}$  with helium carrier gas at a flow rate of 35 ml/min. Hydrogen and air flow rates were 30 and 50 ml/min. respectively. ECD (Ni<sup>63</sup>) was used for cypermethrin analysis on column 5% OV-225. The operating temperatures were: injection port,  $235^{\circ}$ ; column,  $230^{\circ}$ ; and ECD  $300^{\circ}$  with 95% argon -5% methane (carrier gas) at a flow rate of 50 ml/min.

Under these conditions, the retention times were: dichlorvos, 2.05 min.; pirimicarb, 3.15 min.; carbaryl, 5.34 min.; and cypermethrin, 6.16, and 6.85 min. for cis and trans isomers respectivley. The reliability of the analytical method was tested by fortifying the untreated alfalfa sample with known amounts (5  $\mu$ g, 10  $\mu$ g) of dichlorvos, pirimicarb, carbaryl and cypermethrin insecticides. Recovery of the tested insecticides ranged at 80-97%. The results were calculated for individual insecticides from the area displayed by the electronic integrater and statistically analyzed in accordance with the methods recommended by Snedecor and Cochran [11].

#### **RESULTS AND DISCUSSION**

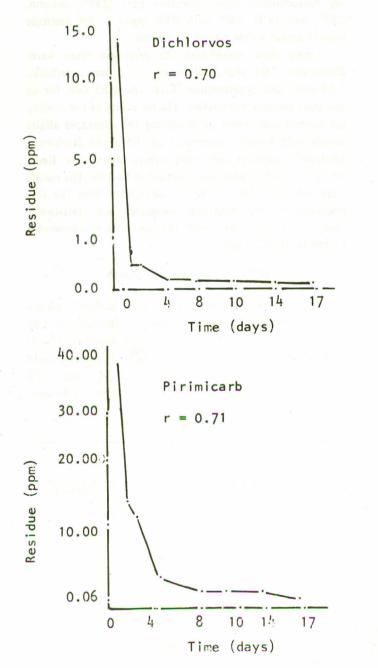
The residual amount of dichlorvos, carbaryl, pirimicarb and cypermethrin insecticides as a function of time after application to alfalfa crop is presented in Table 1. Alfalfa samples collected on the day of the treatment contained high residues of 14.56, 106.34, 36.85 and 10.50 ppm for dichlorvos, carbaryl, pirimicarb and cyper-

Days after treatment	Average maximum temperature ( <sup>o</sup> C)	Average relative humidity (%)	Residue (ppm*)			
			Dichlorvos	Carbaryl	Pirimicarb	Cypermethrin
0	12.6	40	14.6	106.34	36.85	10.5
1	12.8	30	0.51	77.15	14.70	8.68
2	13.7	30 000	0.42	43.33	11.65	8.35
4	14.0	36	ND	36.21	2.20	6.51
8	11.5	50	ND	16.03	0.21	3.83
10	11.6	54	ND	10.84	0.18	3.45
14	12.5	43	ND	8.70	0.10	2.93
17	17.5	42	ND	7.64	0.06	2.01

Table 1. Residual amounts of insecticides at different intervals after application to alfalfa

\*Average of four replicates ND = Not detectable

methrin, respectively. The high percentage of pirimicarb residues might have been due to the fact that the insecticide is readily taken up through the root system on account of its systemic properties. Decline of all the residues started one day after application which was more pronounced in the case of dichlorvos (97%). A sharp decrease in the residues of carbaryl, pirimicarb and cypermethrin was obtained between 4 and 8 days after treatment when precipitation (4.7 mm) was received during the period of the experiment.



Statistical analysis of the data indicated a significant negative correlation (r = -0.84) between the time after spraying and the amount of carbaryl residues. Similar correlations (Fig. 1) were established for pirimicarb (r = -0.71), cypermethrin (r = -0.95) and dichlorvos (r = -0.70). However, no correlation could be established between temperature, relative humidity and the loss of insecticide residues. This might be due to a very narrow range of variations in temperatures and relative humidity prevailing during the experimental period. The effect of high temperature.

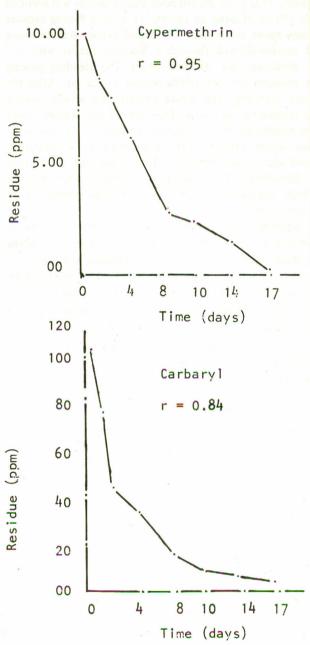


Fig. 1. Decreasing trends of dichlorvos cypermethrin, pirimicarb and carbaryl residues in alfalfa with time after spraying.

ture on the absorption of some of the organophosphate insecticides has been observed [1].

The magnitude of residues durign the 17-day experimental period, with the precipitation indicated in the preceding paragraph, revealed a decrease of 93%, 99.8% and 81% for carbaryl, pirimicarb and cypermethrin, respectively. This showed cypermethrin as comparatively more persistent and displayed more gradual decrease with time amongst the 4 insecticides tested. Residues of dichlorvos on alfalfa reduced well below the maximum resudue limit of 0.5 ppm [5] at two days after application. The dichlorvos residues were not detectable (< 2  $\mu$ g) at 4 days after treatment. However, signs of phytotoxicity developed on the treated crop which lasted for 14 days after application. The persistence of cypermethrin for longer periods is reasonable in view of Bostanian et al's [3] studies on the residues of 4-synthetic pyrethroids on apple foliage. Residues of carbaryl reached well below the tolerance limit of 100 ppm [5] just in two days after application. Among carbaryl and pirimicarb, the latter was found to be the least persistent which is in line with the findings of Szeto [12]. The maximum permissible levels for pirimicarb and cypermethrin have, however, not yet been established.

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