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Residues and persistence of some organophosphorus insecticides applied to cabbage plants

M. A. Abo-El-Seoud,[a] A. M. Shams-El-Din[b], L. N. Danial[a] & S. M. Ahmed[b]

[a]*Agric. Dept. of Soils and Water Res., Atomic Energy Authority, Inshas, Egypt*
[b]*Plant Protection Dept., Fac. of Agriculture, Moshtohor, Egypt*

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Cabbage plants grown in a field experiment were sprayed with E. C. formulations of malathion, pirimiphos-methyl and prothiofos at the rates of 570, 600 and 750 *g a.i. per feddan*; residues of the three insecticides were analysed by GLC. Results revealed that initial deposits varied; the highest deposit was that of malathion followed by pirimiphos-methyl, and the lowest initial deposit was that of prothiofos. Initial deposits on inner leaves were less than the outer leaves. Prothiofos showed more persistence than malathion, the least persistent toxicant was pirimiphos-methyl. Persistence of the toxicants was lower on inner leaves, probably owing to lower initial deposits. Deposits were within the permissible limits after 12, 12 and 15 days for malathion, pirimiphos-methyl and prothiofos, respectively, while on inner leaves, these intervals were 6, 8 and 12 days for the same insecticides, respectively.

INTRODUCTION

Integrated Pest Management (IPM) programmes were introduced in order to minimize dependence solely on chemical control for pests because of undesirable side effects on the environment. Such effects would include the health hazards of human exposure to traces of these toxicants which may have no acute effect, but chronic exposure could result in serious health hazards. Unfortunately, no IPM programmes have been developed for most of the vegetable crops in Egypt. Accordingly it is imperative to determine the time interval between insecticidal application and harvest, needed for the residues of insecticides to fall below the tolerance limits indicated either by national (EPA) or international (FAO–WHO joint committee) organizations.

Cabbage is a popular vegetable crop in Egypt, which is grown in more than one season and usually attacked by aphids, white flies and several species of lepidopterous larvae. Three insecticides are recommended for use on this crop: malathion against aphids, prothiofos and pirimiphos-methyl against mixed infestations. Various researches have been carried out to identify and estimate the deposit and residues of malathion (Trabulsi & Kamel 1983; Jacob & Verma, 1984; Ahmed *et al.*, 1991), prothiofos (Hadjidemetrious, 1988; Hegazy *et al.*, 1988; Al-Samariee *et al.*, 1988) and pirimiphos-methyl (Ahmed *et al.*, 1991; Talekar *et al.*, 1977; Nikolov, 1980). However, no information on the residual persistence of these compounds on cabbage is known to the authors. The present work was designed to investigate the residues of malathion, prothiofos and pirimiphos-methyl on and in the outer and inner leaves of cabbage plants so as to determine the interval between spraying and harvest required for the safe use of this crop.

MATERIALS AND METHODS

Insecticides

Malathion. *S*-1,2-bis(Ethoxycarbonyl)ethyl-*O*,*O*-dimethyl phosphorodithioate. It was used in the form of the E.C. formulation under the trade name of Carbofos, 57% a.i. at the recommended dose of 1 litre/feddan.

Pirimiphos-methyl. *O*-(2-Diethylamino-6-methyl pyrimidin-4-yl *O*,*O*-dimethyl phosphorothioate. It was used in the form of the E.C. formulation under the trade name of Actellic 50% a.i. at the recommended rate of 1·2 litre/feddan.

Prothiofos. *O*-2,4-Dichlorophenyl-*O*-ethyl-*S*-propyl phosphorodithioate. It was used in the form of the E.C. formulation under the trade name of Tokuthion 50% a.i. at the recommended rate of 1.5 litre/feddan.

Spraying and sampling

Cabbage plants (Brunswick variety) were transplanted in field plots in areas of 3 × 3·5 m. Each plot contained

Table 1. Residues and persistance of some organophosphorus insecticides in the outer leaves of cabbage plant

Time after application (h)	Malathion		Pirimiphos-methyl		Prothiofos	
	Concentration (ppm)	% of loss	Concentration (ppm)	% of loss	Concentration (ppm)	% of loss
1	47·3 ± 1·50	0·00	41·6 ± 1·71	0·00	36·2 ± 2·74	0·00
24	36·2 ± 1·26	34·2	28·3 ± 1·53	32·04	27·8 ± 1·28	23·1
72	22·0 ± 0·26	53·6	11·4 ± 0·71	72·71	20·1 ± 1·38	44·6
144	14·3 ± 1·17	69·9	2·88 ± 0·26	93·31	9·53 ± 1·59	73·7
216	7·34 ± 0·87	84·5	2·07 ± 0·45	95·03	6·08 ± 1·08	83·2
288	1·70 ± 0·29	96·4	0·99 ± 0·26	99·38	2·13 ± 0·66	94·1
360	UND	—	UND	—	UND	—

UND: Undetectable by the method used in this work.

around 25 plants. The growing plants were treated with the pesticides under investigation at the recommended doses after the formation of plant heads. For each pesticide, three plots were used and the plots were distributed in a completely randomized pattern.

Representative samples were taken randomly after 1, 24, 72, 144, 216, 288 and 360 h of spraying for the outer leaves. However, samples from the inner leaves were taken after 1, 144 and 216 h of pesticides application. The collected samples were placed in a deep freezer at −18°C until analysis.

Determination of pesticide residues

Extraction. Pesticide residues were extracted according to the procedures of Steinwandter (1985) and concentrated under vacuum to 2–3 ml.

Clean up. The concentrated extract was transferred quantitatively to a glass beaker with 20 ml of *n*-hexane and mixed with 5–10 g activated charcoal and 2 g anhydrous sodium sulphate and the slurry was allowed to settle. The clear layer of the slurry was transferred to a suitable chromatographic column (fitted with a stopcock and packed with silica gel) and allowed to pass slowly through the column (30 drops/min). The charcoal was washed 6 times with 20 ml *n*-hexane each and passed through the column. The combined extract was evaporated under vacuum to dryness and transferred quantitatively with *n*-hexane to a 10 ml volumetric flask to be used for injection in the GC.

Gas chromatography injection. A PYE unicam series 304 GC equipped with N/P detector and Pyrex glass column packed with OV.17 on 80/100 mesh chromosorb was used for determination of pesticide residues. The applied temperature was 260, 255 and 265°C for injection, column and detector, respectively. Flow rate of nitrogen carrier gas was 30 ml/min. Under these conditions, the retention times were 2·99, 2·90 and 4·80 minutes for malathion, pirimiphos-methyl and prothiofos, respectively.

An external standard analysis was used to calculate the recovery rate of pesticide residue. The area of the peak corresponding to pesticide was corrected according to percent recovery to indicate residue determination expressed as ppm or mg/kg.

RESULTS AND DISCUSSION

Residues in outer leaves

Table 1 and Figs 1, 2 and 3 demonstrate the residues of the applied insecticides in outer leaves of cabbage plant up to 360 h (15 days) after spraying. Malathion showed the maximum initial deposit on cabbage leaves. The estimated residues were 47·3, 41·6 and 36·2 ppm

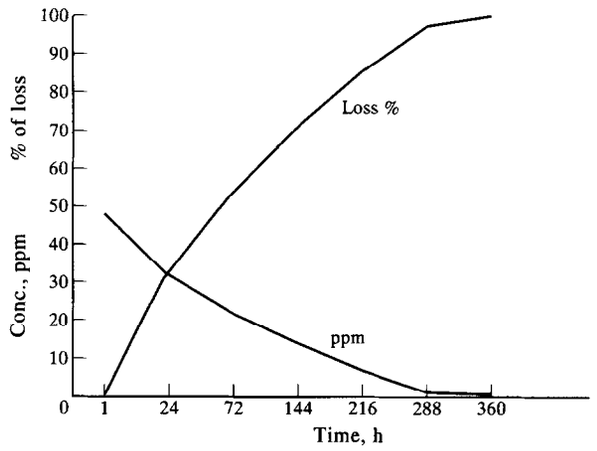

Fig. 1. Persistence and degradation of malathion in outer leaves of cabbage plant.

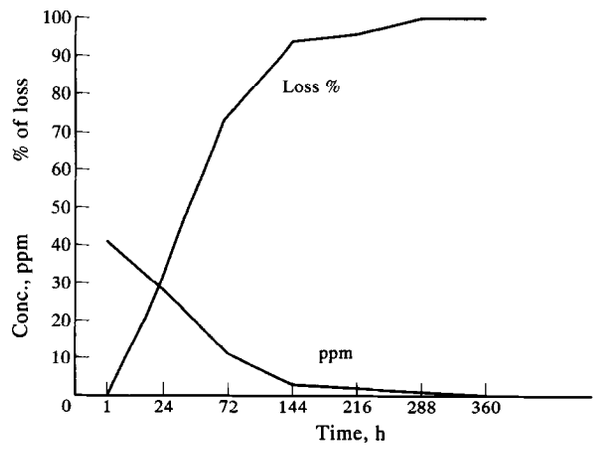

Fig. 2. Persistence and degradation of pirimiphos-methyl in outer leaves of cabbage plant.

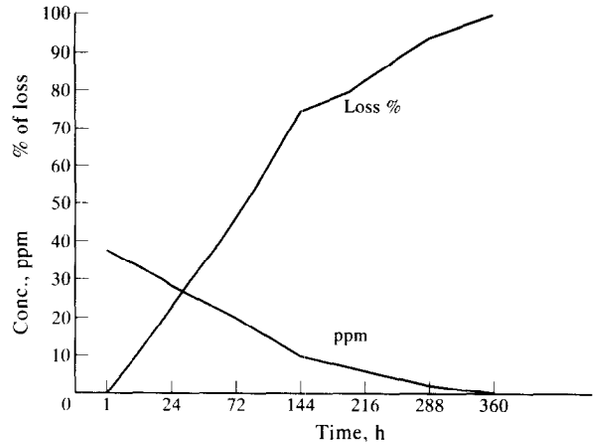

Fig. 3. Persistence and degradation of prothiofos in outer leaves of cabbage plant.

after 1 h of treatment for malathion, pirimiphos-methyl and prothiofos, respectively. The obtained differences in the initial deposits may be attributed to the variations in the formulations. As expected, a gradual and continuous deterioration of the pesticide residues in and on the treated plants was observed as a function of time after application. In this respect, the magnitude of loss was recorded to be 34·2, 32·0 and 23·1% after 24 h of spraying; however, it reached 53·6, 72·7 and 44·6% after 72 h of treatment for malathion, pirimiphos-methyl and prothiofos, respectively. Thus, a sharp decline of residues occurred for pirimiphos-methyl followed by malathion; however, a comparatively slow rate of degradation was noticed for prothiofos. In later determinations, additional decrease in the amount of pesticide residues took place after 144 and 216 h of application; however, the rate of degradation was slower as compared with the first period of 72 h after pesticides application. Minimum residue levels were attained by 288 h (12 days); however, all the applied organophosphorus insecticides became undetectable at the final experimental period, i.e. 360 h (15 days) after application. Generally, the persistence and stability of the treated pesticides in outer leaves of cabbage plant could be arranged in the following order: prothiofos > malathion > pirimiphos-methyl.

Residual impact in inner leaves

Table 2 shows the residues and penetration of the studied pesticides in the inner leaves of cabbage plant. Malathion residues were detected only after 1 h of application; however, no deposits could be found at the experimental times of 144 and 216 h. That means poor penetration of the toxicant into the inner leaves of the cabbage head. The insecticide pirimiphos-methyl was detected in the samples harvested at 1 and 144 h after spraying, while it became undetectable after 216 h of application. On the other hand, prothiofos existed in inner leaves of cabbage plant up to 216 h (9 days) after treatment, indicating more stability and penetration of that pesticide. It may be deduced that the persistence and penetration of such agrochemicals into the inner

Table 2. Residues of some organophosphorus insecticides in the inner leaves of cabbage plant

Time after application (in h)	Malathion (ppm)	Pirimiphos-methyl (ppm)	Prothiofos (ppm)
1	0·798	3·27	4·33
144	UND	0·78	0·642
216	UND	UND	0·068

UND: Undetectable by the method used in this work.

leaves of cabbage plant could be ranked as follows: prothiofos > pirimiphos-methyl > malathion. This trend is supported by the findings of Talekar *et al.* (1977) that deposits of prothiofos were the most persistent residues among 14 insecticides applied to Chinese cabbage. It was noticeable that the sprayed insecticides deteriorated in and on the outer and inner leaves of cabbage plants. However, different rates of degradation were recorded between the individual pesticides throughout the time course of the experiment. Naturally, such variation should be attributed to the chemical and physical properties as well as the nature of the pesticide molecule in relation to the capability of the tested plant to break down such environmental chemicals.

According to the Codex Alimentarius Commission (Anon., 1989) the tolerance limits for malathion and pirmiphos-methyl are 3 and 1 ppm, respectively. In view of these limits and the result obtained in the present work, we could recommend use of the outer leaves of cabbage plant commercially after 12, 12 and 15 days of application; however, the inner leaves could be utilized after 6, 8 and 12 days of spraying with concern to the insecticides malathion, pirimiphos-methyl and prothiofos, respectively as the recommended limits could be reached. In this connection, previous studies mentioned that deposits of malathion were completely degraded after 10 and 14 days of treatment for tomato (Trabulsi & Kamel, 1983) and okra (Jacob & Verma, 1984) plants. Both malathion and pirimiphos-methyl were undetectable in and on tomato fruits (Ahmed *et al.*, 1991) after 12 days of application, while they disappeared from tomato leaves after 15 days of spraying. Further investigations reported that residues of pirimiphos-methyl attain the permissible limit after 14 days of application when applied to onion plant (Hegazy *et al.*, 1988).

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