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Toxicity of field-weathered residues of insecticides to the cabbage butterfly *Pieris brassicae* L.

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Abstract

In biological and chemical assessments of insecticide residues on cauliflower (*Brassica oleracea* var *botrytis* cv 'Snowball'), quinalphos and malathion dissipated quickly, followed by fenitrothion' while endosulfan and phosalone were relatively persistent. Minimum effective level of quinalphos for the neonate larvae was 34·4 to 36·0 times less than its initial deposit on leaves followed by fenitrothion (14·7 to 15·2 times), phosalone (7·5 to 8·8 times), endosulfan (6·5 to 7·2 times) and malathion (1·4 times). Phosalone provided maximum period of protection against the larvae (17 days), while fenitrothion, endosulfan and quinalphos for about 10 days. Malathion was not effective even for full day (0·8 day).

Key words: Endosulfan, fenitrothion, malathion, phosalone, quinalphos, toxicity, persistence, residues, *Pieris brassicae*, cauliflower.

1. Introduction

Assessment of toxicity of field-weathered insecticide residues against an insect species plays a significant role in determining an effective, economical and environmentally safe pest management programme. In Himachal Pradesh, insect pests pose a serious problem in the production of quality seeds of late varieties of cauliflower. Amongst these, the cabbage butterfly *Pieris brassicae* L. is by far the most problematic. Seed crop is affected by the pest during March-April, when sizeable number of larvae cause damage by feeding on leaves, inflorescence and pods. To protect the

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crop, farmers invariably resort to heavy application of insecticides in the area. This endangers not only the bees and other beneficial insects but may pose unseen danger due to pollution of the environment. In the present investigations, efforts were made to evaluate the residues of five promising and popular insecticides, chemically and biologically, on the crop along with their effectiveness against the cabbage butterfly larvae, so that the selection and application of pesticides could be made judiciously.

2. Materials and methods

Cauliflower seed crop using the seedlings of late variety, 'Snowball selection-1', was raised at the College farm in two seasons according to the recommended agronomic practices. The first crop was planted on October 14, 1978, and the second on October, 16, 1979. The entire experiment was laid out in a randomised block design and the treatments, including control, were replicated thrice in 10 × 5 m plots separated from each other by 1 m broad buffer zone. Commercial formulations of endosulfan, fenitrothion, malathion, phosalone and quinalphos at 0·05% concentration were sprayed to 'just run-off' stage with 'Maruti' foot sprayer. In case of the first crop, the sprayings were carried out on February 22 and March 8, 1979 and in the second, on February 23 and March 8, 1980.

Random samples of cauliflower leaves (about 1·5 kg) from 25 different plants (lower, middle and upper portions of individual plant) raised in the field were collected at 0 (2 hr), 1, 3, 5, 7 and 14 days after the first spray, and then at 0, 1, 3, 5, 7, [illegible] and 30 days after the second spray in both the seasons. Samples of each replication of a treatment were chopped and mixed before taking a representative sample of 50 gm for analysis.

Petroleum ether (bp 60-80° C) and acetone were used in the ratio of 7:3 as solvent for all the insecticide extractions. The extraction from samples was done on the same day as received, so as to prevent losses during storage. The method of extraction described by Hameed and Allen[1] was followed with slight modifications.

The extracts were analysed by bioassay using *Drosophila melanogaster* Meig. as per the method of Kavadia and Rattan Lal[2]. The results were verified by gas liquid chromatography using Toshniwal model RL 04/01A equipped with electron-capture detector and tritium source. Glass column (0·6 cm internal dia and 1·2 m long) was fitted with 'Supersorb' coated with 2% silicon and OV-17 (liquid phase: 50% methyl-50% phenyl silicon) conditioned at a maximum temperature of 340° C. The column was later conditioned at 250° C overnight having 100 ml/min of N gas-flow rate. Detector temperature (200° C) and carrier gas-flow rate (60 ml/min) remained constant for all the insecticides, while column temperature (° C) and retention time (seconds) were 150 and 15, 120 and 15, 120 and 21, 145 and 24, and 145 and 24 for endosulfan, fenitrothion, malathion, phosalone and quinalphos respectively. The detector signal was supplied to 10 mV recorder with a pen response of 1·5 seconds. Quantification was based upon peak heights. The comparison was made with standard curves obtained from technical grades of insecticides. Satisfactory recovery (86·60 to 90·55%) of insecticides was obtained by both the methods.

In a separate experiment, intrinsic toxicity of the deposits of insecticides to the neonate larvae was determined by laboratory bioassay, and the actual amounts of insecticides in the deposits so formed from their commercial formulations, giving the desired toxicity, was determined by chemical (GLC) and bioassay methods. Half-life values were determined on the basis of the formula of Hoskins[3] while effective life taken graphically from the values of LD_{90} on Y-axis corresponding to the time of X-axis. Toxicity of field-weathered deposits of all the insecticides was obtained by releasing 20 neonate larvae of cabbage butterfly in petri plates (5 cm dia) on each of the treated and control leaves following 0, 1, 3, 5, 7, 14, 21 and 30 days after the second spray. Such petri plates were then transferred to an incubator at 26 ± 1° C. After 24 hours, mortality counts were recorded.

3. Results and discussion

Results on residue estimations are given in Table I. There seemed no significant difference in the magnitude of initial residues among different insecticides. Whatever little difference noticed could be attributed to the differences in the formulations of these products. However, when the deposits following second sprays were determined, phosalone and endosulfan resulted in relatively high figures than the other three insecticides since they did not dissipate as much as the other treatments before sampled for analyses (see figures on 14th day). The rate of dissipation seemed faster in malathion and quinalphos than fenitrothion, and slower in endosulfan and phosalone. Weather condition during the experimental periods did not reveal any significant impact on the persistence or dissipation of residues by its different components, as no definite relationship could be established. Half-life (Table III) of phosalone was the highest (6-8 days) in both the seasons, followed by endosulfan (4-6 days) and almost equal (2-3 days) in fenitrothion, malathion and quinalphos. These findings approximately agree with the results of Sachan and Srivastava[4], Singh and Kalra[5], and Hameed *et al*[6].

Laboratory bioassay of the toxicity of fresh deposits to the neonate larvae of *P. brassicae* revealed (Table II) that quinalphos, fenitrothion, phosalone and endosulfan were respectively 18, 11·7, 4·9 and 3·7 times more toxic than malathion. A comparison of the toxicity with initial deposits of insecticides, however, revealed that in the case of quinalphos the amount of initial deposit formed under field condition was nearly 61-64 times more than the amount which is required to cause at least 50% mortality of the pest because of its high intrinsic toxicity. Similarly, the initial deposits of fenitrothion were 37-38 times, phosalone 16-19 times, endosulfan 12-14 times and

Table I

Insecticide residues on cauliflower leaves at varying intervals following first and second sprays during 1979 and 1980

Insecticide (0·05 %) concentration	Year	Spray*	Residues (ppm) on the following days after spray**							
			0	1	3	5	7	14	21	30
Endosulfan	1979	I	38·9	29·0	22·1	13·8	8·2	3·6	...	...
		II	42·1	32·7	22·5	13·7	7·9	3·1	...	0·8
			(100)	(100)	(100)	(100)	(98)	(42)	(16)	(0)
	1980	I	37·9	31·4	17·8	13·9	8·1	3·6	...	...
		II	41·3	33·6	18·8	14·1	8·0	3·5	...	0·9
			(100)	(100)	(100)	(100)	(99)	(41)	(13)	(0)
Fenitrothion	1979	I	35·6	25·6	13·7	6·8	4·5	1·3	...	...
		II	35·6	25·0	12·7	6·6	3·8	1·4	...	BDL
			(100)	(100)	(100)	(99)	(76)	(46)	(16)	(0)
	1980	I	34·5	25·8	13·0	6·9	4·7	1·3	...	...
		II	35·6	24·6	13·1	6·5	4·3	1·1	...	BDL
			(100)	(100)	(100)	(95)	(69)	(41)	(18)	(0)
Malathion	1979	I	38·8	25·7	17·5	9·7	3·7	1·1	...	...
		II	39·4	25·0	16·1	8·9	3·4	0·8	...	BDL
			(94)	(90)	(80)	(71)	(29)	(0)	(0)	(0)
	1980	I	38·2	24·7	16·7	10·2	4·2	1·3	...	...
		II	39·7	24·6	16·8	9·5	3·9	0·9	...	BDL
			(95)	(85)	(78)	(65)	(26)	(0)	(0)	(0)
[illegible]	1979	I	36·8	29·1	19·6	16·2	14·1	8·0	...	...
		II	44·1	[illegible]	22·8	18·9	16·2	7·6	...	1·3
			(100)	(100)	(100)	(100)	(98)	(71)	(64)	(32)
	1980	I	[illegible]	[illegible]	[illegible]	17·1	11·8	7·8		...
		II	42·4	[illegible]	[illegible]	17·7	12·0	7·5	...	2·07
			(100)	(100)	(100)	(100)	(100)	(73)	(61)	(29)
Quinalphos	1979	I	38·6	25·6	12·7	8·8	[illegible]	[illegible]	...	...
		II	38·8	24·9	11·8	8·7	[illegible]	[illegible]	...	BDL
			(100)	(100)	(100)	(98)	(74)	(10)	(0)	(0)
	1980	I	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]

* During 1979 1st spray : 22 February and 2nd spray : 8 March. During 1980 1st spray : 23 February and 2nd spray : 8 March.
** Average of bioassay and GLC of 3 replications each. Figures in parentheses : Corrected % kill of the larvae following 2nd sprayings only and of 5 replications each. BDL, below detectable limit.

Weather during the experimental periods

Year	Spray	Temperature° C				Relative humidity (%)		Rainfall (mm)
		Maximum		Minimum		Range	Mean	
		Range	Mean	Range	Mean			
1979	I	12·2–22·8	17·5	0·0–5·5	2·1	41–92	71·9	48·7
	II	13·3–28·0	22·4	0·0–10·3	5·7	42–94	60·3	78·3
1980	I	15·5–31·1	19·6	0·0–10·0	4·7	23–93	56·9	21·4
	II	11·1–29·2	22·0	0·0–14·4	6·4	29–93	57·0	45·5

Table II
Intrinsic toxicity in relation to initial deposits of insecticides

Insecticides		Initial deposits (ppm)				Toxicity of insecticides* to the neonate larvae of *P. brassicae*			
		1979		1980					
		1st spray	2nd spray	1st spray	2nd spray	LD_{50} (ppm) (Fiducial (limits)	Slope	Relative toxicity	LD_{90} (ppm) (Fiducial limits)
Endosulfan	1	38·908	42·078	37·870	41·260	2·958	4·4	3·7	5·815
	2	13·15	14·23	12·80	13·95	(2·8–3·1)			(5·2–6·7)
	3	6·69	7·24	6·51	7·10				
	4	(1 :2)							
Fenitrothion	1	35·600	35·633	34·533	35·633	0·931	3·2	11·7	2·351
	2	38·23	38·27	37·09	38·27	(0·8–1·0)			(1·9–2·8)
	3	15·14	15·16	14·69	15·16				
	4	(1 :2·5)							
Malathion	1	38·825	39·385	38·190	39·676	10·870	3·2	1·0	27·730
	2	3·57	3·62	3·51	3·65	(9·9–11·8)			(22·8–33·7)
	3	1·40	1·42	1·38	1·43				
	4	(1 :2·6)							
Phosalone	1	36·831	43·078	36·600	42·363	2·221	3·8	4·9	4·873
	2	16·58	19·48	16·48	19·07	(2·1–2·4)			(4·1–5·7)
	3	7·56	8·84	7·51	8·69				
	4	(1 :2·2)							
Quinalphos	1	38·592	38·830	37·090	37·871	0·602	5·1	18·0	1·078
	2	64·10	64·50	61·61	62·90	(0·5–0·7)			(0·9–1·2)
	3	35·80	36·02	34·41	35·13				
	4	(1 : 1·8)							

Table III

Persistence and effective lives of insecticides against *P. brassicae*

Insecticide	1979				1980			
	Half-life (days)		Effective life (days)		Half life (days)		Effective life (days)	
	1st spray	2nd spray	1st spray	2nd spray	1st spray	2nd spray	1st spray	2nd spray
Endosulfan	4·02	5·36	10·25	10·95	4·10	5·70	10·10	11·15
Fenitrothion	2·95	3·01	10·50	10·25	2·95	2·80	10·40	10·00
Malathion	2·69	1·59	0·85	0·90	2·86	2·56	0·70	0·95
Phosalone	6·70	6·26	17·60	17·45	6·34	7·60	18·20	18·75
Quinalphos	2·29	2·03	11·20	10·30	2·55	2·38	12·40	11·70

malathion about 3·5 times and therefore, a generalization can be made that if the insecticide is toxic the margin would be higher between toxicity and initial deposit (provided initial deposit remains constant). A further extension of this idea gave more logical answer to the problem. Since LD_{50} values are only an index of intrinsic toxicity, it is of little utility as a guide to likely field performance, for which purpose LD_{95} would be a more appropriate value. However, because of the inherent difficulties in obtaining precision at high mortality levels, LD_{90} termed as 'minimum effective level' (m.e.l.) is taken as a more reliable guide. On the basis of initial deposits of chemicals and their m.e.l.s' these could, therefore, be classified into three categories :

Category	Insecticide
First	
Initial deposit more than 10 times of m.e.l.	Quinlaphos Fenitrothion
Second	
Initial deposit 5 to 10 time of m.e.l.	Phosalone Endosulfan
Third	
Initial deposit less than 5 times of m.e.l.	Malathion

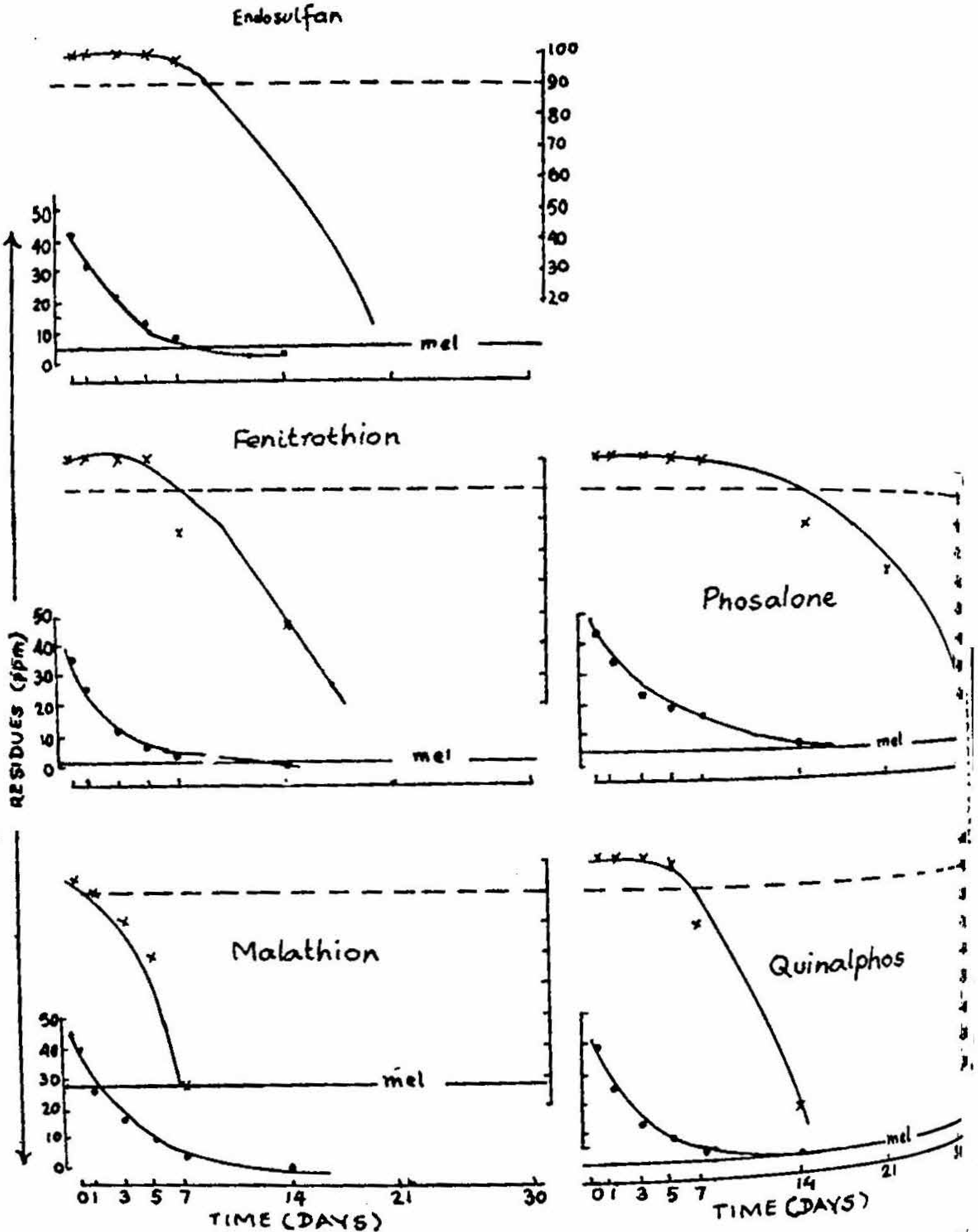

Fig. 1. Persistence as measured biologically and chemically (upper and lower graphs respectively) of insecticdes in 1979. Horizontal lines are shown at 90% mortality of *P. BRASSICAE* and at mini-mum effective level of residues.

The data (Table II) suggest that quinalphos and fenitrothion have comfortable margin to be effective against the pest. This margin is moderate in phosalone and endosulfan but is extremely low in malathion. Since the margin in the case of quinal-phos is appreciably higher as compared to other insecticides, even the lower dose of

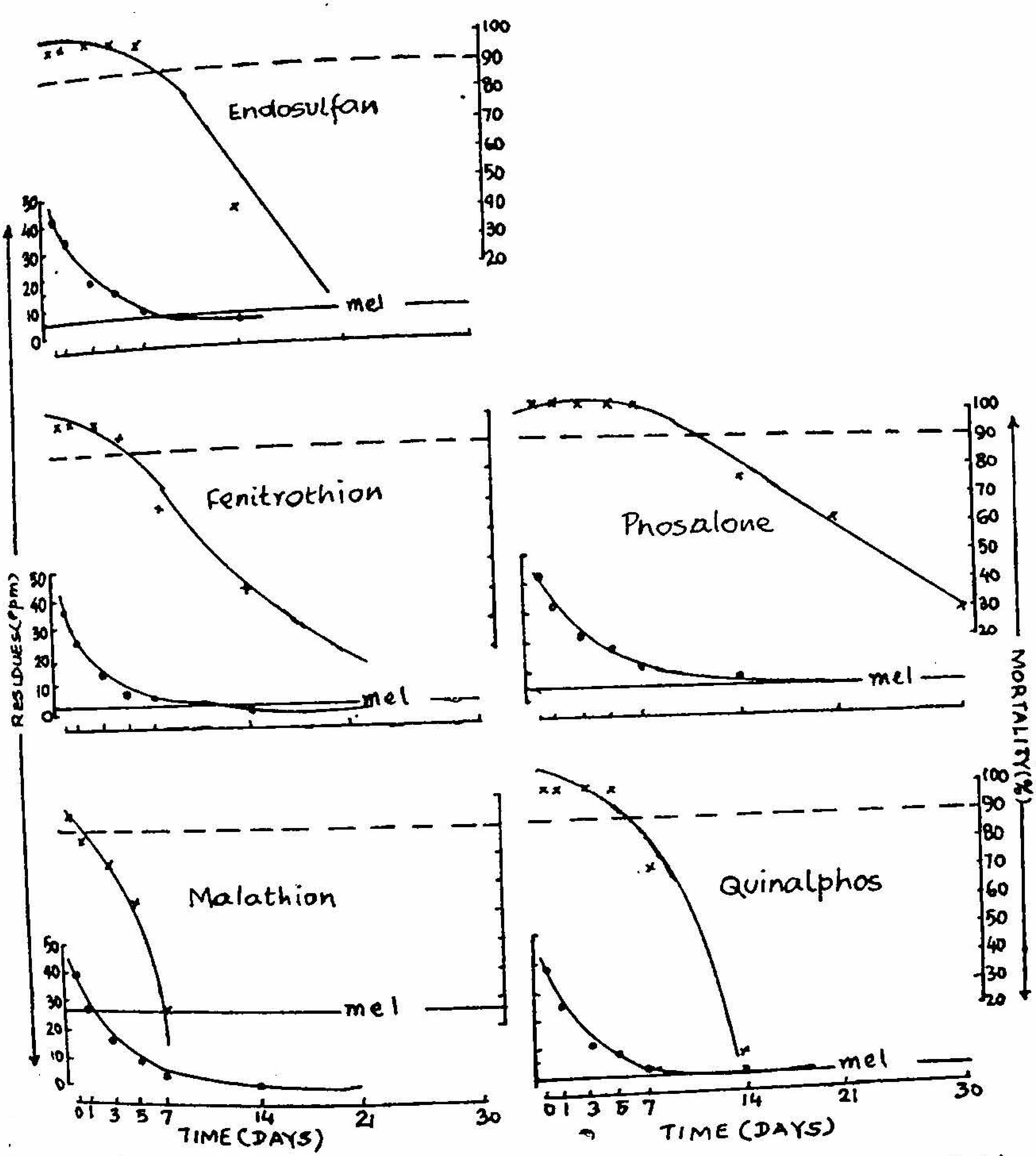

Fig. 2. Persistence as measured biologically and chemically (upper and lower graphs respectively) of insecticides in 1980. Horizontal lines are shown at 90% mortality of *P. BRASSIC- AE* and at minimum effective level of residues.

this compound could be considered to give at least 90% kill of the pest under field conditions.

Intrinsic toxicity of a chemical and its initial deposits, however, are not complete guide to its performance, since the order of biological activity may change with time due to differences in persistence of the deposits[7]. Insecticides with low intrinsic toxicity but with long residual effect may prove better for a particular pest in certain situations than those possessing high intrinsic toxicity which dissipate quickly.

A knowledge of the contributions made by intrinsic toxicity of the initial deposit of an insecticide and its persistence is obviously considered desirable for deciding its use for achieving an effective control of the pest. The LD_{50} value is the lowest for quinalphos (0·602 ppm) and the highest for malathion (10·87 ppm). On the basis of LD_{50} and LD_{90} there is no difference in the ranking order of insecticide, *viz.*, quinalphos > fenitrothion > phosalone > endosulfan > malathion. When toxicity (m.e.l.) and persistence of chemicals are studied together a term what is known as 'effective life' or period of protection could be easily derived. This value gives a correct idea as to what extent or period the residues on the substrate would afford at least 50% protection from the pest infestation. On this basis, hypothesis so formed could be made more realistic. Quinalphos is inherently more toxic chemical to the cabbage butterfly larvae than phosalone but its half-life is about three times less, and its effective life is also about one and a half-times less than that of phosalone (Table III). On this ground, phosalone proves to be a better compound than others and provides protection up to 17 days, while quinalphos, fenitrothion and endosulfan afford about 10–12 days of protection. Phosalone thus, shifted its position from third to first. Despite the half-life of quinalphos and fenitrothion being shorter (2-3 days) than endosulfan (4·7 days), their high intrinsic toxicity gave protection equal to endosulfan. By going through the observations critically, it may, therefore, be concluded that the parameter of effective life gives more realistic picture of its biological effectiveness under field conditions than any other value. On this account' quinalphos, endosulfan and fenitrothion are at par with each other, while malathion cannot be considered effective as its protection period is very little (0·85 days).

Results of the chemical and biological assessments of the residues on the leaves at different intervals throughout the first month period following second sprays (Table I) are also shown graphically in figs. 1 and 2. Positive correlation is observed between mortality of the larvae and residues of insecticides. When the insecticide residues cross m.e.l. mortality also decreases. Fourteen day-old residues did not cause any mortality in malathion, but phosalone recorded the highest mortality (61%). Phosalone remained biologically active up to 30 days, while endosulfan and fenitrothion gave mortality only up to 21 days. Planes and Rivera[8] obtained promising results with phosalone by releasing the larvae on treated leaves of cabbage, while on cauliflower, Atwal and Singh[9] recorded 52·5% mortality with 0·07% spray in field trials. Rivera *et al.*[10] also observed promising results with phosalone, endosulfan and fenitrothion on treated cabbage leaves by conventional methods.

References

1. HAMEED, S. F. AND ALLEN, J. G. — Toxicity and persistence of some organophosphorous insecticides and permethrin on apple fruits for the control of codling moth *Laspeyresia pomonella* (L.), *J. Hort. Sci.*, 1976, **51**, 105–15.

2. KAVADIA, V. S. AND RATTAN LAL — Residues of malathion on Indian rape seed (*Brassica campestris* L. var. *dichotoma* Watt.), *Indian J. Agric. Sci.*, 1967, **38**, 708–13.

3. HOSKINS, W. M. — Mathematical treatment of the rate of loss of pesticide residues, *Pl. Prot. Bull.*, F.A.O., 1961, **9**, 163–168.

4. SACHAN, J. N. AND SRIVASTAVA, B. P. — Studies on the insect pests of cabbage III. Extent of residues of recommended insecticides, *Indian J. Ent.*, 1975, **37**, 353–61.

5. SINGH, G. AND KALRA, R. L. — Dissipation of quinalphos on cabbage (*Brassica oleracea* L. var. *capitata* L.), *Proc. Symp. Nuclear techniques of studies of metabolism effects and degradation of pesticides* held in Tirupati, Dept. Atomic Energy ' Bombay, Feb. 24, 1978 (in press).

6. HAMEED, S. F., SURI, S. M. AND KASHYAP, N. P. — Toxicity and persistence of residues of some organophosphorous insecticides applied for the control of *Dacus cucurbitae* Coq. on fruits of cucumber, *Indian J. Agric. Sci.*, 1980, **50**, 73–77.

7. GRATWICK, M. AND TEW, R. P. — A comparison of the toxicity of various carbamate, organophosphorous and organochlorine compounds to the codling moth, *Proc. 3rd British Insecticides Fungicides Conf., Brighton, U.K.* (1965), 1966, pp. 276–95.

8.* PLANES, S. AND DEL RIVERA, J. M. — Tests on the control of the larvae of cabbage moth, *Pieris brassicae* L. *Blon. Patol. Veg. Ent. Agric.*, 1966, **29**, 307–10.

9. ATWAL, A. S. AND SINGH, K. — Comparative efficacy of *Bacillus thuringiensis* Berlimer and some contact insecticides against *Pieris brassicae* L. and *Plutella maculipennis* (Curtis) on cauliflower, *Indian J. Ent.*, 1969, **31**, 361–63.

10.* RIVERA, DEL, J. M., JUSET, J. J., ROIG, F. J. AND LAFUENTE, M. L. — Effectiveness of several insecticides alone and in combination against larvae of *Pieris brassicae*; *An Inst. Nac. Inst. Agapn.* 1969, **18**, 145–55.

* Original not seen.