J. Indian Inst. Sci. 63 (C), Aug. 1981, Pp. 121-129 C Indian Institute of Science, Printed in India.

### Toxicity and persistence of some organophosphorous insecticides against San Jose scale Quadraspidiotus perniciosus Comstock\*

#### A. K. THAKUR AND S. F. HAMEED\*\*

Department of Entomology and Apiculture, Himachal Pradesh Krishi Vishva Vidyalaya, Palampur 176 062, India.

Received on July 12, 1980; Revised on January 23, 1981.

#### Abstract

Toxicity and persistence of deposits of diazinon, fenitrothion, malathion, methyl-parathion and phosalone at 0.05% following one autumn spray in 1976 on apple leaves and twigs were evaluated against San Jose scale Quadraspidiotus perniciosus Comstock at Solan, Himachal Pradesh. The deposits of insecticides on apple leaves were found to be more compared to those on twigs. Diazinon, fenitrothion, methyl-parathion, and malathion persisted up to 5, 6, 4 and 3 days, respectively following treatment while phosalone persisted up to 12 days. Fenitrothion provided protection up to 25 days to twigs and 27 days to the leaves against the coccid. Methyl-parathion and diazinon were the next effective

compounds. Malathion proved to be the least persistent and the least toxic insecticide. Phosalone, though persisted for periods longer than any other compound, was of little use against the pest.

Key words: Organophosphorus insecticide, toxicity and persistence.

#### L. Introduction

τ

San Jose scale Quadraspidiotus perniciosus Comstock continues to be a serious insect pest of apple in Himachal Pradesh. Leaves and twigs become the first target of its attack before the pest moves on to the fruits. When the fruits are harvested, the pest thrives either on leaves or twigs, and a third generation of the pest emerges out during autumn<sup>1</sup>. The attacked leaves and twigs become spotted, skinny and wither, ultimately affecting the quality of fruits in the following season. Investigations were, therefore, carried out to evaluate the toxicity and persistence of some recommended organophosphorous insecticides on leaves and twigs of apple when sprayed during autumn as a prophylactic measure.

Part of the Ph.D. Thesis submitted to the Himachal Pradesh University, Agricultural Complex, College of Agriculture, Solan, by the senior author under the guidance of the second author.
Present address; Department of Entomology, Academic Complex, Rajendra Agricultural University, Pusa 848125, Bihar.

121

× + - +

I.LSc.-2

#### 2. Materials and methods

Apple trees (cv Red Delicious) were sprayed on 22 September 1976 with the commercial formulations of diazinon, fenitrothion, malathion, methyl-parathion and phosalone in a private orchard at Kasauli (Sular.) with the help of a foot sprayer (Aspee make) to 'run-off' at the recommended rate of 0.05% concentration. Layout and other horticultural operations were according to recommendations<sup>2</sup>. Random samples of 24 twigs (12-15 cm long and 10-15 mm dia) and 100 leaves were collected from four replications per treatment on 0 (immediately after the spray was dry), 1, 3, 7, 15 and 30 days following spraying. The samples were brought to the laboratery where these were divided into 4 lots of 25 leaves and 6 twigs each. From each lot, 15 leaves and 4 twigs were drawn for each replication. From leaves, disks of 1.6 cm dia. were withdrawn and for twigs, length and diameter were recorded for determining the surface area. The samples were later extracted, cleaned up and stored for analysis. Field sample extracts were first analysed by bioassay taking adult males of Drosophila melanogaster Meig as test insect as per the method of 'residue-film' of Kavadia and Rattan Lal<sup>3</sup>. Results obtained by bioassay were confirmed by standard chemical methods of each insecticide<sup>4</sup>. Following the two methods of estimations, diazinon was recovered to the extent of 90  $\pm 1\%$ , fenitrothion and methyl-parathion 88  $\pm 5\%$ , malathion 95  $\pm 2\%$ and phosalone 93  $\pm$  3%.

Intrinsic toxicity of the insecticides was earlier determined by Thakur<sup>4</sup> (Table I). Half-life value of the deposits of each insecticide on apple leaves and twigs was worked

out on the basis of formulae of Hoskins<sup>5</sup>. The values of the effective life of each insecticide were worked out by substituting the log  $LD_{90}$  to 'Y' of the respective time-deposit regression equations (Table II).

#### 3. Results and discussion

Fenitrothion, was found to be more toxic (Table I) to the crawlers of San Jose scale than the other insocticides. Methyl-parathion, diazinon, malathion and phosalone were next in the order of toxicity. There was no change in the ranking order of the chemicals when compared on the basis of their  $LD_{90}$  values.

Chemical estimations of the deposits of insecticides, in all the cases, approximately agreed well with the data obtained from the bioassay of field sample extracts (Table II). The data of the two estimations of each insecticide in both the seasons were positively correlated. There was not much difference in the extent and magnitude of initial deposits of diazinon, fenitrothion and malathion but the order of activity changed with time both on leaves and twigs due to the differences in their persistence. The deposits of all these insecticides dissipated quickly up to 3 days following treatment in spite of increase in minimum temperature and thereafter slowly. Humidity showed considerable variation during the last week prior to final sampling. There was, however, no

Table I

Toxicity of insecticide deposits to the crawlers of San Jose scale Quadraspidiotus perni-

			the second value of the se		
Insecticide	Regression equation	LD <sub>50</sub> (µg/cm²)	Fiducial limits (µg/cm <sup>2</sup> )	LD <sub>90</sub> (µg/cm²)	Fiducial limits (µg/cm <sup>2</sup> )
Diazinon	$Y = 1 \cdot 2599x + 2 \cdot 2231$	0.01.60	0·0107 0·0239	0.1664	0·0659 0·4198
Fenitrothion	Y = 1 5689x + 1 9420	0.0089	0.0065	0.0283	0·0291 0·1169
Methyl-parathion	Y 1.3992x + 2.0396	0.0130	0·0091 0·0188	0.1076	0·0397 0·2917
Malathion	$Y = 1 \cdot 3737 x + 1 \cdot 0386$	0.0765	0·0528 0·1108	0.6555	0·2587 1·6620
Phosalone	$Y = 1 \cdot 3659x + 0 \cdot 7516$	0.1289	0·0911 0·1825	1-1190	0·4617 2·7090

In none of these cases the data were found to be significantly heterogeneous at P = 0.05;

614

123

```
Y = Probit Kill; x = \log \cos c \cdot (\mu g/cm^2) \times 10^4.
* Vide Thakur4.
```

rainfall during the period of experimentation. The figures for average weather condition during this period are given in Table II and illustrated in fig. 1. Malathion could not persist on leaves and twigs after the 15th day while only 0.01 to 0.05  $\mu$ g/cm<sup>2</sup> of the deposits of diazinon, fenitrothion and methyl-parathion could be detected on the 30th day on both the leaves and twigs. Phosalone, however, exhibited maximum persistence on leaves and twigs (0.36 to  $0.40 \,\mu\text{g/cm}^2$  on the 30th day).

The deposits of insecticides on the 15th day (Table II) when subjected to the respective regression equations (Table I), for obtaining corresponding per cent kill of the crawlers, revealed that the deposits as low as  $0.11 \,\mu\text{g/cm}^2$  of methyl-parathion on leaves (Table IV) could give 89.9% mortality, followed by the deposits of fenitrothion  $(0.15 \,\mu\text{g/cm}^2)$ . On twigs, the deposits of diazinon  $(0.10 \,\mu\text{g/cm}^2)$  gave 83.8% mortality followed by methyl-parathion (0.11  $\mu$ g/cm<sup>2</sup>). The deposits of phosalone followed by malathion, however, provided the least expected kill. This showed that the threshold of toxic action on leaves was smaller with methyl-parathion followed by fenitrothion, while on twigs it was diazinon, followed by methyl-parathion. From practical standpoint, these are important considerations because an insecticide is better if its threshold of toxic action is smaller,

Table	II					-		1.4		
Persist	ence	of insecticide	deposits on	apple	leaves	and	twigs during	autumu	in	Himachal

Insecticides	Method of estimation (Plant/Location)		Deposits ( $\mu$ g/cm <sup>2</sup> ) $\pm$ 95% confidence limits at different			
	(Flair Location	.,	0	1	3	
Diariaan	Bioassav	(L)	3·83 ± 0.82	2.09 E 0.45	$0.72 \pm 0.27$	
Diazinon	Chem. assay	(L)	3.11 ± 0.06	1.18 + 0.10	0.28 1 0.10	
			(3.47)	(1.64)	(0.65)	
	Bioassay	(T)	3·56 ± 0·54	2·18 ± 0·42	0·78 ±. 0·27	
	Chem. assay	(T)	2·56 ± 0·92	1.26 + 0.13	$0.60 \pm 0.02$	
			(3.06)	(1.72)	(0· <del>69</del> )	
Fenitrothion	Bioassay	(L)	$4.00 \pm 0.43$	1.92 ± 0.22	$1.01 \pm 0.54$	
	Chem. assay	(L)	4.03 ± 0.60	$2.47 \pm 0.59$	$0.95 \pm 0.24$	
			(4.02)	(2.20)	(0.98)	
	Bioassay	(T)	3·36±0·09	1.76 ± 0.60	$0.66 \pm 0.54$	
	Chem. assay	(T)	3-82 0-33	1·73 ± 0.68	0·53 ± 0·26	
			(3 - 59)	(1 • 75)	(0 - 60)	
Methyl-parathion	Bioassay	(L)	4-56 ± 0-98	$3.41 \pm 0.20$	$1.05 \pm 0.42$	
	Chem. assay	(L)	4·38 ± 0·53	$3.44 \pm 0.53$	1.65 ± 0.05	
			(4 · 46)	(3 · 43)	(1.35)	
	Bioassay	(11)	$4.23 \pm 0.57$	3.20 ± 0.99	$0.83 \pm 0.31$	
	Chem. assay	<b>(T)</b>	$4.27 \pm 0.80$	2 88 ± 0.35	1.18 1. 0.21	
			(4 · 25)	(3.04)	(1.01)	
Malathion	<b>Bioassay</b>	(L)	3.07 ± 0.49	2·67 ± 0·45	1.39 ± 0.38	
	Chem. assay	(L)	3.12 + 0.40	2 42 1 0 32	1-13 1-15	
			(3.09)	(2.55)	(1 · 26)	
	Bioassay	(T)	3.12 - 0.48	2.73 + 0.17	$1.01 \pm 0.25$	
	Chem. assay	(T)	3.05 4 0.29	2.43 - 0.21	1-14 ± 0-29	
			(3.09)	(2.58)	(1.08)	
Phosalone	Bioassay	(L)	$2.91 \pm 0.49$	2·29 ± 0·26	1.80 ± 0.15	
	Chem. assay	(L)	$1.95 \pm 0.39$	$1.46 \pm 0.39$	$0.97 \pm 0.39$	
			(2-43)	(1 · 87)	(1 · 39)	
	Bioassay	(T)	$2.70\pm0.14$	$2.35 \pm 0.41$	$1.64 \pm 0.24$	
	Chem. assay	(T)	$2.65 \pm 0.73$	$1.51 \pm 0.21$	$1.14 \pm 0.26$	
			(2.67)	(1.93)	(1.39)	

124

Average weather conditions: Temp. °C: max. 27.8, min. 11.9, R.H. 86.2, Rainfall O mm, BDL; are average of biorssay and chemical assay; r = Coefficient of correlation.

125

٠

#### Pradesh

Intervais (days)			Time-deposit (td) regression equations
7	15	30	
$0.40 \pm 0.09$	0·11 ± 0·05	0.04 + 0.03	V 4 241 0 041
0.28 ± 0.06	0.16 + 0.10	BDL	I = 4.241 - 0.061x
(0.34)	(0-14)	(0.04)	I = 4.184 - 0.075x
		(0 04)	(r = 0.982)
0·18 ± 0·26	0.06 ± 0.05	0.04 + 0.01	V - 4:157 0:064.
0.30 - 0 06	0.14 ± 0.08	BDL	$V = 4 \cdot 137 = 0.004x$ V = 4.178 = 0.077
(0.24)	(0.10)	(0.04)	$1 = 4^{-1} 10 - 0^{-0} 11x$
		(0 0 1)	(/ == (1.986)
0-36 ± 0-10	0.10 ± 0.04	0.03 + 0.02	Y - 4.227 - 0.055-
0.36 + 0.14	0.21 + 0.16	0.07 + 0.11	$Y = 4 \cdot 297 = 0.053x$
(0.36)	(0.15)	(0.05)	(r = 0.002)
		(	(/ (/ ->))
0.20 = 0.05	0.08 + 0.01	0.04 + 0.01	$Y = 4.125 = 0.060 \times$
0.40 = 0.14	0.19 - 0.03	$0.07 \pm 0.05$	Y = 4.180 = 0.050x
(0.30)	(0.14)	(0.05)	(r = 0.994)
	(***)	(0 00)	(r - 0)(r + 1)
0.36 - 0.05	0.11 + 0.02	$0.02 \pm 0.01$	Y = 4.395 - 0.077x
BDL	BDL	BDL	Y = 4.566 - 0.075x
(0.36)	(0.11)	(0.02)	$(r = 0.999)^{**}$
	(0 11)	(0 02)	
$0.24 \pm 0.05$	0.11 + 0.03	$0.01 \pm 0.02$	Y = 4.335 - 0.079x
0.63 - 0.05	BDL	BDL	Y = 4.460 - 0.098x
(0.44)	(0.11)	(0.01)	(r = 0.992)
	(0.1.)		
$0.55 \pm 0.14$	$0.12 \pm 0.02$	BDL	Y = 4.470 - 0.095x
BDL	BDL	BDL	Y = 4.511 - 0.150x
(0.55)	(0.12)	(0)	(r == 0·993)**
	N		
0.35 - 0.06	0.10 ± 0.02	BDL	$Y = 4 \cdot 419 - 0 \cdot 101x$
0.64 - 0.14	BDL	BDL	Y = 4.488 - 0.147x
().45)	(0.10)	(0)	$(r = 0.995)^{**}$
$1.69 \pm 0.24$	0.74 + 0.05	0.45 ± 0.13	Y = 4.346 - 0.626x
$0.73 \pm 0.39$	0.51 ± 0.18	$0.26 \pm 0.27$	$Y = 4 \cdot 232 - 0 \cdot 026x$
(0.91)	(0.62)	(0.36)	(r = 0.966)
1.68 ± 0.83	$0.70 \pm 0.13$	$0.48 \pm 0.19$	Y = 4.322 - 0.024x
$0.77 \pm 0.12$	$0.52 \pm 0.21$	$0.30 \pm 0.14$	$Y = 4 \cdot 2.3 - 0 \cdot 0.29x$
(0.92)	(0.61)	(6.46)	(r = 0.9.8)

Below Det etable Limits. Y = Log. value of residues,  $x = d_{1}y$  of sampling. Figures in parentheses (T) = Twigs, (L) Leaf. \*\* Significant at 1% level of significance.





Initial deposits of diazinon, fenitrothion and methyl-parathion were more on leaves

than on twigs (Table II). Malathion gave almost similar initial deposits both on twigs and leaves while physalone deposits were slightly more on twigs than on leaves. The variations in the extent and the magnitude of initial deposits on two substrates, however, d'd not seem to be very significant. On the basis of variations in the initial deposits, amongst different insecticides, be it on leaves or twigs, it appeared that except for phosalone all the four insecticides were identical in their commercial formulations. From the data presented in Table III, it is evident that the deposits of all the insecticides were much in excess of the amounts determined for either their intrinsic toxicity (LD<sub>50</sub>) or of the 'minimum effective level' (m.e.l., LD<sub>90</sub>). Initial deposits of fenitrothion both on leaves as well as on twigs were maximum, i.e., 62 to 69 times more than what is actually required for LD<sub>20</sub> values, followed by methyl-parathion (40 to 42 times) and diazinon (18 to 21 times), while malathion and phosalone were almost identical in this respect. When compared with the amounts required for LD<sub>50</sub>, similar trends were observed. However, the margin between m.e.l. and intrinsic toxicity (expressed as ratios) was found to be maximum in diazinon followed by malathion and phosalone which provided equal margins between themselves, and then in methyl-parathion and the least in fenitrothion. Thus, it can be said that the deposits of fenitrothion and methylparathion were maximum and their intrinsic toxicity was also more compared to the rest of the insecticides but the margin between intrinsic toxicity and m.e.l. was minimum, while reverse was true in diazinon followed by malathion and phosalone,

Extent and magnitude of insecticide deposits in relation to their toxicity

Insecticide (at 0.05% conc.)	Initial derosit	No. of times initial deposit		
	(FB/CIII )	LD.	LD <sub>90</sub>	
I. LEAVES				
Diazinon	3-47	216.7	20-8	
Fonitrothion	4.02	451-3	68-9	
Methyl-parathion	4.46	343 • 4	41 • 5	
Malathien	3.09	40.5	4.7	
Phosalonc	2.43	18.8	2.2	
II. TWIGS				
Diaziron	3.06	191-1	18.4	

Feritrothion	3.59	403-3	61.6
Methyl-parathion	4.25	327.1	39.5
Malathion	3.09	40.3	4.7
Phosalon.c	2.67	20.7	2.4

Malathion proved to be the least persistent insecticide both on leaves and twigs (Table IV) as evident from its half-life values  $(2 \cdot 6 \text{ days})$ . Initial deposits of phosalone being m nimum in magnitude  $(2 \cdot 43 \text{ to } 2 \cdot 67 \,\mu\text{g/cm}^2)$  proved to be highly persistent (12 days), but its persistence was of little use owing to its low intrinsic toxicity. Among moderately persistent insecticides, fenitrothion provided 25 to 27 days protection from the attack of crawlers, followed by methyl-parathion (15 to 17 days) and diazinon (12 to 13 days) to the leaves and twigs. Thus, it can be said that 1 or 2 sprays of fenitrothion during autumn could satisfactorily prevent the third generation crawlers from settling or overwintering on apple plants.

#### 128 A. K. THAKUR AND S. F. HAMBED

#### Table IV

Threshold of toxic action and biological performance of insecticide deposits to the crawlers of San Jose scale on apple

Insocticides (at 0.05% conc.)	Deposits (#g/cm <sup>2</sup> ) on the 15th day following spray (22.9.76) Table II	Expocted % kill* of crawlers	Initial deposit** (µg/cm <sup>2</sup> )	Half** life (days)	Effective life ** (days)
Leaves					
Diazinon	0-14	87.8	3 · 47	4.5	13-1
Fenitrothicn	<b>●</b> ·15	97.3	4.02	5.6	27.4
Mothyl-parathior.	<b>●-11</b>	89.9	4.46	4.0	16-7
Malathion	0.15	60.2	3.09	2.6	6.1
Phoselore	0-62	82.4	2.43	11·7	8.0

-		
	-	HOK.
-		

Diazir.on	0.10	83.8	3.06	4.4	11-8
Fenitrothion	0.14	96.9	3.59	5.5	25.4
Methyl-parathior.	0-11	89.9	4.25	3.5	15-0
Malathion	0-10	56-3	3.09	2.6	5.6
Phosalone	0-61	82.1	2 · 67	11.5	8.1

\* Vide regression equations of Table I.

\*\* Average of bio as d chemical assays.

#### Acknowledgement

Authors are grateful to the Aspee Research Foundation, Malad, Bombay, for financing the project and awarding a Senior Research Fellowship to the first author.

.

.

.

#### References

I. DINABANDHOO, C. L.	The biology of San Jose scale, Quadraspidiotus perniciosus Constock (Hemiptera: Coccidae) and its control with particular reference to the evaluation of organophosphorous insecticides at the pre-bloom stage, M.Sc. (Agri.) Thesis, Himachal Pradesh University, Agri- cultural Complex, Solan, 1971,
2.	Package of practices for fruit crops of Himachal Pradesh, Publi- cation of Directorate of Extn. Edu. Agri. Compl., H.P.U., 1975, pp. 22-27,
3. KAVADIA, V. S. AND RATTAN LAL	Residues of malathion on Indian rape seed (Grassica campestris L. var. dichotoma Walt.), Indian J. Agri, Sci., 1961, 38, 708-713.
4. TAKUR, A. K.	Toxicity, persistence and harvest residues of some organophosphorous insecticides on apple for the control of San Jose scale Quadraspi- diotus perniciosus Comstock, Ph.D. Thesis, Himachal Preadsh University, Agricultural Complex, Solan, 1978.
5. HOSKINS, W. M.	Mathematical treatment of loss of pesticide residues,, Pl. Prot. Bull., F.A.O., 1961, 9, 163-168.

#### Editor's Note

While recommending the paper for publication, one of the referees disagreed with the authors on the process of insecticide extraction. His observations are : Insecticide extraction and its loss during process will remain a constant factor for all the insecticides included in trial, as different insecticides have different solubilities even in the same solvent; slight difference in this will alter the results and finally the interpretation.

The authors preferred publishing the following reply: It is known that insecticides from the treated leaves and twigs cannot be fully and completely removed by the solvent. Solubility of insecticides in solvents, clean-up procedures, method of analyses, sensitivity, etc., account for proper detection of the residues. In the present studies, specific solvent (Pet. ether 60-80° C for diazinon; benzene for fenitrothion and methylparathion : CC4 for malathion and acetone for phosalone) as recommended for each insecticide and separate specific recommended methods of analysis were adopted for different insecticides. The percentage recovery determined for each insecticide separately was found satisfactory, and all calculations were based on this. By bioassay and specific colorimetric method, the estimations were quite satisfactory.

With which view do our readers agree?

ILSc.-3