Pakistan J. Sci. Ind. Res., Vol. 30, No. 12, December 1987

Res., 8, 71 (1987).

# RESIDUAL BEHAVIOR OF THE INSECTICIDE PERMETHRIN IN TOMATOES, SOIL AND DIFFERENT pH EMULSIONS

A.A. Barakat, Pardul Khan and A.M. Abdul Karim

Regional Agriculture and Water Research Centre, P.O. Box 17285 Riyadh 11484, Saudi Arabia

(Received September 29, 1986; revised June 28, 1987)

Tomato plants grown in the field and greenhouse were sprayed with 0.2 % Kavil (10 % EC permethrin) and residue analysis was performed in fruits and soil at 0, 1, 2, 5, 7, 9 and 13 days post treatment. Permethrin residues were also monitored in aqueous buffers of pH 5, 6, 7 and 8.

The data showed that permethrin persisted longer in soil and tomatoes grown under greenhouse conditions than in the field. Permethrin was more stable in low pH emulsions.

Key words: Tomatoes, soil, pH buffers, persistence, permethrin, insecticide.

#### INTRODUCTION

The increasing use of pesticides on agricultural crops has necessitated a constant effort to be made to use pesticides least hazardous to consumers. Permethrin, a synthetic pyrethroid insecticide, has a high level of activity against a wide range of insect-pests and low mamalian toxicity. The persistence and degradation of permethrin under different environmental conditions have been studied by different researchers [1,5]. The degradation of permethrin on cotton plants is related to high temperature, moisture and microbial activity [7,9].

The main objectives of the present investigation were to study and compare the persistence and degradation of permethrin on tomatoes grown under greenhouse and field conditions and the behaviour of permethrin in the soil and its stability in buffer solutions of different pH under controlled conditions. The results of this investigation should help producers identify safe periods for harvesting permethrin treated tomatoes.

#### MATERIAL AND METHODS

Field and greenhouse experiments were conducted at the Regional Agriculture and Water Research Centre, Riyadh, Saudi Arabia. Tomato plants at the stage of physiological maturity were sprayed with 0.2 % Kavil (permethrin 10 % EC), till runoff, using a manual blast sprayer. Some plants were left unsprayed as control. Five samples each of tomato and soil (under the plants) were collected from randomly selected locations in the experimental plot at 0, 1, 2, 5, 7, 9 and 13 days' post treatment. The samples of tomato and soil were then separately mixed together thoroughly and approximately 2 kg. were taken from each as representative samples which were used in triplicate for residue analysis. Soils from the field and greenhouse were sandy with pH 8.

The effect of different pH on the behaviour of permethrin insecticide was studied under aqueous conditions. Aqueous buffers (5 litre) of pH 5, 6, 7, and 8, having an ionic strength of 0.2M were prepared [6] and stored in coloured bottles. Analytical grade permethrin, diluted with acetone was added to each bottle to yield  $100 \mu g/1$  of permethrin. After thorough mixing, the bottles were stored at room temperature (25°). Samples in triplicate from each pH buffer (emulsion) were collected at 0, 6, 9, 13, 16, 23, 27, 30 and 60 days' post treatment for permethrin residue analysis.

*Extraction from tomatoes.* A 50-g tomato sample was well macerated and blended with 100 ml hexane at high speed for 2-3 min. The hexane extract was filtered through glass wool on a Buchner funnel and, this procedure of extraction with hexane was repeated twice. The hexane filtrates were combined and concentrated with a rotary vacuum evaporator (40-50°).

Clean up. A chromatographic column (30x2 cm) was prepared by filling the glass column with anhydrous sodium sulphate (2 cm) followed by 15 cm deactivated florisil (5 % H<sub>2</sub>O to activated florisil) and an additional layer (2 cm) of anhydrous sodium sulphate. The column was prewashed with 50 ml hexane. The concentrated (5 ml) sample extract was transferred to the column and allowed to penetrate the upper portion of florisil. The sample was then eluted with 200 ml hexane + diethyl ether (10:1). The eluent was collected and evaporated to dryness on rotary vacuum evaporator (40-50°) for GLC analysis. *Extraction from soil.* A 25-g soil sample was extracted with 100 ml hexane by mechanically shaking for 4-5 hr. before filtration on Buchner funnel.

*Clean-up:* The soil extract was cleaned up in accordance with the method described for tomatoes.

Extraction from aqueous solution. A 100 ml aqueous sample from each fortified buffer emulsion was extracted thrice each with 30 ml hexane. The extracts were received through anhydrous sodium sulphate and evaporated to dryness under vacuum rotary evaporator  $45^{\circ}$ . The sample extract was dissolved in acetone and diluted to a known volume for GLC analysis.

Gas chromatographic analysis. GLC analyses were made on a Hewlett-Packard 5830A gas chromatograph, equipped with an EC detector (Ni63), fitted with a 1.8m x 4mm i.d. glass column, and packed with 5 % OV-225 on 100-120 mesh chromosorb W HP. The GLC operating temperatures were: injection port,  $250^{\circ}$ ; column,  $230^{\circ}$ ; and ECD  $300^{\circ}$  with argo-methane (95:5) carrier gas at a flow rate of 50 ml/min. Under these conditions the retention times of permethrin were 7.91 for cis and 9.07 min. for trans-isomers. The reliability of the analytical method was tested by fortifying untreated tomato, soil and water samples with known amounts of permethrin followed by extraction and analysis on GLC under the same conditions.

### **RESULTS-AND DISCUSSION**

Permethrin residues in tomato fruits at different intervals after treatment are shown in Table 1. The data indicated variation in the residue status of tomatoes grown under two different environmental conditions. The halflife time (t 1/2) of permethrin in tomatoes grown in the field was less than two days while it was about seven days under greenhouse conditions. The maximum permissible limit of 0.40 ppm in tomatoes [4] was obtained at two and seven days after application under field and greenhouse conditions respectively. This is longer than the three-day withholding period recommended by Grounds [5] for glasshouse tomatoes treated with permethrin. The persistence of permethrin on fruits of okra at an effective application rate is seven days [2]. A waiting period of four days is suggested for permethrin-treated okra fruits.

The concentration of the trans-isomer of permethrin decreased faster than the cis-isomer in greenhouse grown tomatoes. This is in agreement with the findings of Williams [9] and Smith [7] who found that the trans-isomer was generally less persistent than the cis-isomer.

Permethrin residues at different intervals in soil under the treated plants are presented in Table 2. The rate of disappearance of permethrin in the soil from the field was similar to the one for fruits, but faster than in the greenhouse soil through the first nine days after application. This might be due to the high temperature  $(30^{\circ})$  outside in the field as compared to low temperature  $(24^{\circ})$  inside the greenhouse. The cis: trans-isomer ratio decreased with time only in the soil collected from the greenhouse. Southwick *et al.* [8] have shown that high degradation is related to high temperature and the decrease in cis: trans-isomer ratio with time is largely due to the cis-to-trans isomerization of permethrin.

The stability of permethrin in different pH emulsions under controlled conditions is shown in Table 3. As expected, the data indicated a gradual decrease of total permethrin with time at all pH values. The percent decrease of permethrin was more pronounced in emulsions at elevated pH. The half-life period was only four-five days at pH 6, 7 but 10 - 11 at pH 8 and 23 at pH 5. The effect of pH on cis. and trans-isomer ratio of permethrin showed that the trans-isomer was less stable than the cis-isomer to higher pH values. The influence of water pH on the stability of

Table 1. Average permethrin residue values in tomato fruits at different times after treatment.

Days		Field	EFFRENCEN	Gre	enhouse	×		
after			Pe	Permethrin (ppm)				
treatment	Cis	Trans	Total	Cis	Trans	Total		
0	0.11	0.29	0.40	0.49	0.90	1.39		
1	0.14	0.29	0.43	0.40	0.72	1.12		
2	0.04	0.10	0.14	0.26	0.51	0.77		
5	0.04	0.10	0.14	0.31	0.60	0.91		
7	0.03	0.07	0.10	0.18	0.33	0.51		
9	0.06	0.09	0.15	0.15	0.24	0.40		
13	0.02	0.3	0.05	0.04	0.06	0.10		

Table 2. Average permethrin residue values in soil.

Days		Field		Greenhouse					
after				Permethrin (ppm)					
treatment (in hours)	Cis	Trans	Total	Cis	Trans	Total			
0	0.060	0.120	0.180	0.049	0.096	0.145			
1	0.056	0.114	0.170	0.016	0.031	0.047			
2	0.024	0.048	0.072	0.038	0.072	0.110			
5	0.023	0.050	0.073	0.069	0.111	0.180			
7	0.014	0.030	0.044	0.048	0.074	0.122			
9	0.024	0.037	0.061	0.041	0.045	0.086			
13	0.10	0.019	0.029	0.007	0.011	0.018			

Table 3. The stability of permethrin in different pH emulsions.

			pH 5	dauonto	Doe no pH	6		pH 7		pH	1810 moiter	
Days	10 (°0E)	anutanure	e tugh ten	might be due to the high re		*Permethrin %						Clean
after treatment	Cis	Trans	Total	Cis	Trans	Total	Cis	Trans	Total	Cis	Trans	Total
0	25	75	100	25	.75	100	25	75	100	25	75	100
3	22	59	81	30	66	96	28	60	88	21	44	65
6	24	48	72	18	22	40	15	28	43	22	49	71
9	25	57	82	. 23	17	40	16	14	30	22	41	63
13	30	64	94	17	10	27	12	5	17	12	0 tol 5(7)	19
16	24	46	70	14	17	31	13	3	16	10	5	
20	18	52	70	14	10	24	13	3	16	15	10	25
23	17	35	50	18	6	24	10	3	13	11	4	15
27	5	13	18	17	7	24	8	3	11	11	4	15
30	9	21	30	13	a sitt <b>1</b> to	24	5	3	8	6	4	10
60	13	17	30	2	1	3	2	3	5	3	1	4

\*Average of the samples.

insecticides has been studied by Chapman [3] who found that half-life measured at pH 8 were generally smaller than that at lower pH values.

## REFERENCES

- 1. N.P. Agnihotri, V.T. Gajbhiye, H.T. Jain, K.P. Srivanstava and S.N. Sinha,, J. Entomol. Res., 7(1): 10-14 (1983).
- M.D. Awasti, L. Anand, J. Entomol. Res., 7(1): 55-59, 1983.
- R.A. Chapman and C.M. Cole, J. Environ. Agr. Wastes, 17(5): 487-504 (1982).

- 4. R. Duggan, Food Chemical News, Inc., Washington, D.C. 20013 (1982).
- 5. P.R. Grounds, N.Z.J. Exp. Agr., 10(4): 425-428, 1983.
- C.W. Robert, (ed.), Handbook of Chemistry and Physics, 58th ed. CRC Press, Cleveland, Ohio 44128, U.S.A. (1978).
- 7. S. Smith and G.H. Willis, Soil Sci., 136(1): 26-32, 1983.
- L.M. Southwick, S. Smith and G.H. Willis, Environ. Toxicol. Chem., 2(1): 29-34 (1983).
- J.H. Williams and M.J. Brown, J. Agr. Fd. Chem., 27(1): 130-132 (1979).