

PERSISTENCE STUDIES OF INSECTICIDES: VI. DEGRADATION OF METHOXYCHLOR
ON WHITE PINE LEADERS (*Pinus strobus* L.) AFTER AERIAL APPLICATION FOR
CONTROL OF WHITE PINE WEEVIL (*Pissodes strobi* Peck) IN ONTARIO,
SPRING 1974.

By

K.M.S. SUNDARAM

Chemical Control Research Institute
Environment Canada - Forestry Service
25 Pickering Place
Ottawa, Ont., Canada. K1A 0W3

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INTRODUCTION

Pine is a prominent and valuable component of our natural forests ranking third behind spruce and fir in volume and comprising 10% of the total merchantable timber in central and eastern Canada. Among the 90 or so insects that cause significant injury to these conifers, especially to eastern white pine (*Pinus strobus* L.), no insect is more devastating than the white pine weevil, *Pissodes strobi* (Peck). By attacking and killing the leader, the top part of the main stem, the weevil seriously affects tree form and consequently the commercial and aesthetic value of the tree. In poorly stocked plantations, repeated weeviling of trees 1 to 10 meters (3.28 to 32.8 ft) in height can result in a commercially worthless stand of trees.

The Chemical Control Research Institute (CCRI) recognizing the destructiveness of the insect, initiated over 5 years ago control measures using various types of insecticides under the leadership of Dr. R.F. DeBoo. The control methods adopted so far gave reasonably good protection to white pine stands from weevil attack. Many useful publications on this aspect dealing with the application techniques, formulation developments, efficacy of different insecticides, their residual qualities, fate and persistence have appeared since 1971 from this Institute. The success and failures met during the past five years in combating the weevil pest by chemical control methods were summarized recently by DeBoo and Campbell (1974a, 1974b) and Sundaram (1974, 1975). This report describes a similar weevil control spray program carried out during the spring of 1974 at Ramsayville near Ottawa using the insecticide methoxychlor in an oil formulation.

MATERIALS AND METHODS

Experimental Design

Plots of semi-mature white pine trees in a 49 ha (120 acres) pine plantation near Ramsayville (Fig. 1) in the National Capital Commission greenbelt forest was sprayed with methoxychlor emulsifiable concentrate (E.C.) on the morning of April 28, 1974 for the purpose of:

- (1) studying the efficacy of the compound as an emulsifiable concentrate dissolved in oil for weevil control,
- (2) determining the deposit and residue dissipation rates in and on the leaders and
- (3) the extent of penetration of the insecticide molecules into the cuticular layers of the leader.

The compound was applied at the rate of 2.8 kg AI in 37.5 l No. 2 fuel oil/ha (2.5 lb AI in 4 gal. No. 2 fuel oil/acre) using a boom and nozzle equipped Cessna AgTruck aircraft (Fig. 2). The field plot arrangement, preparation of spray formulations, details on spray application, equipment used, meteorological conditions* at the time of treatment etc are described in detail by DeBoo and Campbell (1974b). Samples of 8 - 10 uniform size (25-30 cm) leaders were collected

* The meteorological conditions during the aerial spray at Ramsayville on the morning of April 28, 1975 were as follows:

Wind speed	0 - 8 km/hr (0-5 miles/hr)
Temp	12.2° C (54° F)
R.H. (%)	67

randomly from the sprayed and control plots for residue analysis before treatment (prespray) and at intervals of 1 hr (0 day), 1, 3, 7, 11, 16, 25, 36, 50, 64 and 90 days after treatment. The check plot was situated (Fig. 1) about 3.2 km (2 miles) south of the treated area and was free from any methoxychlor contamination.

Analytical Procedure

Leader samples collected from the treated plot at different intervals were cut into small pieces (ca 1 cm in length) by a hand-clipper, mixed well and analysed for surface (dislodgable or solvent removable) and total (dislodgable or surface plus penetrated) residues of o,p-MC, p,p'-MC and MCE*.

An aliquot of the leader pieces (20 g) in duplicate were taken in sealed Mason jars and shaken for 10 min in a Fisher-Kendall mixer with 200 ml of acetonitrile. The solution containing the surface deposits of the insecticide residues were decanted and another 200 ml of fresh solvent was added and the sample was homogenized in a Sorvall Omni-Mixer at high speed for 5 min to bring out the penetrated methoxychlor residues. The acetonitrile extract was filtered under suction using "S and S Shark-skin" filter paper. The extracts containing the surface deposits and the penetrated residues were partitioned individually with water-hexane mixtures, the hexane layers were dried with anhydrous sodium sulphate, cleaned up by Florisil column chromatography and analysed using gas-liquid chromatography (GLC) according to the analytical methodology developed

<u>o,p</u> -MC	=	2,2-bis(<u>o,p</u> -methoxyphenyl)- 1,1,1-trichloroethane
<u>p,p'</u> -MC	=	2,2-bis(<u>p</u> -methoxyphenyl)- 1,1,1-trichloroethane
MCE	=	2,2-bis(<u>p</u> -methylphenyl)- 1,1-dichloroethylene

recently at this Institute (Sundaram 1973).

In all the samples studied, surface deposit and the penetrated residue levels of the insecticide isomers (o,p and p,p'-MC) and MCE were measured whenever their presence was above the detectable limit (> 0.01 ppm) of the gas chromatograph used and their sum is reported as the total methoxychlor residues found in pine leaders analysed.

The leader samples from the untreated plot did not contain any measurable MC residues throughout the sampling period but the prespray samples collected a few hours prior to the aerial application showed an "apparent" residue concentration of 0.03 ppm of p,p'-MC probably due to the ground spraying conducted by the Ontario Ministry of Natural Resources during the spring of 1973.

TABLE 1

Methoxychlor Residues on and in White Pine Leaders

No	Days After Spraying	Moisture Content (percent)	Methoxychlor Internal Deposit (ppm) (As sampled)				Methoxychlor Surface Deposit (ppm) (As Sampled)				Methoxychlor Total Deposit (ppm) (As Sampled)			
			MCE	<u>o</u> , <u>p</u> -MC	<u>p</u> , <u>p'</u> -MC	Total	MCE	<u>o</u> , <u>p</u> -MC	<u>p</u> , <u>p'</u> -MC	Total	MCE	<u>o</u> , <u>p</u> -MC	<u>p</u> , <u>p'</u> -MC	Total
1	Prespray	59							0.03	0.03			0.03	0.03
2	0*	64	0.05	0.15	1.33	1.53	0.10	0.72	3.97	4.79	0.15	0.87	5.30	6.32
3	1	61	0.08	0.10	1.10	1.28	0.08	0.29	3.50	3.87	0.16	0.39	4.60	5.15
4	3	57	0.26	0.27	3.05	3.58	0.10	0.09	1.25	1.44	0.36	0.36	4.30	5.02
5	7	58	0.14	0.17	1.05	1.36	0.17	0.08	0.55	0.80	0.31	0.25	1.60	2.16
6	11	61	0.11	0.10	0.76	0.97	0.13	0.06	0.47	0.66	0.24	0.16	1.23	1.63
7	16	58	0.08	0.07	0.66	0.81	0.03	0.02	0.23	0.28	0.11	0.09	0.89	1.09
8	25	48	0.07	0.04	0.56	0.67	0.04	0.02	0.33	0.39	0.11	0.06	0.89	1.06
9	36	44	0.04	0.04	0.54	0.62	0.08	0.02	0.31	0.41	0.12	0.06	0.85	1.03
10	50	38	0.02	0.04	0.31	0.37	0.04	0.03	0.19	0.26	0.06	0.07	0.57	0.70
11	64	39	0.03	0.03	0.14	0.20	0.02	0.02	0.04	0.08	0.05	0.05	0.18	0.28
12	90	45	T	N.D.	0.05	0.05	T	T	0.07	0.07	T	T	0.12	0.12

T = Trace (< 0.01 ppm)

N.D. = Not detected

* = Sampling was done one hour (i.e. 0.04 day) after the spraying.

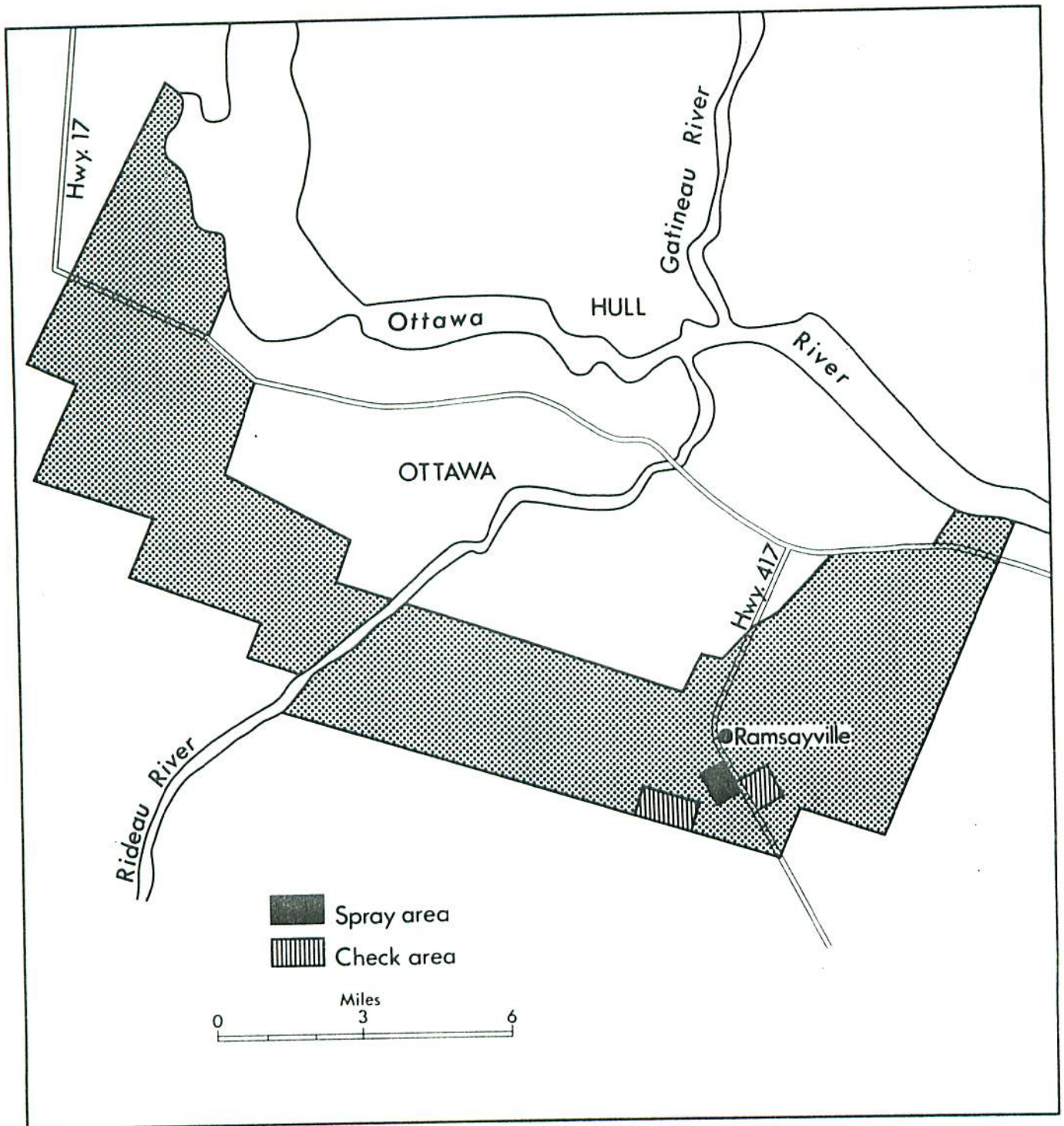


Fig. 1 Plot Design for Methoxychlor Spraying to White Pine Weevil Control in Ramsayville Area - Spring 1974.



Fig. 2. Cessna AgTruck Aircraft Equipped with Boom and Nozzle for Spraying.

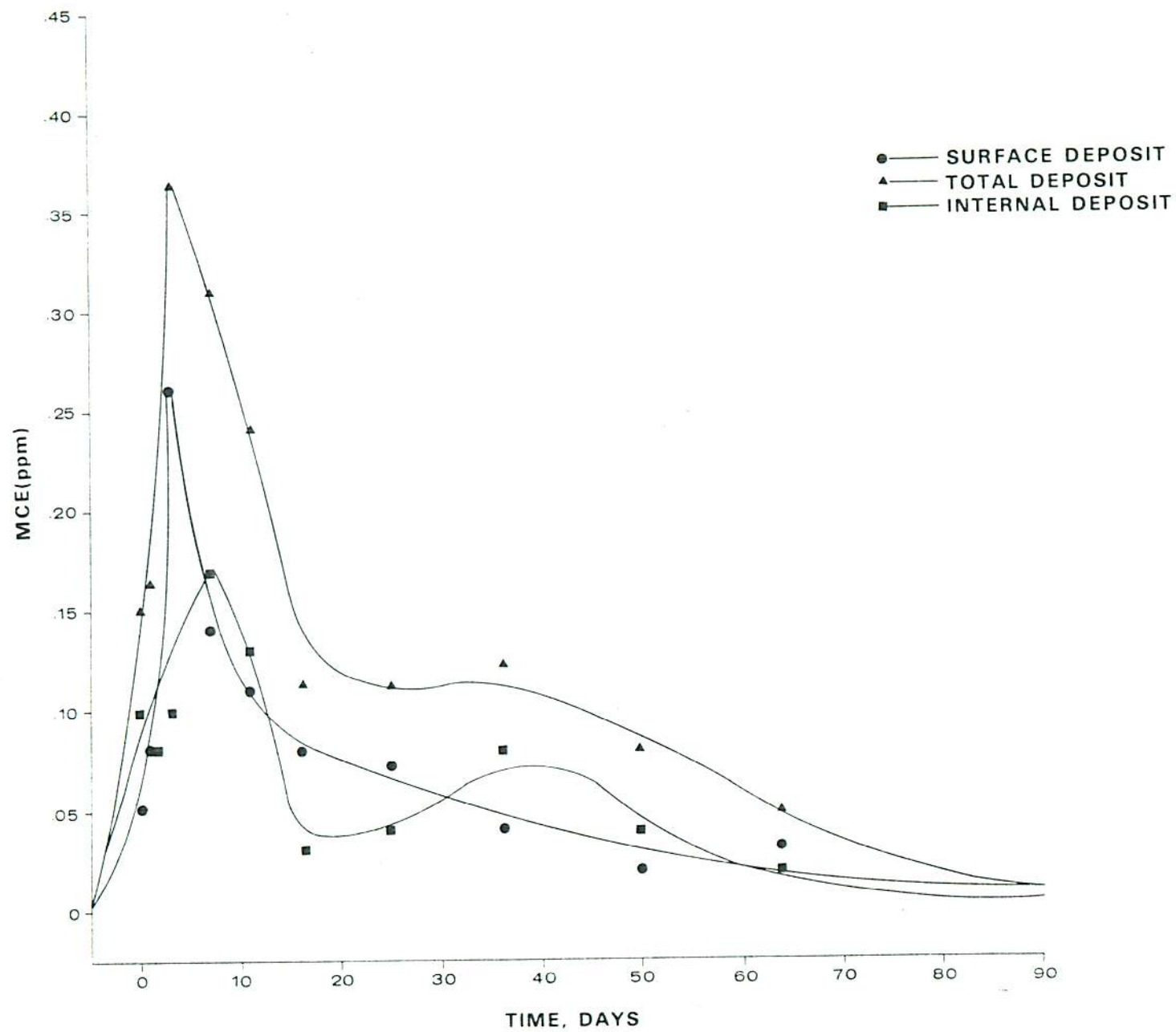


Fig. 3. Residual methoxychloroethylene in pine leaders.

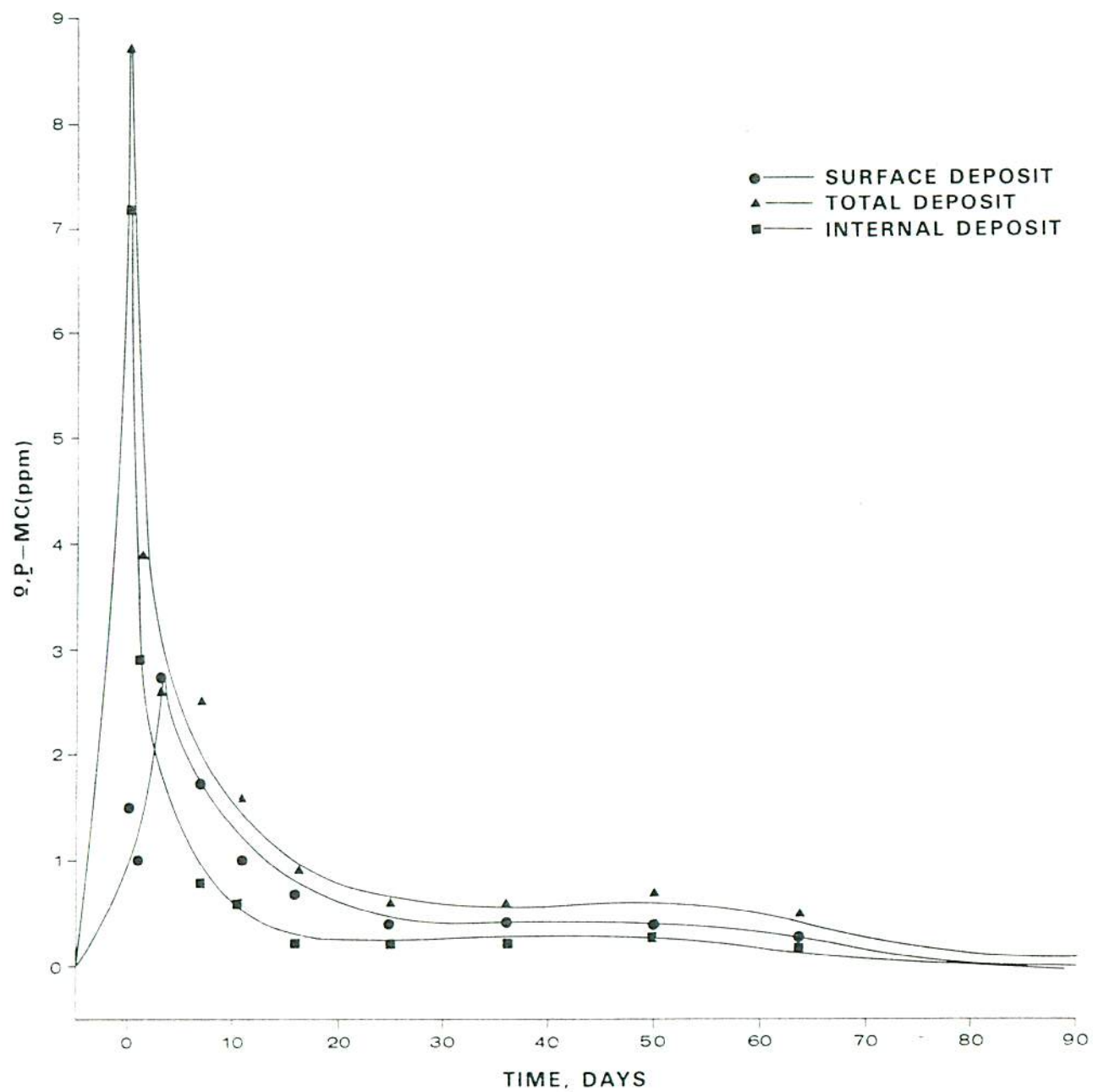


Fig. 4. Residual o,p-Methoxychlor in pine leaders.

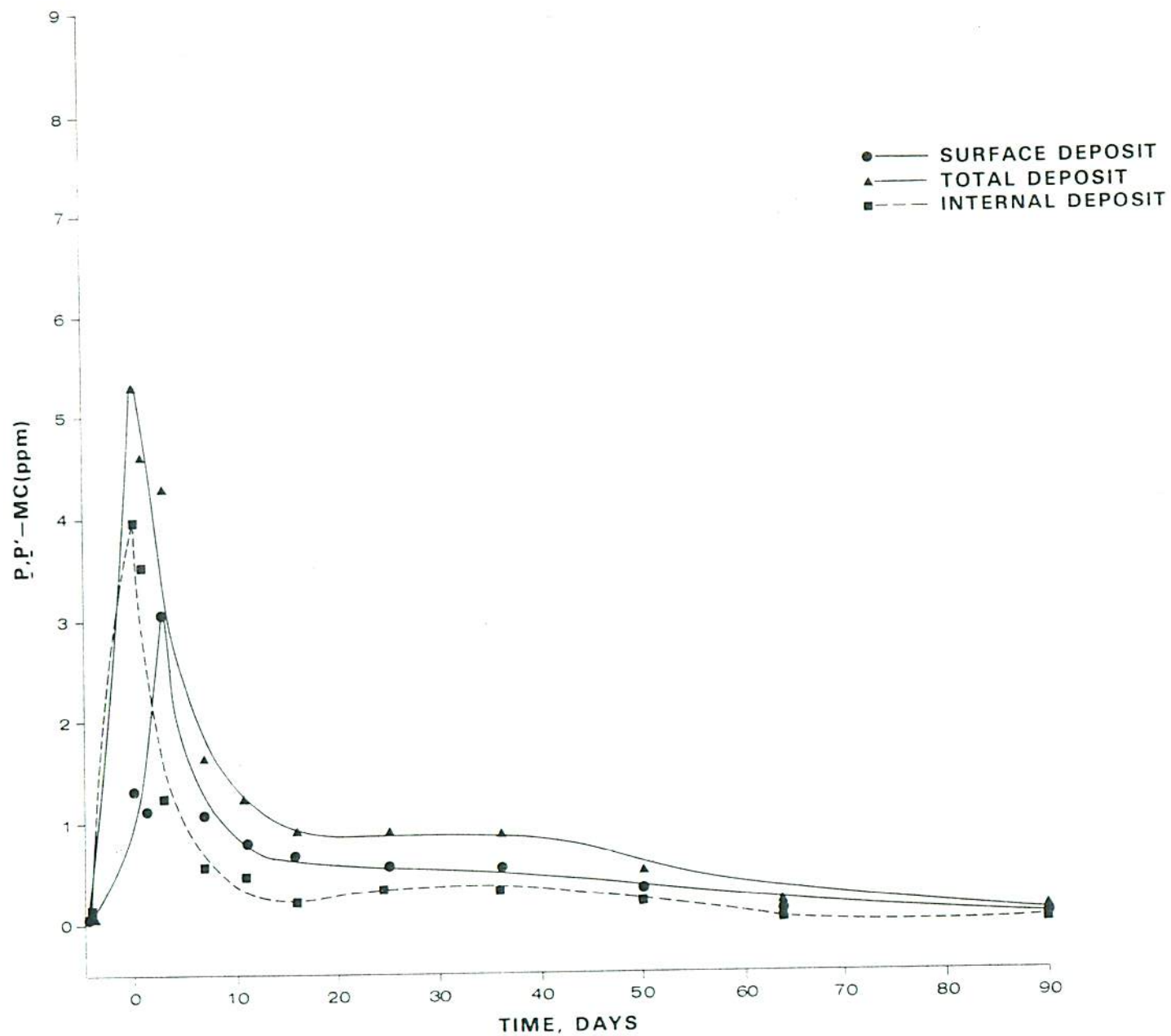


Fig. 5. Residual p,p'-Methoxychlor in pine leaders.

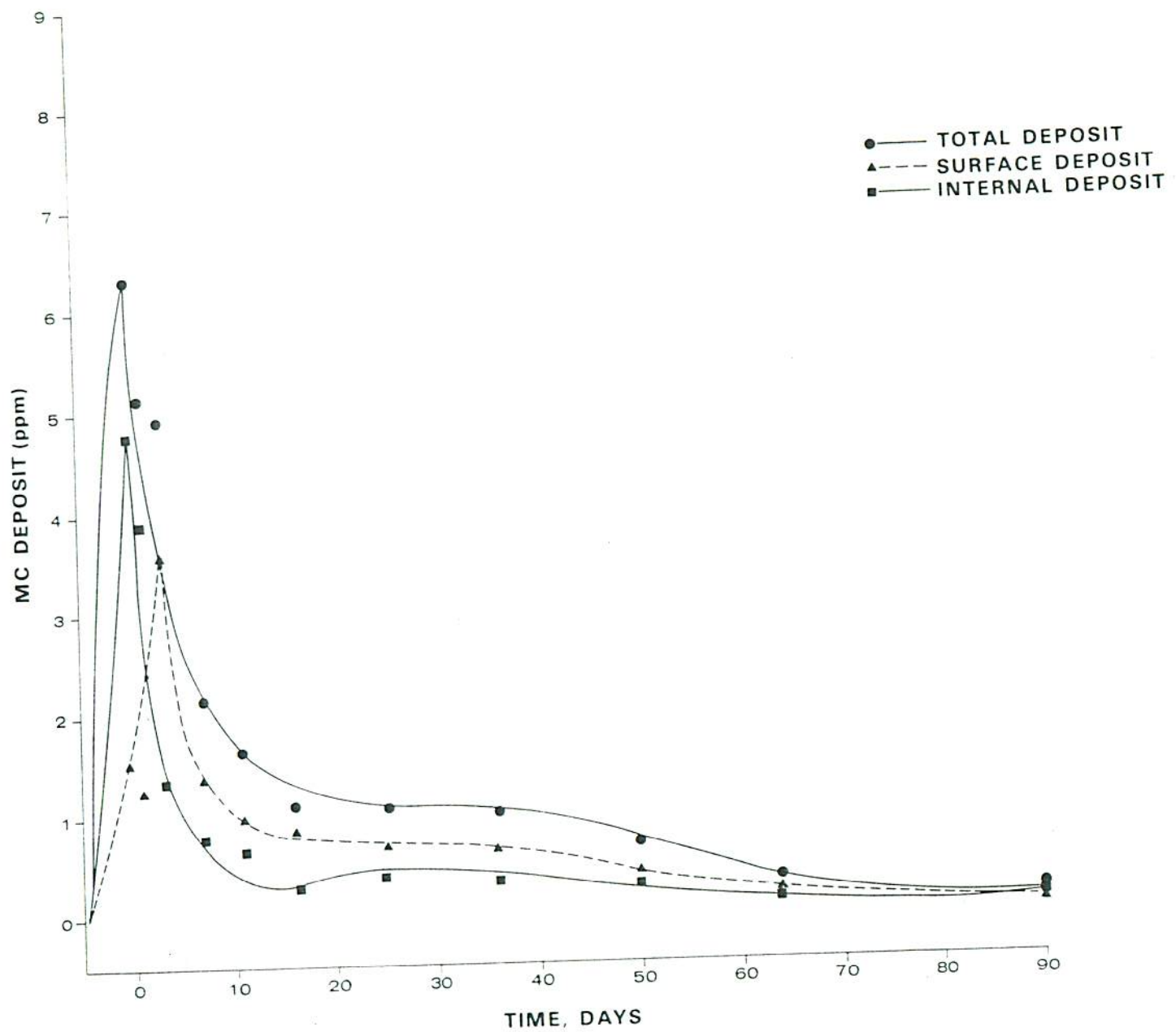


Fig. 6. Residual Methoxychlor (MCE + o,p-MC + p,p'-MC) in pine leaders.

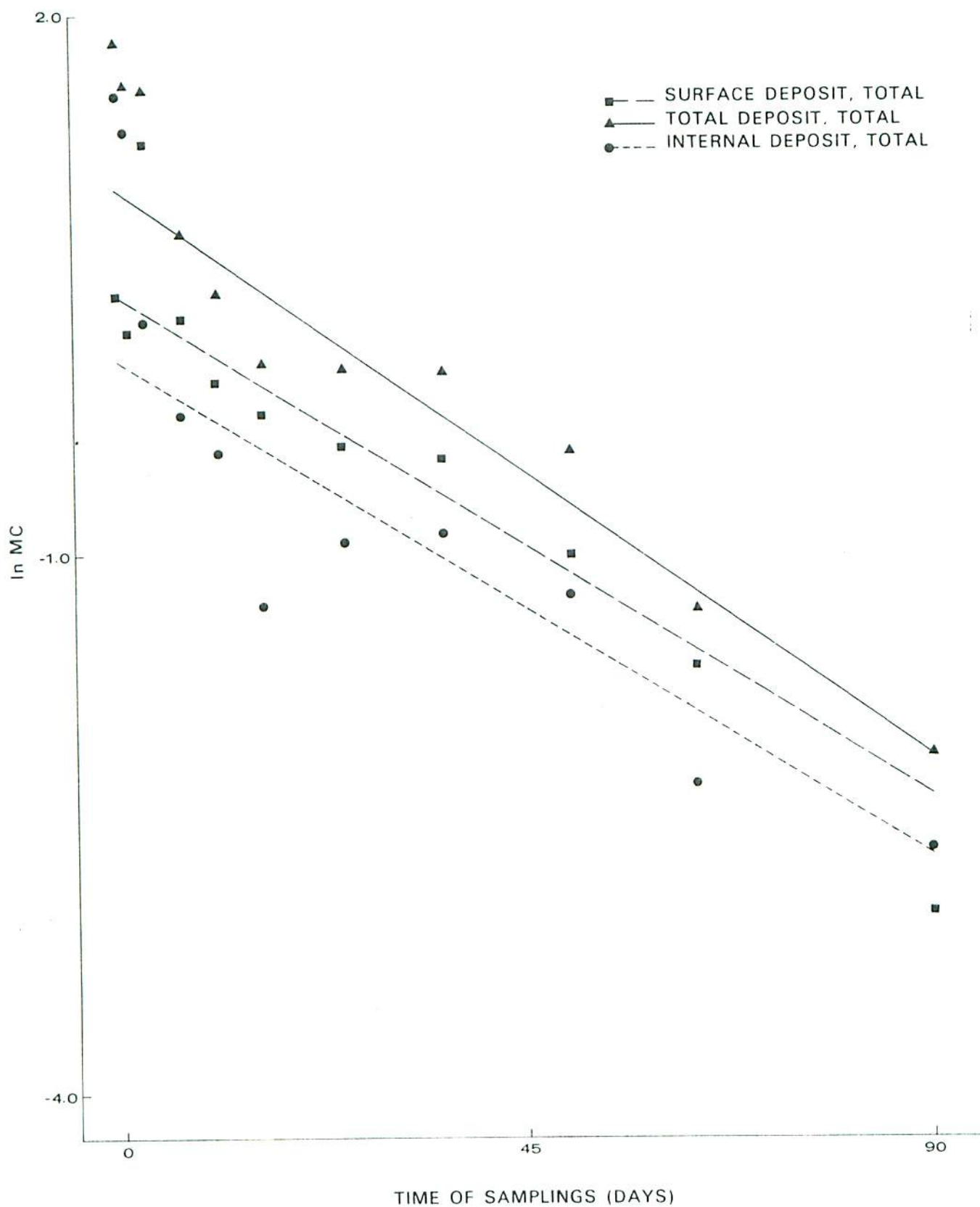


Fig. 7. Plot of $\ln MC$ vs Time to show the kinetic behaviour of methoxychlor dissipation.

On the third day, the total MC concentration observed was the maximum at 3.58 ppm when the penetration and accumulation of the insecticide molecules were completed. The percent individual amounts of the MCE, o,p- and p,p'-isomers observed were ca 7, 8 and 85 respectively, again showing, as observed earlier in the surface deposits, an enormous increase (233%) in the concentration of the olefin from the recorded initial level. The disappearance of the persisting subsurface total residue was comparatively slow (half life ca 7.5 d vs 1.5 d for the surface deposit) to the surface deposit and did not show a smooth exponential decrease due to the peak observed on the third day. Detectable amounts (0.05 ppm) of the p,p'-isomer was found even after 90 days.

The last column in Table 1 gives the total (surface + internal) methoxychlor (MCE + o,p-MC + p,p'-MC) residues present in the white pine leaders analysed. A maximum concentration of 6.32 ppm comprising ca 2% of MCE, 14% of the o,p-isomer and 84% of the p,p'-isomer was observed on the zero day. As observed earlier, the MCE concentration rose to a maximum of 0.36 ppm on the third day although the total concentration of the insecticide decreased to 5.02 ppm from the initial level of 6.32 ppm. Residue data show a rapid decline in the total residue levels especially after the third day and on the seventh day a loss of 66% has occurred from the initial deposit level. Afterwards the rate of loss was not very significant and a small but measurable amount of the insecticide lingered up to the last day of sampling. The degrading residue half-life found when plotting MC (total) vs time (days) was ca 5 days compared to the $T_{\frac{1}{2}}$ of 1.5 and 7.5 days respectively

for the surface and internal deposits. The ratio of the chemical half-lives found for the three residue data (total, surface and internal) were 1: 0.3 : 1.5. The overall residue level observed in the present investigation was much lower (nearly half, 6.32 ppm vs 12.82 ppm) compared to the value recorded in 1973 under similar experimental spray conditions.

The degradation patterns of the MC-isomers and its olefin metabolite in the internal surface and total deposits are shown in Figs. 3-6. Both the isomers show somewhat exponential decay patterns but this is not the case with the olefin metabolite (Fig. 3) because of its formation from the parent *p,p'*-isomer accompanied by dissipation after the third day of application. Plots of ln MC vs days for the three total deposits (surface, internal and surface + internal) are shown in Fig. 7 to demonstrate first-order dissipation kinetics in spite of the variations encountered in the residue data during analysis. Although the points are scattered, the overall kinetic behaviour is apparent.

Efficacy of Methoxychlor Treatment for Weevil Control

Systematic and periodic observations on the fluctuation of insect populations during the years 1973 and 1974 at the Ramsayville experimental and check plots, and careful counting of weeviled trees during the pre-spray and post-spray periods at these plots formed the basis for evaluating the spray efficacy (for more details see DeBoo and Campbell 1974b). The percent weeviling of the leaders during the period was calculated and Abbott's formula (1925) used to obtain changes in leader injury for the two years 1973 and 1974 as shown below:

$$\text{Percent reduction between years} = \left[\frac{\% \text{ Weeviled in 1973} - \% \text{ Weeviled in 1974}}{\% \text{ Weeviled in 1973}} \right] \times 100$$

Analysis of the results of 1974 aerial application of methoxychlor showed that the percent weeviled in 1973 pre-spray period was 11 and in 1974 post-spray i.e. after the insecticide was applied, the number decreased to 5 showing a fall of 6 percent, thereby giving a 55% $[(11-5/11) \times 100]$ reduction in weeviling during the intervening period. Similar results obtained from the control plot showed an average 100% increase in the number of weeviled trees. The reduction in weevil injury of 55% observed in the 1974 spray operation at Ramsayville is far below the accepted level of 85% protection observed earlier (DeBoo and Campbell 1972, 1974a) using the same insecticide. Evidently the treatment used in 1974 was found to be ineffective. Considering the morphology and the mode of weevil behaviour, it appears that the chemical was not available on the leader surface in sufficient quantities (low zero day residue level) for a sufficient period of time (low half life) for the weevil to come in contact with the toxin. For the acceptable 85% leader protection, the initial deposit concentration on the leader surface should be ca 15-20 ppm and the residue should be sufficiently concentrated to act as a contact toxin and be active on the leaders for at least 10 days after the application. Unless these two conditions are satisfied adequately, our combat against pine weevil will be ineffective resulting in failures as observed now and the weevil will have an upper hand and we will be forced to find consolation very often in Murphy's law (DeBoo and Campbell 1974b).

The overall results of the 1974 spray application of methoxychlor for weevil control was rather disappointing in spite of its proven efficiency observed in the past two years. Recent GLC analysis of the spray mixtures

used in the 1974 spray program showed that many of them contained on an average below the required amount instead of the normal application dose level of 2.8 kg AI/ha (2.5 lb AI/acre). This could explain the low initial residue levels observed on the leader surface and for the low half-life of the compound in the substrate; consequently accounting for its ineffectiveness in weevil control. The efficacy of an insecticide also depends to some extent on the formulation used. An E.C. formulation in oil used in the 1974 spray program appears to be rather incompatible on smooth waxy leader surfaces due to poor retention of spray drops. Probably much of the insecticide deposited initially could have dripped off due to presence of the emulsifier accounting for the rapid loss of the compound from the substrate. An oil-based formulation without an emulsifier would increase the retention and deposition characteristics of the spray drops which in turn will increase the initial deposit level of the toxicant and its residue half-life thereby enhancing the efficacy of the insecticide in white pine weevil control.

SUMMARY

High-value white pine plantation near Ramsayville east of Ottawa was treated with methoxychlor E.C. in an oil formulation to control white pine weevil infestation. The reduction in weeviled trees was only 55% showing that the new formulation did not provide sufficient protection against weevil attack probably due to the problems encountered in preparing the spray mixture and the poor retention of the deposited material on leader surface. The maximum initial deposit (total) was only 6.32 ppm which decreased rapidly at the beginning with a half-life of 5 days, thereafter gradually to 0.12 ppm after 90 days. The maximum surface deposit and internal residue levels of the compound were 4.79 and 3.58 ppm respectively. The dissipation rate of methoxychlor deposit on the leader surface was much higher than the internal residue, the degrading deposit half-life was 1.5 days and the persisting residue half-life was 7.5 days.

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