A PRELIMINARY REPORT ON THE PERSISTENCE OF METHOXYCHLOR

FOR THE CONTROL OF WHITE PINE WEEVIL IN

PLANTATIONS

BY

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Information Report CC-X-31

November 1972

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INTRODUCTION

White pine (<u>Pinus</u> <u>strobus</u> L.) is a valuable commercial tree species widely distributed in eastern North America. The white pine weevil, <u>Pissodes</u> <u>strobi</u> Peck, is the major insect pest of this species throughout its range. Damage to the leaders of trees results in degradation of quality in the main stem which, in turn, diminishes the value of logs for the lumber industry (Brace 1971). During the past two decades, weevil damage was minimized by aerial applications of DDT [2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane] (Connola et al 1955, Kirby et al 1962). Since the use of the compound has been discontinued due to its accumulation and biological magnification in the environment (Metcalf et al 1972), currently control is sought in Ontario with spray applications of methoxychlor [2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane], a less hazardous and more readily biodegradable material than DDT. Recently, several authors (Metcalf 1966, Warner 1967, Burdick et al 1968, Moubry et al 1968, Menzie 1969, Hunt and Sacho 1969, Kapoor et al 1970, Kennedy et al 1970, Reinbold et al 1971, Edwards and Glass 1971, Merna 1972) favoured this compound as an effective replacement for DDT in the control of various insect pests. Howse and Sippell (1971) have shown that aerial applications of methoxychlor at 2 to 3 lbs per acre do not reduce weevil damage to acceptable levels. Recently DeBoo and Campbell (1971, 1972) have shown that efficient and timely application of an aqueous emulsion of methoxychlor by use of a hydraulic ground sprayer at the rate of 1 to 2 lb(s)/acre reduced weevil infestation by 95-100%.

Although the insecticide is commonly used for the control
of white pine weevil (loc. cit.), elm bark beetles (Kapoor et al 1970
and the references cited therein) and other insect pests (Chemical
Control Research Institute 1972), very few reports have been published
on the distribution, fate and persistence of methoxychlor sprays
under forest conditions. The present study was undertaken in
conjunction with the current research program of this Institute on
methoxychlor with the following major objectives:

(1) to evaluate quantitatively, under field conditions,
the toxicity of methoxychlor on sprayed leaders* and associated foliage
at varying intervals of time and to correlate these measurements
with reduction in weevil infestation and mortality;

(2) to study the persistence and possible degradation routes
of the insecticide and its disappearance rate in the forest environ-
ment;

(3) to evaluate the insecticide as a possible replacement for
DDT and other chlorinated hydrocarbons in controlling forest insect
pests, with minimal hazard to the environment.

<center>MATERIALS AND METHODS</center>

Experimental Plan

Field experiments were conducted in a white pine (Pinus
strobus L.) plantation during the period May to September 1972 at the
Orr Lake Forest, approximately 14 miles northwest of Barrie, Simcoe
County, Ontario. A plot measuring approximately 0.4 acre, having
11 rows, each containing 110 trees, with the mean height of

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*The term 'leader' in this report refers to the leading or top shoot
of white pines including bark and wood but NOT the associated foliage.

10' and DBH of <u>ca</u> 2.2", was established for the study. Another identical plot situated a mile away from this and free of insecticide served as the control.

Spray Applications

Spraying was done on the morning of May 9, 1972, coinciding with maximum adult weevil activity and under favourable meteorological conditions. Methoxychlor (25 EC) was supplied by Green Cross Products, Toronto. The spray mixture was analysed by GLC after necessary cleanup, and found to contain 22.10% of <u>p,p</u>' and 1.20% of <u>o,p</u>-methoxychlor isomers. The sprays were applied by a truck-mounted hydraulic sprayer at the rate of 100 gallons of water emulsion containing 2.0 lbs of methoxychlor (25 EC) per acre. A detailed account of the spray application technique is discussed by DeBoo and Campbell (1971, 1972). For brevity and to avoid repetition, the technique is not fully described here. Care was taken to direct the spray stream uniformly to the upper whorl of branches, with particular attention given to the leaders. Each tree top was sprayed to the dripping point.

Sampling Procedure

At various intervals [-2 (prespray), 0, 1, 3, 6, 12, 18, 24, 36, 72 and 144 days (postspray)] following the application, samples of leaders and foliage were collected using a pole-pruner, from ten randomly chosen trees within the plot and from the control area for the determination of the insecticide residues. Prespray samples were collected two days before the treatment. The samples of the leaders and foliage, from the control and sprayed

plots were composited separately in polythene bags, stored in coolers at near 0°C and transported immediately by commercial carrier to the Institute's Chemical Laboratory in Ottawa for analysis. Most samples reached Ottawa within a 24-hour period.

Extraction Procedure

In the laboratory, the composited leaders and foliage were chopped separately into tiny pieces by hand pruners. Each sample was mixed thoroughly until a homogeneous mixture was obtained. Three 10 g replicates of each sample (leaders and foliage) were weighed and placed in 0.5-liter glass stoppered pyrex conical flasks and macerated overnight (ca 16 hrs) with 200 ml of 1:1 methylenechloride:methanol (V/V) solvent mixture*. The crude slurry, after ca 15 hour interval, was drawn through a narrow fritted glass funnel containing a 10 cm column of anhydrous sodium sulphate (15 g) to absorb the water present in the extract. The residue and the column were washed twice with 20 ml of the solvent mixture. The residue was then discarded. The combined extract and the washings were flash evaporated just to dryness

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*Other solvents such as benzene and hexane and solvent systems such as chloroform:methanol 1:1 (V/V), hexane-methylenechloride 1:1 (V/V) and acetone:hexane 1:1 (V/V) were also tried as extracting solutions. The solvent system used was found to be efficient for extraction of methoxychlor residues from both leaders and foliage. Because of its high dielectric constant, nonpolar moieties present in the samples were not co-extracted, and consequently column poisoning was minimal, and recovery precision good.

under reduced pressure at room temperature and the residue in the flask diluted to a convenient volume (ca 5 ml) with hexane.

Analytical Procedure

For quantitation of methoxychlor residues in the extract, the one-step Florisil column method of Langlois et al (1964) was employed with minor modifications. Florisil, 60/100 mesh, activated commercially at ca 500°C, was reheated at 135°C for a period of 24 hours. Upon cooling to room temperature, the adsorbent was partially deactivated by the addition of water at the rate of 5 ml per 100 g Florisil. It was then held in an air-tight container, and allowed to equilibrate during a 12-hour tumbling period. Thirty grams of deactivated Florisil was poured into a chromatographic 20 mm x 260 mm Pyrex column fitted with fritted glass disc and Teflon stopcock at one end and 300 ml glass reservoir at the other. Ten grams of anhydrous sodium sulphate was added to the column and the contents were packed uniformly using an automatic mixer. Tightness of packing contributed greatly to the retention of chlorophyll and other impurities in the column thus leading to satisfactory cleanup in most cases. If interference still occurred in GLC analysis, especially with foliage samples, solvent partition (Sundaram 1972) using acetonitrile was necessary in addition to column cleanup for the removal of such interfering materials. The column was prewashed with 25 ml of hexane and the washings discarded. The methoxychlor sample in hexane was then introduced quantitatively to form the top layer.

The column was eluted with 450 ml of 1:4 dichloromethane:hexane (V/V) elution mixture (Frank et al 1970) at a percolation rate of 3-6 ml/minute. In some instances additional elution mixture or changes in polarity of the elution mixture was necessary to obtain reasonable recovery. The eluate was concentrated just to dryness in a flash evaporator at room temperature and the residue dissolved to 2 ml of hexane (diluted more if necessary) and transferred quantitatively to a stoppered centrifuge tube for subsequent gas chromatographic analysis.

Since DDT residues may be present as ubiquitous environmental micropollutants, frequent checks for their presence were made by carrying through the described procedure above, and eluting the adsorption column with 200 ml of hexane and injecting the concentrated eluent into the gas chromatograph. No peaks corresponding to DDT isomers and or their olefin metabolites were found, consequently no further attempts were made to detect them in the samples analysed.

A Hewlett-Packard Model 5750 gas liquid chromatograph equipped with a 63 Ni electron capture detector was used for all quantitative assays of methoxychlor residues. Operating parameters were as follows:

Column: 4' x 0.25" Pyrex glass packed with 3.8% SE30 on Chromosorb W, 60-80 mesh, AW-DMCS, preconditioned 48 hours at 230°C.

Temperature (°C):   Injection ports 210-220

                                            Column oven   190

                                              Detector   280

Carrier gas: Argon/methane (95/ 5%) pressure of

                                              50 psi and flow rate of 50 ml/min.

Instrument settings: Attenuation and range, 16 x 10;

                                              pulse rate 50

Injection volumes were kept constant at 4 µl for both sample solutions and comparison standards. Where necessary, sample solutions were diluted until chromatographic responses were within the linear range of the detector. Under these conditions the ratio of relative retention times were: p,p'-methoxychlor ethene [2,2-bis-(p-methylphenyl)-1,1-dichloroethene] (hereinafter referred to as MCE), 1.00; o,p-methoxychlor, [2,2-bis(o,p-methoxyphenyl)-1,1,1-trichloro-ethane], (hereinafter referred to as o,p'-MC), 1.13 and p,p'-methoxy-chlor (hereinafter referred to as p,p-MC), 1.61. Since all analyses were carried out under isothermal and isobaric conditions, peak heights alone were used for quantitation by comparing with calibrations for MCE, o,p-MC and p,p'-MC. Quantitative p,p'-MC standards were injected on the same day the samples were analysed to provide corrections as necessary for the day-to-day fluctuations in operating conditions.

The overall recovery of p,p'-MC ranged between 70-75% ($\bar{x}$ = 72.5%), for several spiked samples of leaders and foliage with the techniques described above. The data presented in this report does not include recovery corrections. Several revisions of the

method were made to improve the recovery of the insecticide from fortified samples but none was satisfactory.

All solvents used were either pesticide grade chemicals or had been fractionally distilled in glass. The anhydrous sodium sulphate used was of reagent grade, heated at 400°C overnight and stored in a glass-stoppered bottle. Laboratory sources of contamination were found to be minimum.

Kinetics of Insecticide Residue Disappearance

The disappearance of most pesticide residues appears to depend on first order reaction kinetics (Ebeling 1963 and the references cited therein on p. 117, Ruzicka et al 1967, 1968). The rate equation for such a reaction can be represented as:

$$\ln [A]/[A_o] = -kt$$

where the initial concentration (zero day for the foliage and one day for the leaders -- see table 1) of the insecticide is $[A_o]$, after time t, the residue concentration drops to $[A]$, and k is the rate constant of the reaction. A plot of $\ln [A]/[A_o]$ (logarithm of residual insecticide or preferably its percentage) versus the time of exposure (days) yielded a straight line and k was evaluated from its slope. The half-life $(t_{0.5})$ of methoxychlor, i.e., the time in which half the insecticide originally present has disappeared, was calculated from the equation

$$t_{0.5} = 0.693/k$$

The decay pattern of methoxychlor isomers followed close to first order kinetics. Similar study was not made for the olefin metabolite of the insecticide.

RESULTS

Methoxychlor residues (p,p'-MC, o,p-MC, MCE and their total) found in leaders and foliage of white-pine trees at various times after spraying are given in Table 1. All samples were collected around 9 a.m. on the collection day to minimize errors that might arise due to time variations. This precaution facilitated the standardization of all residue data for comparison and interpretation. The analytical results are expressed in ppm of the mass of the samples as collected and are the mean of 2-3 replicates. The deviation of individual values from the mean was ca 15%. Concentration values below 0.03 ppm are recorded as traces due to analytical sensitivity of the GLC instrument used. Leader and foliage samples from the control plot gave negative results for methoxychlor residues, hence are not recorded. Similarly prespray samples also did not contain any insecticide residues. None of the samples analysed contained any detectable DDT residues (p,p-DDT; o,p-DDT and DDE).

Plots of percent residual insecticide, i.e., $[A]/[A_o] \times 100$ vs time (days) (see Table 1) showing the decay pattern of p,p'-methoxychlor in leaders and leaves are shown in Fig. 1. Similar decay patterns for the o,p-isomer are exhibited in Fig. 2. Both isomers showed initially a linear and later, a curvilinear decrease of concentration with time. Uptake and rate of fall of the p,p'-isomer in the foliage were greater than in the leaders. A nonuniform fall in concentration of the o,p-isomer was observed (Fig. 2) in leaders. This was a-typical in comparison to the other isomer. Except for experimental

error involved in the measurements of very low concentrations of the
isomer present (see Table 1), no satisfactory explanation could
be offered for the deviations. No such variance was observed in the
dissipation of the o,p-isomer from the leaves. Logarithmic plots of per-
cent residual insecticide, i.e., ln ([A]/[A$_o$] x 100) against time t
(days) are shown in figs. 3 and 4 for the methoxychlor residues in leaves
and leaders were linear indicating that dissipation of the
insecticide from foliage and leaders obeyed nearly first-order
kinetics, an observation in conformity with those of Ebeling (1963) and
Ruzicka et al (1967, 1968). Due to fluctuations in the measured
concentrations of the o,p-isomer, appreciable deviations are
observed (Fig. 4) in the logarithmic plot of the o,p-isomer against
time. Plots of formation and disappearance of MCE (methoxychlor-
ethene) in sprayed foliage and leaders against time t (days) are re-
presented in Fig. 5. Initial metabolite concentration in leaders
was low (0.25 ppm), but reached a peak value of 1.66 ppm after 12 days,
and disappeared completely after 72 days. In foliage, on the
other hand, the concentration of MCE reached a maximum of 14.32
ppm on the third day from the initial value of 2.81 ppm, showing
a pronounced peaking in the curve. It gradually fell to 0.51 ppm
after an interval of 72 days and then disappeared completely.

TABLE 1

Mean Values of Methoxychlor Residues Found in Foliage and Leaders of White Pine Trees at Various Times After Treatment[*]

Time Relative to Application (Days)	Leaders p,p'-MC ppm	Percent Residual	o,p-MC ppm	Percent Residual	MCE ppm	Total[†] ppm	Leaves p,p'-MC ppm	Percent Residual	o,p-MC ppm	Percent Residual	MCE ppm	Total[†] ppm
-2**	N.D.	---	N.D.	---	N.D.	---	N.D.	---	N.D.	---	N.D.	---
0	78.70	---	0.95	---	0.25	79.90	512.16	100.00	5.44	100.00	2.81	520.41
1	111.00	100.00	1.55	100.00	0.70	113.25	498.65	97.36	5.39	99.08	7.50	511.54
3	104.13	93.81	0.88	56.97	1.60	106.61	477.00	93.14	5.00	91.91	14.32	496.32
6	100.35	90.41	0.86	55.48	1.65	102.86	416.00	81.23	3.79	69.67	12.83	432.62
12	95.00	85.59	0.84	54.19	1.66	97.50	389.00	75.95	1.98	36.40	4.11	395.09
18	70.00	63.06	0.72	46.45	1.22	71.94	312.10	60.92	1.16	21.32	3.96	317.22
24	57.56	51.86	0.61	39.55	1.10	59.27	248.00	48.42	0.85	15.63	2.99	251.84
34	44.00	39.64	0.30	19.36	0.50	44.80	145.00	28.31	0.59	10.85	2.55	148.14
72	6.50	5.86	0.03	1.36	0.08	6.61	18.00	3.51	0.03	0.55	0.51	18.54
144	N.D.	---	N.D.	---	N.D.	---	T	---	N.D.	---	N.D.	---

* All sampling was done ca. 9:00 a.m. on the collection day. Concentrations are expressed in ppm and were calculated on a wet-weight basis. Residue values recorded represent the mean of 2 or 3 determinations. The deviation of individual values from the mean was ca. 15%. Samples from control plot gave negative results for methoxychlor. In kinetic study, $[A_o]$, the initial concentration of o,p- and p,p'-MC for leaders and leaves were taken as 1.55 and 111.00 (1 day); 5.44 and 512.16 (0 day) ppm, respectively.

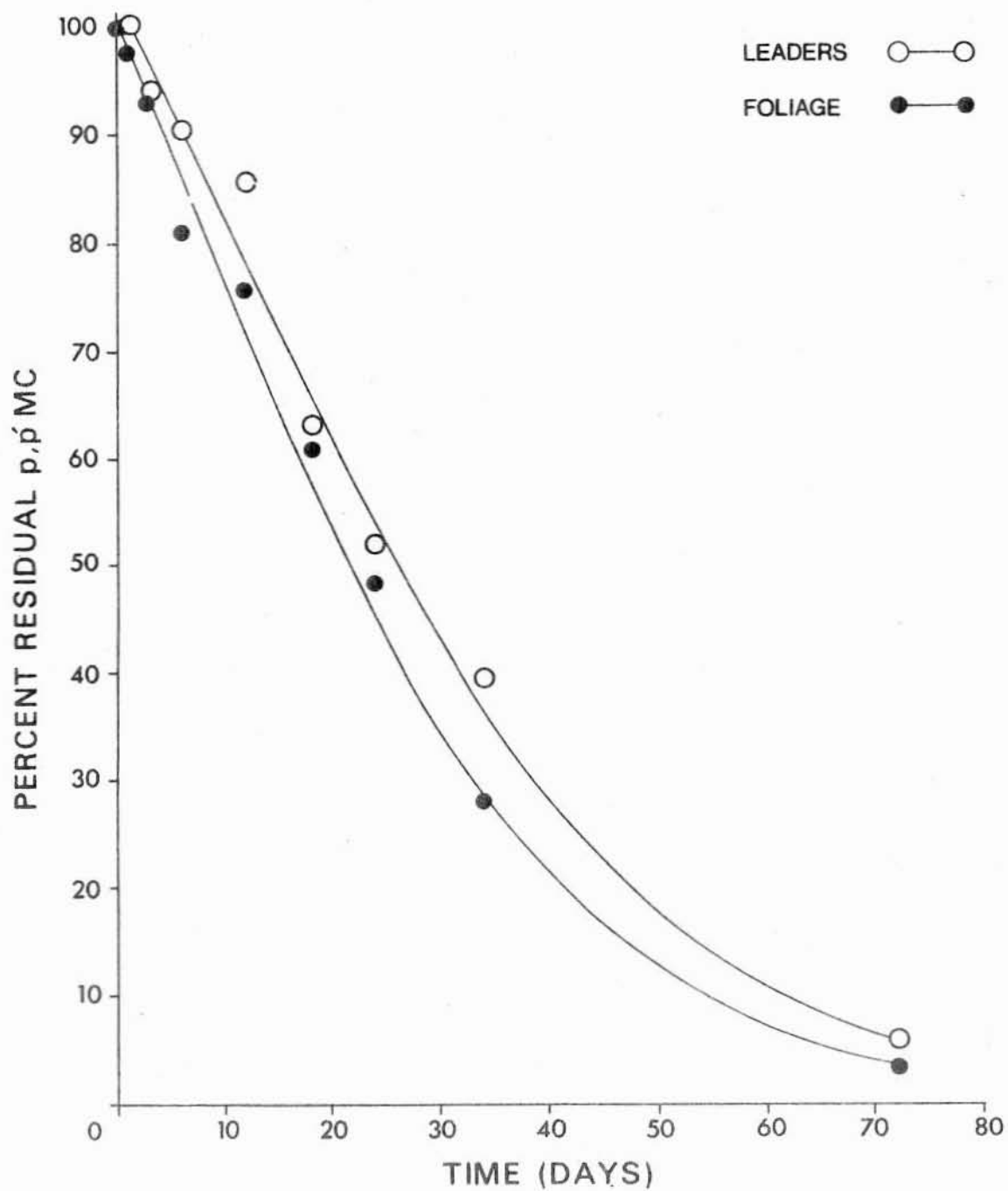** Prespray samples   † Recorded as p,p'-MC   N.D. = Not Detected   T = Traces(< 0.03 ppm)

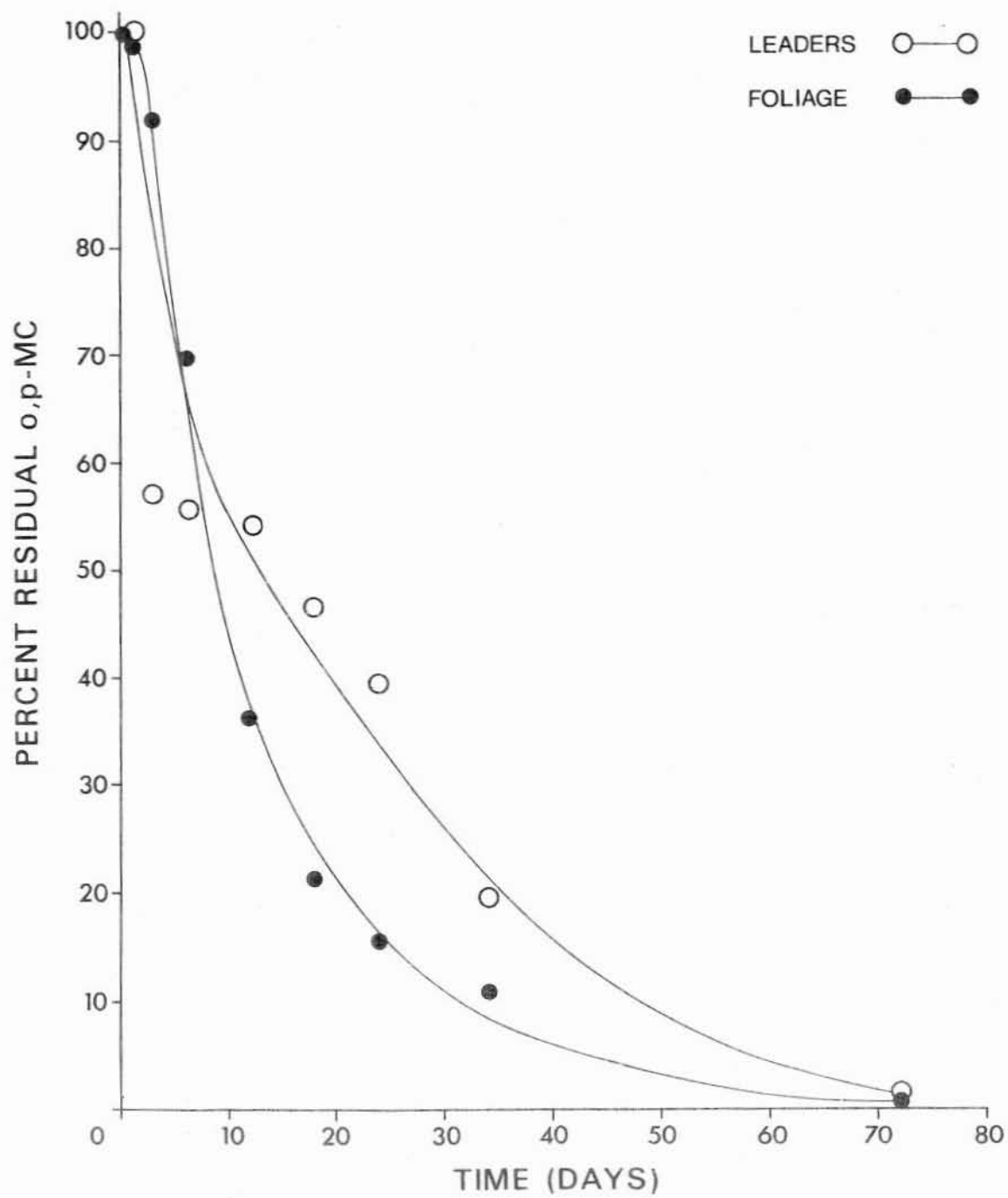Fig. 1: Percentage of p,p'-methoxychlor in leaders and foliage.

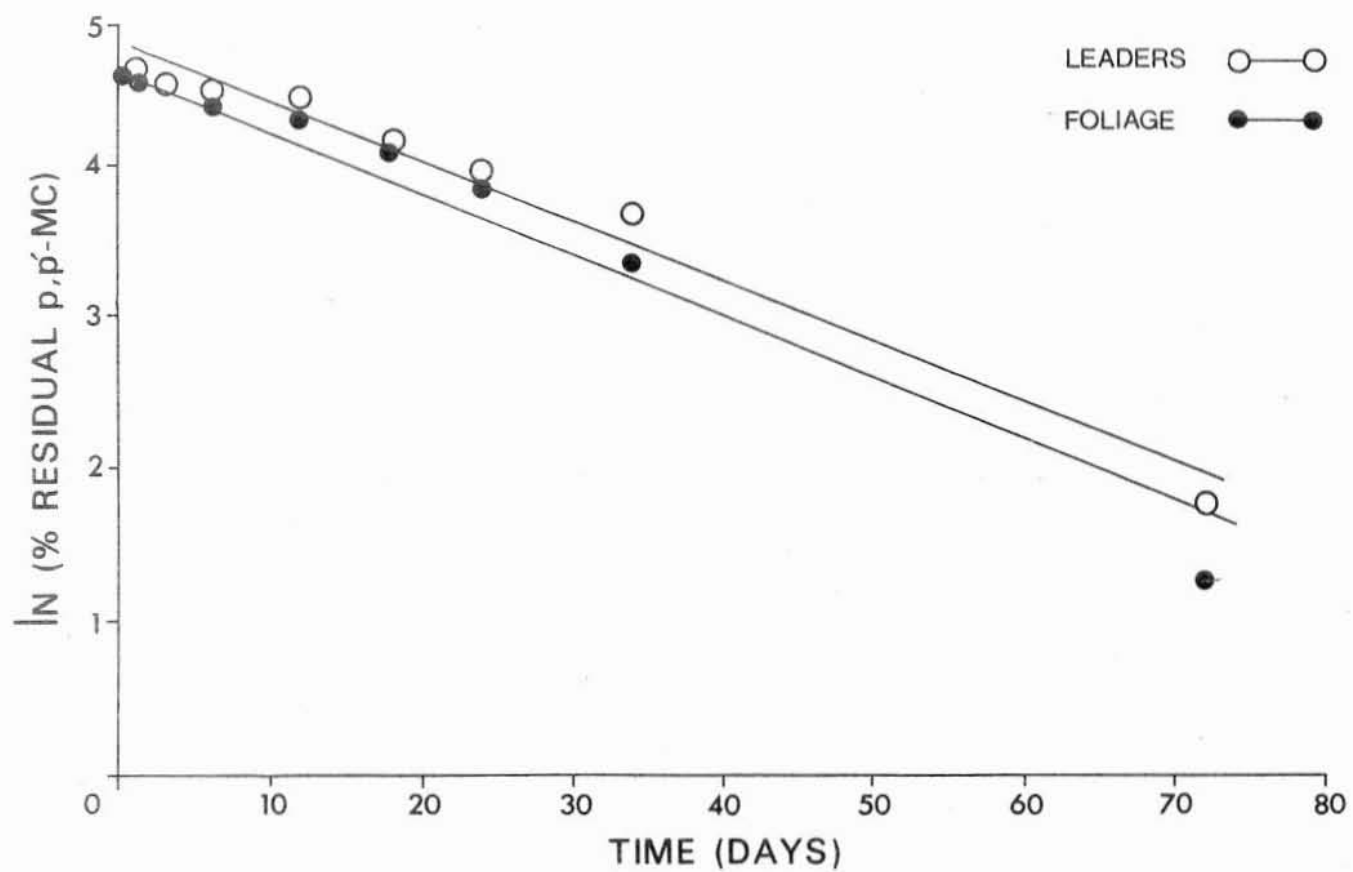Fig. 2. Percentage of residual o,p-methoxychlor in leaders and foliage.

Fig. 3. Logarithmic rate of loss of p,p'-methoxychlor in leaders and foliage.

Regression equations for the straight lines are: $Y = 4.80 - 0.039x$ (leaders)
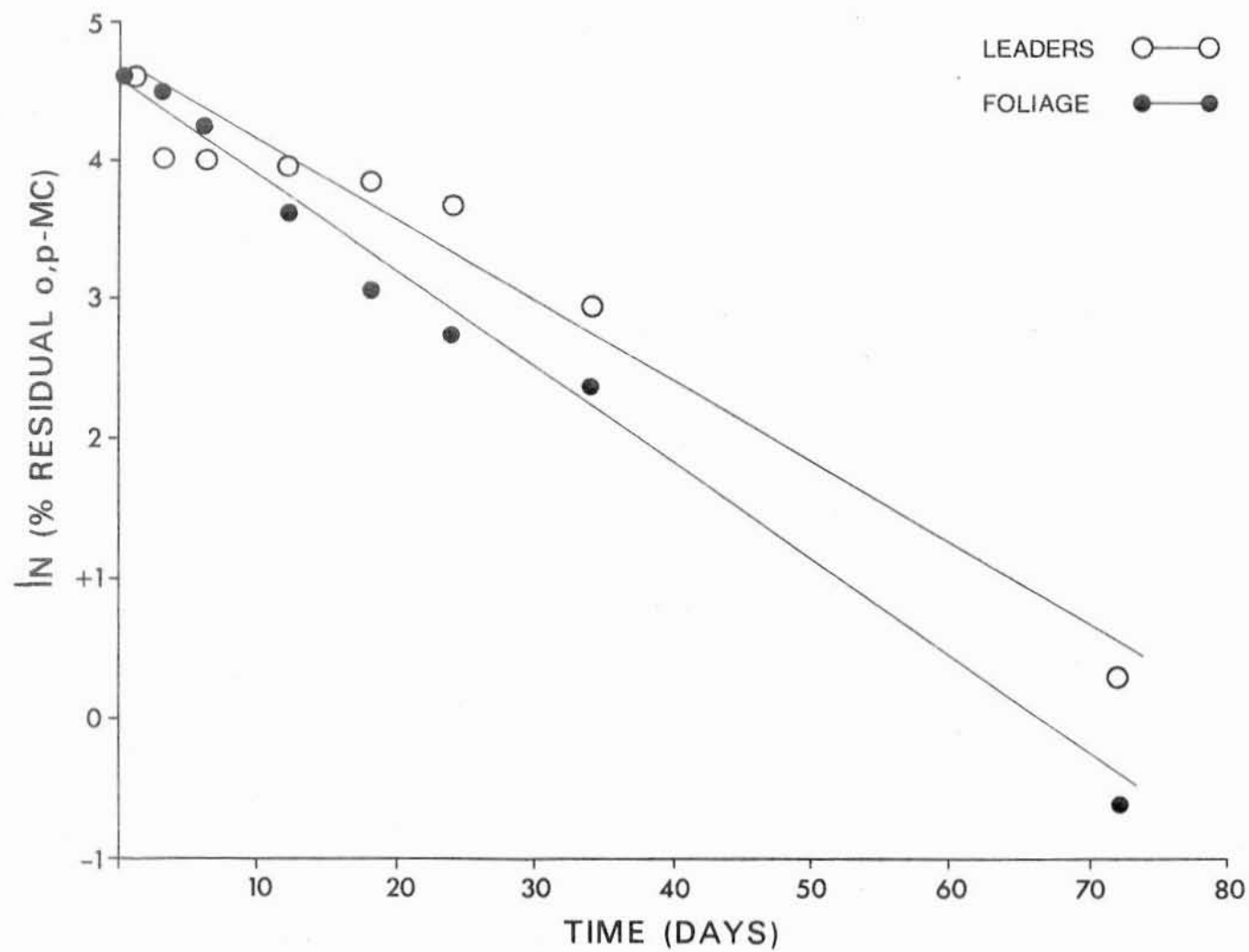
$Y = 4.76 - 0.046x$ (foliage)

Fig. 4. Logarithmic rate of loss of o,p-methoxychlor in leaders and foliage.

Regression equations for the straight lines are: $\mathbf{Y} = 4.62 - 0.056x$ (leaders)
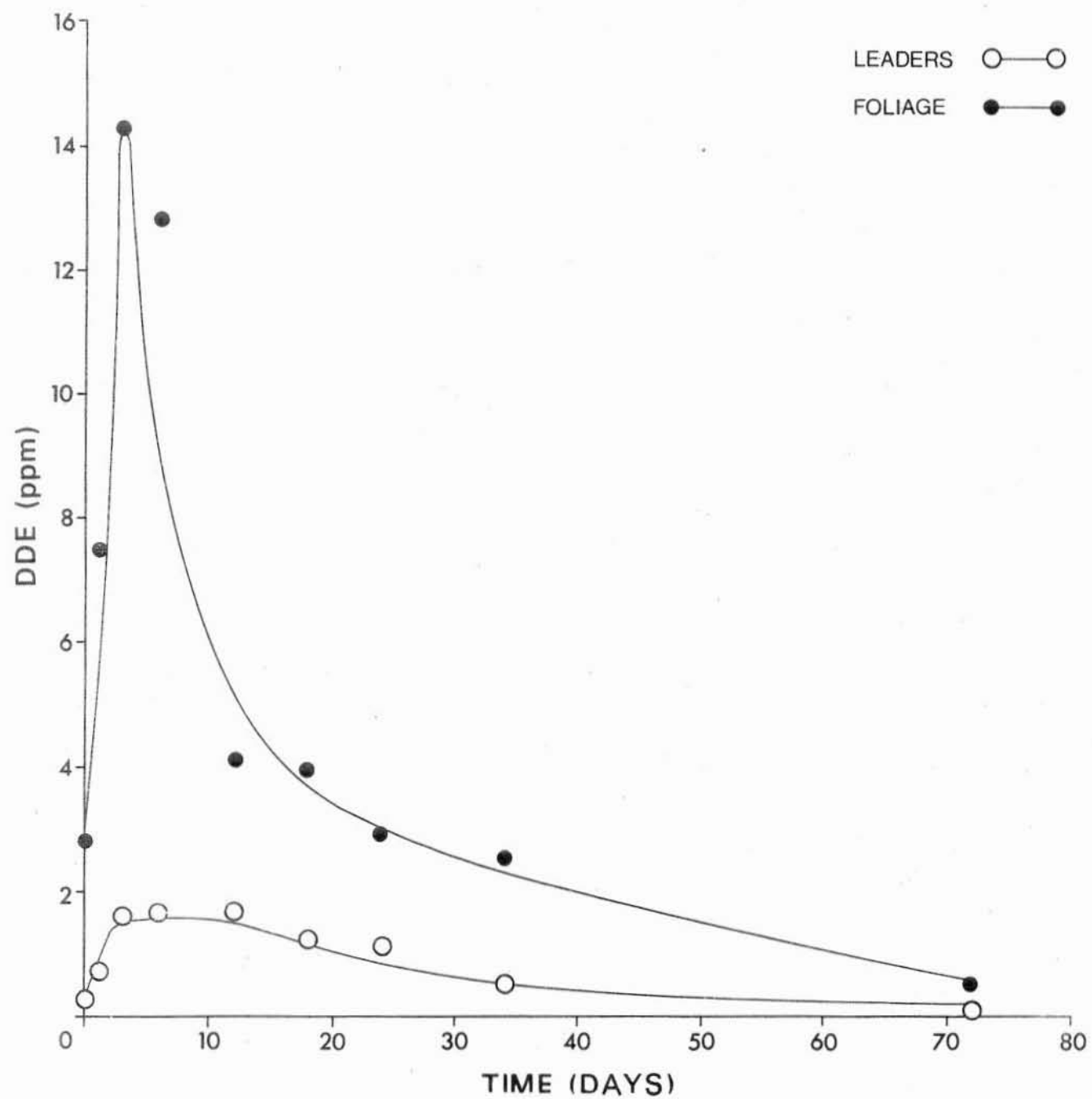$Y = 4.61 - 0.072x$ (foliage)

Fig. 5. Formation and disappearance of methoxychlorethane (MCF) in leaders and foliage.

DISCUSSION

Distribution of methoxychlor residues

The initial deposit of methoxychlor residues (Table 1)
found on day zero in leaders and foliage of white pine trees
varied considerably. The leaders contained only 79.90 ppm
(column 5) whereas the foliage concentrated a substantial
amount, nearly 6.5 times more (520.41 ppm - column 9) of the
insecticide. The large amount of initial deposit on the
foliage showing a peak concentration, could be attributed to
adsorption of spray droplets on pubescence (Hardee et al 1963)
and presumably also through solution of the toxicant on the
waxy leaf surface of coniferous foliage (Ebeling 1963, Yule
and Duffy 1971). Metcalf et al (1956) and Crafts (1960)
pointed out that the highly lipoidal nature of some foliage
cuticle and apolar nature of leaf surfaces greatly favoured
adsorption and retention of insecticide residues. The increase
in concentration of the pesticide in the leaders from 79.90 to
a peak of 113.25 ppm on the first day after spray, was due to run
off of the trapped pesticide emulsion from the foliage to the
adjoining leaders. Although technical methoxychlor contains ca
12% of the o,p-isomer (Metcalf 1955), the sample used for
spraying contained only 6% of the isomer. This is reflected in
the analytical data presented in Table 1, wherein the p,p'-methoxychlor
constituted the bulk of the residue compared to the minimal

amounts of the o,p'isomer present in the samples. The olefin meta-bolite MCE, formed by enzymatic dehydrochlorination (Kapoor et al 1970) and photodecomposition (Li and Bradley 1969) from the p,p'-MC, was found initially in traces in leaders (0.25 ppm) and foliage (2.81 ppm), gradually rose to 1.66 ppm in leaders after 12 days and to 14.32 ppm in leaves after only 3 days (see Fig. 5) and disappeared completely after 72 days. The rise and fall in concentration of the olefin in the substrates substantiated, as observed earlier (loc. cit.), its formation from the p,p'-isomer through bio- and photo-transformations. The large amount of MCE in the foliage was primarily due to the high concentration of the parent material observed in the leaves.

Persistence of methoxychlor residues

Kapoor et al (1970) and Reinbold et al (1971) esta-blished that methoxychlor, unlike DDT, is rapidly biodegradable through attack by the multifunction oxygenase enzymes found in plant and animal tissues. The disappearance rate of the insec-ticide in leaves and leaders (Table 1), vary considerably between the two. In most instances the rate of disappearance of the residues in foliage was faster than in leaders. The percent residual p,p'-MC in leaders after 12 days of spraying was found to be 85.59 ppm compared to 75.95 ppm in the foliage. A similiar disap-pearance pattern was observed for the o,p-isomer. The greater amount of initial deposit of the insecticide in leaves accounted for its rapid loss. Detectable amounts of the residues were present in leaders and foliage up to 70 days; beyond this period,

they disappeared to infinitesimal amounts from the system through various physicochemical processes such as enzymatic degradation to form phenolic derivatives by 0-demethylation, which can be conjugated and eliminated (Kapoor et al 1970), photodecomposition causing the formation of olefins, phenols and ketonic compounds* (Li and Bradley 1969), weathering by rain and wind, growth (leaders grew an average of 18" during May-September), volatilization, humidity (RH observed during the experimental period was around 65%) and chemical decomposition including hydrolysis. The curvilinear relationship of the percent residual methoxychlor isomers to time (Fig. 1 and 2) when the residue loss data were plotted as linear coordinates confirmed the rapid and rather uniform disappearance of the insecticide from the leaders and foliage. The times for 50% disappearance of the p,p'-isomer of methoxychlor in foliage and leaders read from these graphs were 21.5 and 26.0 days respectively.

The decay data of methoxychlor isomers compiled in Table 1 were used to plot ln [% residual insecticide] against time. Straight lines were obtained (Figs. 3 and 4) demonstrating that the process followed first-order kinetics. Rate constants recorded in Table 2 varied depending upon the sample and the isomer species involved. The o,p-isomers from the leaves and leaders had high

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*Recent studies of solution-based photolysis of methoxychlor at this laboratory followed by U.V. and I.R. analysis of the decomposition products, indicated the presence of polar moieties such as phenolic and carbonyl compounds, probably formed by various stepwise processes such as -0 demethylation, dehydrochlorination, hydrolysis and oxidation.

k values (k = 0.66 per day) compared to the p,p_'-MC k values

(k = 0.044 per day), showing the rapid disappearance of the former

from the samples studies. Furthermore, half-lives ($t_{0.5}$) calculated

from the equation

$$t_{0.5} = 0.693/k$$

showed comparatively low values for the o,p-isomer. The mean

half-life for the p,p'-isomer in leaders and leaves was low (15.83

days) confirming its rapid decay from the samples analysed.

Efficacy of methoxychlor treatment

The results of methoxychlor application at the rate of

2 lbs/acre (aqueous emulsion) by a hydraulic sprayer for the control

of white pine weevil during the current year at the Orr Lake Forest

are shown in Table 3. No insecticide applications were made in the

two previous years. From the results, it is apparent that after the

insecticide application, only 1 out of 200 trees examined on August

16, 1972 (i.e., 99.5% reduction) was weeviled showing that the

methoxychlor treatment provided excellent protection of white pines

against weevil attack. Low mammalian toxicity [LD_{50} for rats is

6000 mg/kg (O'Brien 1967)], rapid rate of disappearance, low half-

life, high reduction weevil population etc., qualifies methoxychlor

as one of the safest and most effective insecticides for plantation

pest control. Recent studies of DeBoo and Campbell (1972) showed

that spray applications of methoxychlor, even at 1.0 or 1.5 instead

of 2.0 lb/acre, appeared to be equally effective in protection of

leaders of white pines from attack by the white pine weevil. Addi-

tional large-scale field evaluations and appropriate monitoring of

TABLE 2

Kinetic Data for the Decay of Methoxychlor Residues

Isomer and sample species	k, day^{-1}	$t_{0.5}$ (days)
p,p'-MC (foliage)	0.047	14.75
o,p-MC (foliage)	0.073	9.49
p,p'-MC (leaders)	0.041	16.90
o,p-MC (leaders)	0.059	11.75

TABLE 3*

Methoxychlor Application, White Pine Weevil, Orr Lake

Year of Application	No. of trees checked	No. of trees weeviled	% weeviled
1970	351	112	31.9
1971	351	105	29.6
1972	200	1	0.5

*DeBoo, R. F. 1972   Personal Communication

possible deleterious side-effects to non-target organisms would
be necessary prior to wide-scale adoption and recommendation of
methoxychlor treatment for control of white pine weevil.

SUMMARY AND CONCLUSIONS

1. Applications of an aqueous emulsion of methoxychlor at the
    rate of 2.0 lbs/acre by hydraulic sprayer provided adequate
    protection of leaders of white pines from attack by the
    white pine weevil.

2. The residue levels in ppm of the insecticide in leaders and
    foliage was followed at increasing time intervals by solvent
    extraction, cleanup and quantitation by GLC analysis.

3. White pine foliage collected large amounts of methoxychlor
    (520.41 ppm) compared to leaders (113.25) but the rate of
    loss in the former was greater than in the latter. The
    residues persisted in detectable amounts (0.03 ppm) for
    about 70 days and then disappeared due to various physical
    and metabolic processes such as weathering, photodecomposition,
    biodegradation, etc.

4. Plots of the residual methoxychlor versus time as linear
    coordinates yielded curvilinear relationships; from the
    graphs the time for 50% disappearance of the insecticide
    was found to be 21.5 days in foliage and 26.0 days in
    leaders.

5. The decay process of the insecticide nearly followed first-
    order rate law. The average rate constant for the o,p-isomer
    was comparatively high (0.066 day^{-1}) to the p,p'-isomer

(0.044 day^{-1}). The average kinetic half-life for the latter isomer in leaves and leaders was low (15.83 days) confirming the rapid disappearance of methoxychlor from the system and justifying its low persistence and safety in certain components of the forest environment.

LITERATURE CITED

Brace, L. G. 1971. Effects of white pine weevil damage on tree
height, volume, lumber recovery and lumber value in
eastern white pine. Dept. Env., Can. For. Serv.
Inf. Rept. No. 1303, 33 pp.

Burdick, G. E., H. J. Dean, E. J. Harris, J. Skea, C. Frisa and
C. Sweeney. 1968. Methoxychlor as a blackfly larvicide,
persistence of its residues in fish and its effect on
stream arthropods. New York Fish and Game J. 15:
121-142.

Chemical Control Research Institute. 1972. Compendium on pesticides
for use in Canada - 1971 - for forests, trees, shrubs
and ornamentals. Dept. Env., Can. For. Serv. Inf.
Rept. No. CC-X-19, 129 pp.

Connola, D. D., T. McIntyre and G. G. Yops. 1955. White pine weevil
control by aircraft spraying. J. Forestry 53: 889-891.

DeBoo, R. F. and L. M. Campbell. 1971. Plantation research: IV.
Field evaluation of insecticides for control of white
pine weevil (Pissodes strobi) in Ontario, 1971.
Dept. Env., Can. For. Serv. Inf. Rept. No. CC-X-11,
22 pp.

DeBoo, R. F. and L. M. Campbell. 1972. Plantation research: VI.
Hydraulic sprayer applications of insecticides for
control of white pine weevil (Pissodes strobi) in
Ontario, 1972. Dept. Env., Can. For. Serv. Inf.
Rept. No. CC-X-24, 15 pp.

Ebeling, W. 1963. Residue Reviews, Vol.3, Academic Press, N.Y.,
p. 116.

Edwards, W. M. and B. L. Glass. 1971. Methoxychlor and 2,4,5-T
in Lysimeter percolation and run-off water. Bull.
Environ. Contam. Toxicol. 6:81.

Frank, R., H. E. Braun and J. W. McWade. 1970. Chlorinated hydro-
carbon residues in the milk supply of Ontario, Canada.
Pesticides Monit. J. 4: 31-41.

Hardee, D. D., E. W. Huddleston and G. G. Gyrisco. 1963. Initial
deposit and disappearance rates of various insecticides
as affected by forage crop species. J. Econ.
Entomol. 56: 98-101.

Howse, G. M. and W. L. Sippell, 1971. White pine weevil aerial
spraying operations, Ontario, 1971. Rept. Meeting
Interdepartmental Committee Forest Spraying Operations,
Canadian Forestry Service Mimeograph Rept., Appendix
21, 3 pp.

Hunt, L. B. and R. J. Sacho. 1969. Response of robins to DDT and
methoxychlor. J. Wildl. Mgmt. 33: 336-345.

Kapoor, I. P., R. L. Metcalf, R. F. Nystrom and G. K. Sangha.
1970. Comparative metabolism of methoxychlor, methio-
chlor, and DDT in mouse, insects and in a model eco-
system. J. Agr. Food Chem. 18: 1145.

Kennedy, H. D., L. L. Eller and D. F. Walsh. 1970. Chronic effects
of methoxychlor on bluegills and aquatic invertebrates.
U. S. Dept. Interior, Bur. Sport Fish. Wildl. Tech.
Paper 53, 18 pp.

Kirby, C. S., A. A. Harnden and L. S. MacLeod. 1962. Control of
    white pine weevil. Can. Dept. For., Bi-monthly Prog.
    Rept. 18(5): 2.

Langlois, B. E., A. R. Stemp and B. J. Liska. 1964. Analysis of
    animal food products for chlorinated insecticides.
    J. Milk and Food Technol. 27: 202.

Li, C. F. and R. L. Bradley, Jr. 1969. Degradation of chlorinated
    hydrocarbon pesticides in milk and butteroil by ultra-
    violet energy. J. Dairy Sci. 52: 27-30.

Menzie, C. M. 1969. Metabolism of pesticides. U. S. Bur. Sport
    Fish. Wildl., Spec., Sci. Rept. - Wildl., pp. 127 and
    487.

Merna, J. W., M. E. Bender and J. R. Novy. 1972. The effects of
    methoxychlor on fishes. I. Acute toxicity and break-
    down studies. Trans. Am. Fisheries Soc. 101: 298-301.

Metcalf, R. L. 1955. Organic Insecticides. Interscience Publishers,
    New York, p. 133.

Metcalf, R. L., T. R. Fukuto, R. B. March and E. L. Stafford. 1956.
    The systemic behaviour of Systox thiol isomer sulfoxide
    and methosulfate in plants. J. Econ. Entomol. 49: 738.

Metcalf, R. L. 1966. Metabolism and fate of pesticides in plants
    and animals. In: Scientific aspects of pest control,
    p. 230. Publication 1402. National Academy of Sciences,
    Washington, D. C.

Metcalf, R. L., I. D. Kapoor and A. S. Hirwe. 1972. Development of
    biodegradable analogues of DDT. Chem. Tech., pp. 105-109.

Moubry, R. J., G. R. Myrdel and A. Sturges. 1968. Residues in
food and feed - rate of decline of chlorinated hydro-
carbon pesticides in dairy milk. Pesticides Monit.
J. 2: 72-79.

O'Brien, R. D. 1967. Insecticides, Action and Metabolism.
Academic Press, New York and London, p. 110.

Reinbold, K. A., I. P. Kapoor, W. F. Childers, W. N. Bruce and
R. L. Metcalf. 1971. Comparative uptake and biode-
gradability of DDT and methoxychlor by aquatic
organisms. Bull. Ill. State Natural History Survey
30:405.

Ruzicka, J. H., J. Thomson and B. B. Wheals. 1967. The gas chroma-
tographic determination of organophosphorus pesticides.
Part II. A comparative study of hydrolysis rates.
J. Chromatog. 31: 37-47.

Ruzicka, J. H., J. Thomson and B. B. Wheals. 1968. The gas chroma-
tographic determination of organophosphorus pesticides.
Part V. Studies under field conditions. J. Chromatog.
33: 430-434.

Sundaram, K. M. S. 1972. A study of DDT residues in the brain
tissues of small wild mammals. Dept. Env., Can. For.
Serv. Int. Rept. No. CC-16, 51 pp.

Warner, R. E. 1967. Environmental micropollutants, Bull. World
Health Organ. 36: 181.

Yule, W. N. and J. R. Duffy. 1971. The persistence and fate of feni-
trothion insecticide in a forest environment. Dept. Env.,
Can. For. Serv., Inf. Rept. No. CC-X-10, 16 pp.