A STUDY ON THE COMPARATIVE DEPOSIT LEVELS AND PERSISTENCE OF TWO METHOXYCHLOR FORMULATIONS USED IN WHITE PINE WEEVIL CONTROL

by

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Report CC-X-142

April 1977

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ABSTRACT

The deposition levels of methoxychlor [2,2-*bis*(p-methoxyphenyl)-1,1,1-trichloroethane] and its persistence in white pine (*Pinus strobus* L.) leaders were investigated in two pine plantations, one sprayed with an oil formulation of the insecticide during the spring season of 1975 and the other with an emulsion formulation in the autumn of 1974. The quantity deposited and the dissipation rate in the spring spray were high compared to the fall. No single correlation could be established between the observed deposition levels, insecticide persistence, spray formulation and period of spray application. A comparison of the efficacy of two spray operations will be possible after statistical evaluation of weevilled trees found in the two spray plots.

RESUME

Les doses reçues de méthoxychlore (trichloro-1, 1, 1 bis (p-méthoxyphényl)-2, 2 éthane) et la rémanence de cet insecticide dans les pousses apicales du pin blanc (*Pinus strobus* L.) ont été étudiées dans deux plantations de pins, l'une vaporisée avec une préparation à l'huile au cours du printemps 1975 et l'autre avec une émulsion au course de l'automne 1974. La quantité de produit déposé et la vitesse de dispersion ont été plus élevées lors de l'arrosage du printemps que lors de celui de l'automne. Aucune relation n'a pu être établie entre les doses reçues, la rémanence de l'insecticide, sa préparation et la période d'arrosage. Une comparaison de l'efficacité des deux arrosages sera possible après une étude statistique des arbres attaqués par les charonçons dans les deux parcelles traitées.

INTRODUCTION

Eastern white pine (*Pinus strobus* L.) is found extensively throughout most of eastern Canada from the Atlantic Provinces to south eastern Manitoba. A serious insect pest of this tree species is the native white pine weevil [*Pissodes strobi* (Peck)]. Commercial loss from white pine weevil attack takes two forms - host trees are stunted due to loss of the terminal shoot or leader by insect attack causing a reduction in the volume of recoverable wood, and the wood that can be harvested from weevilled trees is of poor quality.

The adult weevils overwinter in litter on the forest floor and become active on warm days in spring as the snow disappears. They crawl or fly to the terminal shoot of the host tree, where they feed and lay eggs in chewed-out cavities. During the five or six weeks after hatching, the larvae feed in the cambial region, then build pupal chambers in the wood and transform to adults. The adults emerge in early fall and reach the forest floor to overwinter in the litter thus completing the annual life cycle.

Current research (DeBoo and Campbell 1974a, 1974b) at the Chemical Control Research Institute (C.C.R.I.) has shown that timely application of either an aqueous emulsion or an oil formulation of methoxychlor [2,2-*bis*(p-methoxyphenyl)-1,1,1-trichloroethane], using aircraft or mistblower, especially when the adult weevils are in the open *i.e.*, during the early spring or fall periods, produced a good reduction in weevil population and protected the pines against the insect pest. During the fall of 1974 and spring of 1975, experimental aerial spray

programs using oil and emulsion formualtions of methoxychlor were continued by DeBoo *et al* to study the efficacy of different formulations of the insecticide for control of the white pine weevil in relation to the period of application. This study was conducted in conjunction with the above spray program and with the co-operation and assistance of the scientists involved to find pertinent information on:

1. The chemical aspects of the fall of 1974 and spring of 1975 spray applications, especially the seasonal influence if detectable, on the persistence and decomposition of methoxychlor on the tree leaders or terminal shoots and
2. A critical evaluation of the deposit residue levels of the toxicant in relation to time of application (fall and spring) and spray formulation type (oil solution and emulsion), and possible correlations, if any, on observed residue patterns with these two variables.

MATERIALS AND METHODS

Experimental Design

Two pine plantations each about 30 miles from Ottawa, one to the south east of Ramsayville and the other to the west at Constance Bay were selected for aerial application of methoxychlor insecticide. The Ramsayville site was sprayed in the fall of 1974 using an aqueous emulsion of technical methoxyclor containing xylene as the solvent and Atlox as emulsifier at the rate of 2.24 kg AI/ha. The Constance Bay plantation was sprayed in the spring of 1975 using a technical methoxychlor in Arotex® aromatic solvent at the rate of 2.80 kg AI/ha. Both spray applications were carried out using a Cessna 185 aircraft fitted with 4 micronair AU 3000 units under favourable meteorological conditions. Details of plot design, spray application technique, plan of operation, etc. are discussed by DeBoo and Campbell (*loc. cit*).

Sampling of Pine Shoots

Pre and post spray samples of pine leaders from the check and spray blocks at various intervals (see Tables I and II) were taken according to the established methods (Sundaram 1973). Samples were stored in polyethylene bags in a cooler containing ice cubes and transported immediately to the Institute's laboratory for analysis.

Extraction and Gas-Liquid Chromatographic (GLC) Analysis

Recent publications (Sundaram 1973, Sundaram 1975) describe in detail the extraction and GLC analysis of methoxychlor isomers* (*o,p*-MC and *p,p'*-MC) and the metabolite methoxychlor ethylene† (MCE) from pine leaders. Reference should be made to those publications for details of the analytical method developed for pine leaders including GLC parameters.

Solvents and Chemicals

All solvents used were either pesticide grade (Burdick and Jackson, Muskegon, Mich. or Caledon Laboratories, Georgetown, Ont.) or had been fractionally distilled in glass using the middle-cut. The Florisil adsorbent was obtained from Fisher (F-100, 60-100 mesh), heated to 300°C for 24 hours and partially deactivated by adding dropwise 5 mℓ of distilled water to 100 g of the material in a Fisher-Kendall mixer. The anhydrous sodium sulphate (Fisher, S-421) used was reagent grade, heated at *ca* 150°C overnight and stored in a glass-stoppered bottle.

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* *o,p*-MC = 2,2-*bis*(*o,p*-methoxyphenyl)-1,1,1-trichloroethane

* *p,p'*-MC = 2,2-*bis*(*p*-methoxyphenyl)-1,1,1-trichloroethane

† MCE = 2,2-*bis*(*p*-methylphenyl)-1,1-dichloroethylene

Table I

Methoxychlor Residues* in White Pine Leaders from Ramsayville Plot - Fall 1974

Days Relative to Application	Methoxychlor Concentration (ppm)			
	MCE	*o,p*-MC	*p,p'*-MC	Total MC
Pre-spray	T	T	0.16	0.16
0**	0.02	1.80	39.00	40.82
1	0.35	1.75	36.25	38.35
3	0.45	1.63	33.27	35.35
5	0.77	1.33	24.62	26.72
8	1.43	1.20	17.90	20.53
12	0.58	0.71	12.25	13.54
17	0.44	0.55	8.10	9.09
25	0.34	0.42	6.80	7.56
31	0.21	0.36	6.75	7.32
40	0.10	0.29	6.05	6.44
50	0.05	0.25	5.20	5.50
60	T	0.18	4.45	4.63
76	T	0.14	4.30	4.44
94	N.D.	0.11	2.75	2.86

* Mean of three replicated trials.

** Spray date - August 30, 1974, 0800 hrs.

Dose - 2.24 kg/ha of methoxychlor (E.C.) in water. T - Traces (<0.05 ppm)

N.D. - Not detected. Average moisture content of the leaders 46%.

Table II

Methoxychlor Residues* in White Pine Leaders from Constance Bay Plot - Spring 1975

Days Relative to Application	Methoxychlor Concentration (ppm)			
	MCE	*o,p*-MC	*p,p'*-MC	Total MC
Pre-spray	T	T	0.05	0.05
2**	2.40	5.62	75.20	83.22
3	4.33	3.98	59.95	68.26
6	5.21	2.40	35.77	43.38
10	6.11	1.99	20.84	28.94
13	4.64	1.41	9.22	15.27
16	3.24	1.21	7.79	12.24
20	2.94	1.48	6.11	10.53
25	1.37	0.98	4.41	6.76
30	0.09	0.62	3.28	3.99
40	0.05	0.19	2.05	2.29
51	0.06	0.10	1.04	1.20
67	T	0.05	0.91	0.96
80	T	T	0.44	0.44
100	N.D.	N.D.	0.12	0.12

* Mean of three replicated trials.

** Spray date - May 10, 1975, 0800 hrs.

Dose - 2.80 kg/ha of methoxychlor in Arotex oil. T - Traces (<0.05 ppm)

N.D. - Not detected. Average moisture content of the leaders 54%.

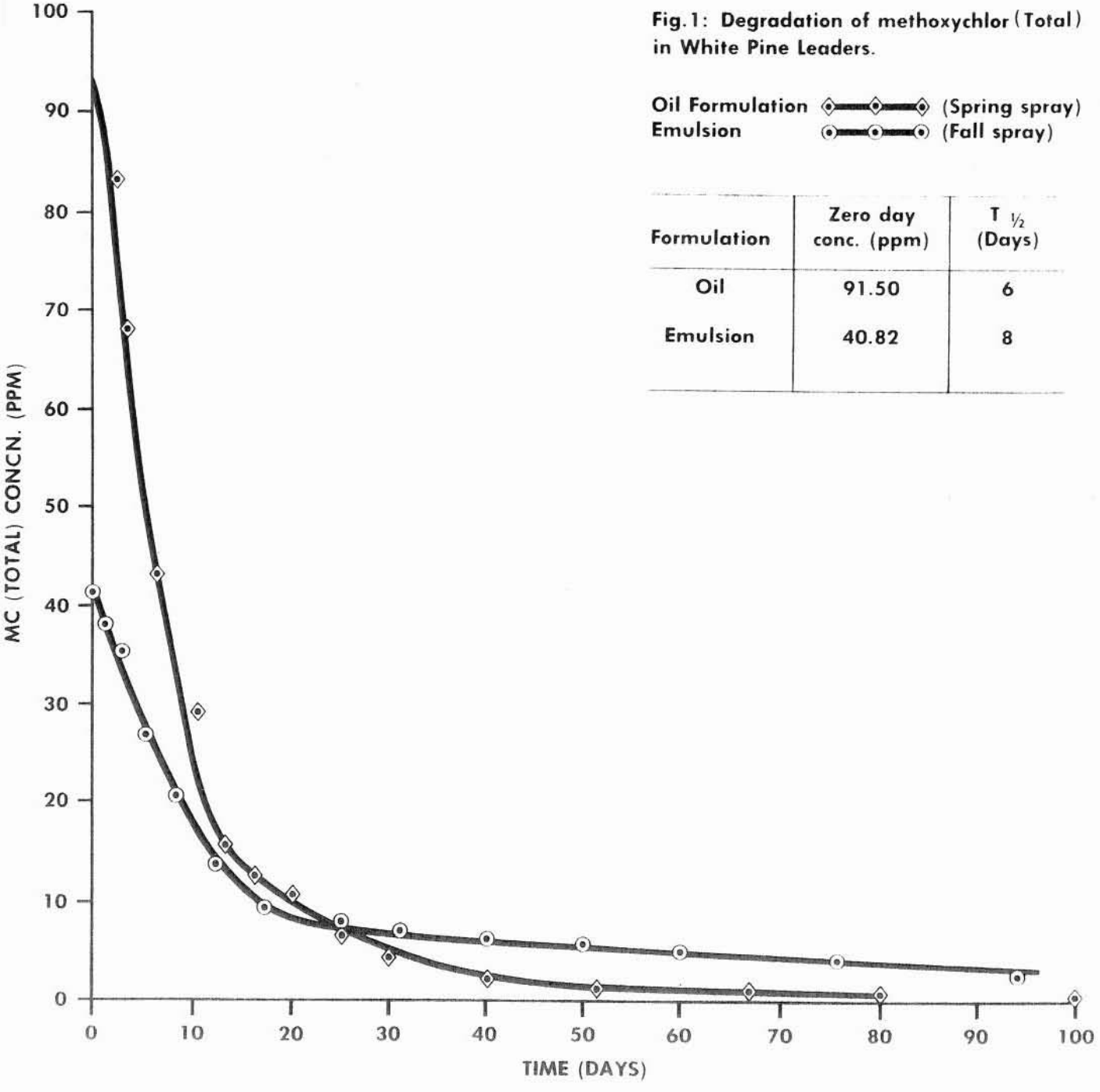

Fig. 1: Degradation of methoxychlor (Total) in White Pine Leaders.

Oil Formulation ◇—◇—◇ (Spring spray)
Emulsion ⊙—⊙—⊙ (Fall spray)

Formulation	Zero day conc. (ppm)	$T_{1/2}$ (Days)
Oil	91.50	6
Emulsion	40.82	8

RESULTS AND DISCUSSION

Analytical Method

Methoxychlor residues (*o,p*-MC, *p,p'*-MC and MCE) found in the white pine leaders collected from the plantations sprayed with the emulsion and oil formulations are recorded in Tables I and II respectively. The concentration levels are expressed in units of parts per million (ppm) *i.e.*, microgram per gram of fresh weight of the primary shoots of white pine. The minimum detection limit that could be achieved in the GLC analytical method used for the two methoxychlor isomers (*o,p*-MC and *p,p'*-MC) and the ethylene metabolite (MCE) was 0.05 ppm. It is evident from the results that the prespray samples of leaders from both spray plots had been exposed previously to methoxychlor sprays. The leader samples from the check plot did not contain any detectable levels of the insecticide residues and are not recorded in this publication.

Deposition Levels of Methoxychlor

The quantity of pesticide deposited on target areas in aerial application depends upon a number of interrelated factors such as spray formulation, equipment and atomization, prevailing meteorological conditions at the forest canopy, spray method and topography of spray area. Apart from the meteorological conditions, the other factors are to a large extent controllable, especially in an experimental spray program. The spray deposit assessment, conducted under such controlled conditions, will be useful in evaluating the coverage, persistence and biological effectiveness of any pesticide spray.

Under similar micro-meteorological conditions existing in the plantation canopy during the fall and spring spray operations, the amounts of methoxychlor deposited on the leaders differed with the type of formulation used. The zero day deposition level (extrapolated from the graph in Fig. 1) with the oil formulation was nearly 2.3 times as heavy (91.50 ppm *vs* 40.82 ppm) as deposits with the emulsion formulation. Comparing the amounts of insecticide released on the pine shoots, although the application rate of oil formulation was 1.25 times that of emulsion, the oil formulation, in general, gave greater deposit levels (230%). This could be due to greater viscosity and wettability coupled with less in volatilization and drift potential. It has been observed that oil formulations of DDT usually gave a higher deposition level compared to aqueous formulations. Emulsions are more readily atomized into fine droplets and the water base is lost very rapidly except under conditions of high relative humidity. However it should not be overlooked that levels of the deposition of pesticides on the target areas should be evaluated primarily in terms of biological effectiveness in controlling the weevil population.

Methoxychlor Persistence

Persistence, *i.e.*, the property of a chemical to remain in or on the target area in an unaltered and biologically active form depends upon envrionmental factors, mode of application, dosage and nature of the chemical. It is seen from the results in Tables I and II, that the disappearance rates of the insecticide in leaders varied considerably between the spring and fall applications. In spite of the low initial deposit

level (40.82 ppm) observed on zero day at the Ramsayville plot (Table I) after fall application, the rate of disappearance was less rapid than that at the Constance Bay plot which received a much heavier initial deposit of 91.50 ppm (Table II) on day zero during the spring 1975 spray program. After 40 days, the deposit levels of total methoxychlor in the former was 0.44 ppm, a decrease of only 84% from the initial level of 40.82 ppm, compared to a rapid decrease of 97.5% in the latter from 91.50 ppm to 2.29 ppm showing that the fall spray deposit levels were more persistent in the leader samples than the spring spray deposits. Nearly three months after spraying, the concentration of total methoxychlor in Ramsayville leader samples read from Fig. 1 was *ca* 3.5 ppm compared to 0.5 ppm in the leaders from Constance Bay and it is evident that the terminal deposit levels did not depend on initial concentrations. But more likely on weather conditions as temperature, sunlight and percipitation. The lower temperature and precipitation in fall decreased the evaporation and removal of methoxychlor from leaders and accounted for the higher residue levels found in the Ramsayville samples. Detectable amounts of the residues were present in both leader samples up to the final day of sampling.

The curvilinear relationship obtained by plotting the total methoxychlor concentration (ppm) against time (days) (Fig. 1) confirmed the rapid loss of the insecticide after the spring application compared to the fall one. The curve is steeper with a greater slope in the former than in the latter. The time for 50% disappearance (half-life period, $T_{\frac{1}{2}}$) of the insecticide in leaders read from the graphs for spring (oil formulation) and fall (emulsion) spraying were 6 and 8 days respectively. Even though the half-life of both were not far different, 90%

disappearance was much longer in fall application - 65 days *vs* 16 days.

Mechanisms of removal of methoxychlor from the pine leaders, as pointed out earlier (Sundaram 1975) included volatilization, weathering, photolysis, chemical and bacterial decompositions. During the summer months, the physical factors (climatic parameters such as light, temperature, humidity, vapour pressure, rain and wind and leader growth - *ca* 45 cm in May to August) could have played a dominant part in the rapid dissipation of the insecticide residues from leaders. By the fall time apart from the microbial activity, the climatic parameters probably did not exert a strong influence on insecticide breakdown accounting for its prolonged persistence in the leaders. However, persistence of a given chemical cannot be assumed for one area on the basis of results from use in dissimilar localities, dosages and formulations.

CONCLUSION

Extensive field studies (DeBoo and Campbell 1972, 1974a, 1974b) have shown that spraying white pine plantations in early spring with methoxychlor effectively controlled the weevil infestation and provided adequate leader protection. Although initial deposit levels obtained in spring application using an oil formulation were high, the dissipation rate was also equally high. Deposits from the fall spraying, using an emulsion formulation of methoxychlor, although only half as heavy initially as those from the spring application, persisted in biologically active states for a longer period of time without deteriorating due to physical, environmental and metabolic factors. The accurate field record of tree infestations for the fall of 1974 and spring of 1975 are not yet available. When the data are gathered and evaluated statistically, the information will be useful in understanding the intensity of weevil infestations in the two experimental pine plantations and the overall usefulness and efficacy of the seasonal (spring/fall) application and the two types of formulations (oil and emulsion) of the insecticide used in white pine weevil control programs in pine plantations.

ACKNOWLEDGEMENTS

The research reported herein forms a part of a collaborative research program undertaken jointly by the author and Dr. R.F. DeBoo of this Institute to study the physicochemical and biological effects of various chemicals in plantation pest control methods.

The author is indebted to Mr. L.M. Campbell (formerly of C.C.R.I.) and Mr. R.A. Brunette of Ontario Ministry of Natural Resources for providing the leader samples used in this study.

The technical assistance of Messrs. P.E. LeCompte, M. Bryan and G. Lafrance is greatefully acknowledged.

Appreciation is extended to Mr. W.W. Hopewell, Drs. J.A. Armstrong, C.H. Buckner and R.F. DeBoo for reviewing this report.

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