PERSISTENCE STUDIES OF INSECTICIDES : I. AERIAL APPLICATION OF METHOXYCHLOR FOR CONTROL OF WHITE PINE WEEVIL IN ONTARIO, 1973

BY

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INTRODUCTION

Among the various conifers found in Canada, the pines play an important part in the economic and industrial development of the nation by providing valuable lumber. Eastern white pine (*Pinus strobus* L.) found extensively throughout most of eastern Canada, is frequently degraded by the attack of an insect pest known as the white pine weevil, *Pissodes strobi* (Peck) (Coleoptera: Curculionidae) (Brace 1972). For more than 60 years the weevil has wrought havoc on reforestation programs and considerable efforts are being made, since the problem was first encountered, to develop practical methods of control of weevil infestations (Sutherland and DeBoo 1973). The usual protective treatment is the application of various toxic chemical sprays to susceptible pine stands during late April and early May. Until 1968, aerial application of some organochlorine insecticides such as lindane, DDT, etc., constituted the most large scale treatments in Ontario plantations. The current ban on the use of DDT resulted in an increased interest in the use of methoxychlor as a biodegradable replacement. Methoxychlor has been used for the past few years in forest pest control (Sundaram et al 1972), but usage has been limited until recently because of less effectiveness and greater cost than DDT.

Recently, DeBoo and Campbell (1971, 1972) have shown that efficient and timely application of an aqueous emulsion of methoxychlor [2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane] by hydraulic ground sprayer at the rate of 1 to 2 lb(s) AI/acre reduced weevil infestation nearly 100%. Recent persistence studies (Sundaram et al 1972) of the

insecticide in white pine leaders have shown that it is less persistent than DDT and readily degraded with a low half life to non-toxic metabolites proving thereby that the compound is environmentally safe. Also the toxicant is sufficiently residual to span most of the adult weevil activity. Current research at the Chemical Control Research Institute (C.C.R.I.) centers on improving the methoxychlor application techniques for large-scale operational treatments using aircraft for the control of white pine weevil. During the summer of 1973 (May-September), an experimental aerial spray program using methoxychlor was continued by C.C.R.I. to study the efficiacy of aerial application of the toxicant for control of the white pine weevil (DeBoo and Campbell 1972, 1973). This report summarizes:

(i) the chemical aspects of that spray operation, especially the methodology development for the quantification of the toxicant residues,

(ii) its persistence and fate and finally,

(iii) the efficacy of the chemical as an insecticide in white pine weevil control.

MATERIALS AND METHODS

Experimental Plan

White pine weevil airspray experiments were conducted during April at the Kirkwood Forest Management Unit of the Ontario Ministry of Natural Resources, north of Thessalon and approximately 50 miles east of Sault Ste Marie. A plot, designated as KE3, measuring 100 acres having

approximately 500 white pine trees/acre, with the mean height of 15' and DBH of ca 4" was chosen for the spray study. Another similar plot (LC1) situated ca 9 miles north of Thessalon and free of the insecticide served as the control. The two plots, KE3 and LC1, were separated from one another far apart to minimize boundary effects and possible contamination by insecticide drift from other plots.

Methoxychlor Application

Spraying was done on the morning (0800 hrs) of April 30, 1973, coinciding with maximum adult weevil activity and under favourable meteorological conditions. Technical methoxychlor (95% purity) was supplied by DuPont of Canada Ltd., Toronto. The gas-liquid chromatographic, (GLC) analysis showed that the material contained 87% *p,p'*-MC (methoxychlor), 9% *o,p*-MC, 0.7% MCE (methoxychlorethylene) and the rest being unidentifiable isomers and reaction products. The spray mixture was prepared by dissolving 2.5 lbs of the technical insecticide/acre in a mixture of 1 gallon of Esso No. 2 fuel oil and 0.75 gallon of xylene as cosolvent and the resulting formulation was sprayed using a Stearman aircraft fitted with 4 micronair (A.U. 2000) units. The application was made in two aircraft sorties during the same morning to provide a clear starting point for the persistence study of the toxicant in white pine leaders.

Sampling Plan

At various intervals [-2(pre-spray), 0, 1, 4, 9, 15, 20, 26, 35 and 50 days* (post-spray)] following the spray application, uniform samples of leaders (10" length, mass ca 20 g) were collected using a pole-pruner from fifteen randomly chosen trees covering the entire area within the plot and from the control area for the determination of methoxychlor residues. All samples were collected usually within a one-hour period to minimize errors that may arise in final calculation of residue concentrations due to time variations. Pre-spray samples were collected one day earlier to the treatment. The leader samples from the control (LC1) and sprayed (KE3) plots were composited separately in polythene bags, stored in coolers at near 0^{o} C and transported immediately by commercial carrier to the Institute's Laboratory in Ottawa for analysis. Most samples reached Ottawa within a 24-hour period.

Analytical Procedure

No reliable and sensitive analytical procedure using GLC

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* Quantification of methoxychlor residues in leaders were attempted for 65, 90 and 120 day samples. Because of the low concentration of the insecticide present (ca 0.02 ppm, wet weight) and of the high background in the GLC instrument observed, while analysing the concentrated eluate after cleanup, the results of the analysis were considered as insufficiently accurate and are not included in this report.

technique has been found in the literature for the estimation of methoxychlor residues from white pine leaders containing appreciable amounts of terpene resins. The method developed recently by Sundaram et al (1972) was reasonably satisfactory but imprecise and needed modification to increase the overall extraction efficiency and improvement in column cleanup to remove interfering substances.

The essential principles involved in methodology development for analysing methoxychlor residues from plant materials are:

(1) Extraction of the insecticide by a suitable solvent or solvent mixture.

(2) Partition the residues into a nonpolar phase for removal of fats and other interfering substances from solvent extracts.

(3) Removal of final traces of plant fats, chlorophyll and other resinous materials having electron affinity which interfere in GC analysis, by passing the solvent through an absorbent column and finally,

(4) Elution of the adsorbed insecticide residues with suitable solvent or solvent mixtures followed by concentration and analysing the concentrated eluate by GLC using an electron capture detector.

A number of preliminary experiments were conducted to work out a satisfactory analytical method for the extraction and analysis of methoxychlor residues (*p,p'*-MC, *o,p*-MC and MCE) from white pine leaders by spiking 25 g of chopped leaders with 5 mg of *p,p'*-MC and varying the four operational steps recorded above, to attain satisfactory recovery and quantitation. The preliminary experiments conducted are summarized

in Table 1, and the analytical procedure developed on the basis of these trials is fully described below and schematically illustrated in Fig. 1.

Extraction Method

In the laboratory, the leader samples were cut into tiny pieces (< 1 inch in length) by hand clippers, mixed well and transferred to a Hobart grinder (Hobart Mfg. Co., Toronto, Food Cutter Model # 84142). The leader pieces were ground for 2-3 min until a homogenous mixture was obtained. An aliquot (10 g) was taken for moisture determination (AOAC 1955). Two 25 g duplicates of ground samples were weighed and transferred to a Sorvall Omni-Mixer container (500 ml) and 200 ml of acetonitrile (residue free solvent, distilled in glass and supplied by Caldeon Laboratories, Georgetown, Ont.) was added. The sample was extracted at high speed (#6) for 3 min and the acetonitrile extract was filtered through a Buchner funnel (23J) using Whatman No. 1 filter paper, retaining as much of the leader tissues as possible in the Sorvall container. The tissues were again blended with another 200 ml of acetonitrile for 2 min at high speed and the resulting extract after filtration under suction, was added to the first. The combined extracts were flashed to a small volume (50 ml) and transferred quantitatively to a separatory funnel (2000 ml.). Six hundred ml of distilled water, 200 ml of hexane (Caldedon) and 10 ml of saturated sodium sulphate solution were added to the separatory funnel and the mixture was shaken vigorously for 5 minutes and allowed to stand overnight. The hexane and water phases were separated. The former was shaken twice with 100 ml of

water, adding these washings to the first aqueous phase. The combined water layers were re-extracted twice with 100 ml of hexane, and the extracts were added to the original hexane solution. The aqueous phase was then discarded. The total volume of hexane (ca 420 ml including rinsings) was dried by passing through a column of granular anydrous Na_2SO_4 (100 g) (Fisher, S-421). The dried extract was reduced to ca 50 ml by flash evaporation.

Cleanup Procedure - column chromatography

To remove any coextracted impurities that may interfere with EC detector in GLC analysis, the hexane solution (equivalent to 25 g of leader) was further cleaned up by using a preconditioned and partially deactivated Florisil (Fisher, F100; 60/100 mesh, equilibrated to contain 5% H_2O) column.

Twenty-five grams of Florisil sandwiched between 10 g of Na_2SO_4 were poured into a "shell" design chromatographic 20 mm x 260 mm column (Scientific Glass, Bloomfield, N.J., JD-4030) fitted with fritted glass disc and Teflon stopcock at one end and 300 ml glass reservoir at the other. The contents of the column were packed uniformly using an automatic mixer. The column was washed twice with 100 ml of hexane, discarding the washings and the concentrated sample in hexane was introduced. Methoxychlor residues (*o,p*-MC, *p,p'*-MC and MCE) were

eluted with 600 ml of 15% benzene in hexane * (V/V) at a percolation rate of 3-5 ml/min. The eluate (> 640 ml) was collected and reduced to 10 ml (2.5 g/ml) using a rotary vacuum evaporator for gas chromatographic analysis. All the steps involved in the analysis of methoxychlor residues are given in Fig. 1.

Gas Chromatographic analysis

Each leader extract after cleanup was analysed twice by gas-liquid chromatographic (GLC) techniques. The GLC conditions used in the present investigations are shown in Table 2. Standard 4 ul injections of extract at a concentration of 2.5 g/ml were analysed first, peak sizes and retention times were compared with standard calibrations for *p,p'*-methoxychlor (*p,p'*-MC), *o,p*-methoxychlor (*o,p*-MC) and methoxychlorethylene (MCE), then the extract was diluted or concentrated and injection volume varied to fit the linear calibration

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* A number of solvents and solvent mixtures (Table 1) were tested for efficiency in eluting methoxychlor residues from the adsorbent and final selection of 15% benzene in hexane (V/V) was found to be satisfactory in spite of the large volume of the solvent mixture used in each elution. Another promising solvent mixture worth considering is 500 ml of 5% diethyl ether in hexane (V/V).

range of the standards. In some samples, (especially samples collected 20 days after the spray and more so at low volumes of the extract) interference due to peak overlapping (thereby masking the feeble MCE response) and GC coextractive background increase (Fig. 2) (S/N ratio < 2) were observed even with the cleanup, and were unavoidable. Spot checks, to confirm the absence of DDT's were made on the same extracts as described earlier (Sundaram et al 1972).

Under the present chromatographic conditions (Table 2) the ratio of relative retention times for *p,p'* methoxychlorethylene [2,2 bis-(*p*-methylphenyl)-1,1-dichloroethylene; hereinafter referred to as MCE] 0.44; *o,p'*-methoxychlor, [2,2-bis (*o,p*-methoxyphenyl)-1,1,1-trichloroethane; hereinafter referred to as *o,p*-MC] 0.69 and *p,p'*-methoxychlor [2,2-bis (*p*-methoxyphenyl)-1,1,1-trichloroethane; hereinafter referred to as *p,p'*-MC] 1.00 (Fig. 3). 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.

The overall recovery of *p,p'*-MC ranged between 75-85%. ($\bar{x}$ = 82%) for several spiked samples of leaders with the extraction technique described above. The data presented in this report does not include recovery corrections.

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 in the present investigation. The anyhdrous sodium sulphate (Fisher, S-421) used was of reagent grade, heated at ca 150° C overnight and stored in a glass-stoppered bottle.

Laboratory sources of contamination were found to be minimum.

RESULTS

Table 3 shows the methoxychlor residues (*o,p*-MC, *p,p'*-MC and MCE) in ppm found for wet (as sampled) and oven-dry white pine leader samples. The concentration levels expressed on wet mass basis will be helpful for ecological interpretations whereas residue levels calculated on oven-dry samples will be useful for comparative studies. Residue concentrations of oven-dry leaders were calculated by taking into consideration their moisture content.

Each residue value recorded in Table 3 is the average of at least two determinations. Individual values which deviated more than 15 percent from the mean are excluded in averaging. Residue levels below 0.03 ppm are recorded as traces due to the limitations of the cleanup technique employed and the sensitivity of the gas chromatographic equipment used. Pre-spray (Table 3) and control samples did not contain any insecticide. Zero day samples were collected 45 minutes after the spray operation. None of the leader samples contained any detectable DDT residues.

Residue concentration (ppm) of *o,p*-and *p,p'*-MC in wet and dry leader samples (Figs. 4 and 5) show exponential decrease of residue levels

TABLE 1

Analysis of Methoxychlor from White Pine Leaders* - Trials

Extraction Solvent	Partition	Column Cleanup	Eluate	Recovery %	Comments
CH_2Cl_2:CH_3OH(1:1 V/V) (200 ml)	Nil	Forisil (5%) 30 g	CH_2Cl_2:Hexane (1:1 V/V)(500 ml)	70	Solution coloured; high background interference in GC
"	Hexane, Water	"	"	70	" "
"	Nil	Charcoal:Celite (6:4)	"	40	Solution clear; low background but poor recovery due to adsorption on charcoal
Ethyl acetate (200 ml)	Nil	"	Hexane (500 ml)	55	Solution clear; minimum interference; poor recovery
"	Hexane, Water	"	"	50	" "
"	Nil	Florisil (5%) 30 g	"	55	Solution slightly coloured; minimum background interference; poor recovery
"	Nil	"	Benzene (500 ml)	60	Solution highly coloured; appreciable interference; poor recovery
CH_3CN (200 ml)	Nil	Charcoal:Celite (6:4)	Hexane (500 ml)	45	Clear solution, low background; poor recovery
"	Hexane, Water Na_2SO_4 (aq)	Florisil (5%) 30 g	"	70	Light green colour solution; low interference; satisfactory recovery
"	"	"	Benzene (500 ml)	78	Solution highly coloured; appreciable interference, satisfactory recovery
"	"	"	15% Benzene in hexane (600 ml)	80	Very light colour solution; minimum interference; good recovery
CH_3CN (2 x 200 ml)**	"	"	"	82	" "

* 25 g of chopped (Hobart) and composited leader samples were spiked with 5 mg of p,p'-MC and homogenized for 10 min. in a Sorvall, using a solvent medium.

** Analytical procedure developed on the basis of this trial experiment.

TABLE 2

Gas Chromatographic Conditions

Instrument	Hewlett-Packard (Avondale, Pa.) model 5750
Detector operation	Pulse mode of ^{63}Ni (10 mCi) twin electron capture detector
Liquid phase*	4% DC-200/6%-QF-1
Support	Chromosorb W, 60/80, AW-DMCS, preconditioned. 48 hrs at 230°C.
Column	Pyrex glass, 48 x 0.25"
Flow rate	44 ml/min
Carrier gas - Argon/Methane	
95/5% pressure of 40 psi	
Temperature (°C)	
Column oven	190
Injection port	210
Detector	250
Instrument Settings	
Attenuation	32
Range	10
Pulse rate	150
Chart Speed	0.25"/min
Recorder	Tracor Westronics MT
Sensitivity 50% f.s.d. given by	0.60 ng of p,p'-methoxychlor (response varied with detector conditions)

* Other liquid phases such as 4% SE-30/6% QF-1 and 3% DC-200 were tried after coating on Chromosorb W. The SE-30 QF-1 column was not sensitive and the retention times were high for methoxychlor isomers. The separation of the isomers in DC-200 column was not satisfactory. Hence 4% DC-200/6% QF-1 column was used throughout the present investigation. The relative retention times for this column with reference to DDE=1 were found to be: DDD=1.31, o,p-DDT = 1.46, p,p,-DDT = 1.77, o,p-MC = 1.89 and p,p'-MC = 2.67.

TABLE 3

Methoxychlor Residues Found in White Pine Leaders

Time Relative to Application (Days)	Leader Mass (g)	Moisture Content (Percent)	Concentration (ppm) - wet mass			Total MC (Σ *o,p* and *p,p'*)	Residual MC (*o,p* + *o,p'*-MC) (Percent)	Concentration (ppm) - dry mass			Total MC (Σ *o,p* and *p,p'*)	Residual MC (*o,p* + *p,p'*-MC) (Percent)
			MCE	*o,p*-MC	*p,p'*-MC			MCE	*o,p*-MC	*p,p'*-MC		
-1*	25.0	56	N.D.	N.D.	N.D.	N.D.	0	N.D.	N.D.	N.D.	N.D.	0
0	25.0	56	0.10	0.92	11.90	12.82	100	0.22	2.09	27.05	29.14	100
1	25.0	55	T	0.89	10.80	11.69	91	T	1.98	24.00	25.98	89
4	25.0	57	0.05	0.76	7.08	7.84	61	0.12	1.77	16.47	18.24	63
9	25.0	56	0.40	0.58	3.20	3.78	30	0.91	1.32	7.27	8.59	30
15	25.0	56	0.25	0.23	2.28	2.51	20	0.57	0.52	5.18	5.70	20
20	25.0	57	T	0.18	1.22	1.40	11	T	0.42	2.84	3.26	11
26	25.0	57	N.D.	0.12	0.44	0.56	4.4	N.D.	0.28	1.02	1.30	4.5
35	25.0	63	N.D.	0.09	0.20	0.29	2.3	N.D.	0.24	0.54	0.78	2.6
50	25.0	64	N.D.	0.06	0.15	0.21	1.6	N.D.	0.17	0.42	0.59	2.0

* Pre-spray and control samples

N.D. = Not detected

T = Traces (< 0.03 ppm)

TABLE 4 *

Efficacy of Methoxychlor Treatment by Hydraulic Sprayer and Aircraft for White Pine Weevil Control

Methoxychlor applied by hydraulic sprayer at the rate of 2.0 lbs/acre in 100 gal. water, Orr Lake - 1972

Year	No. of trees checked	No. of trees weeviled	% Trees weeviled	0-day residue concn. (ppm)	$t_{\frac{1}{2}}$ (days)	Reduction in weeviled leaders (%)
1970 (Prespray)	351	112	31.9	--	--	--
1971 (Prespray)	351	105	29.6	--	--	--
1972 (post-spray)	200	1	0.5	600	15.8	98

Methoxychlor applied by aircraft at the rate of 2.5 lb/acre in 1.75 gal. fuel oil and xylene, Kirkwood F.M.U. (Thessalon) - 1973

1972 (Prespray)	2033	261	13	--	--	--
1973 (Postspray)	2126	56	2.6	12.82	5.0	80

* DeBoo, R.F. 1973. Personal communication.

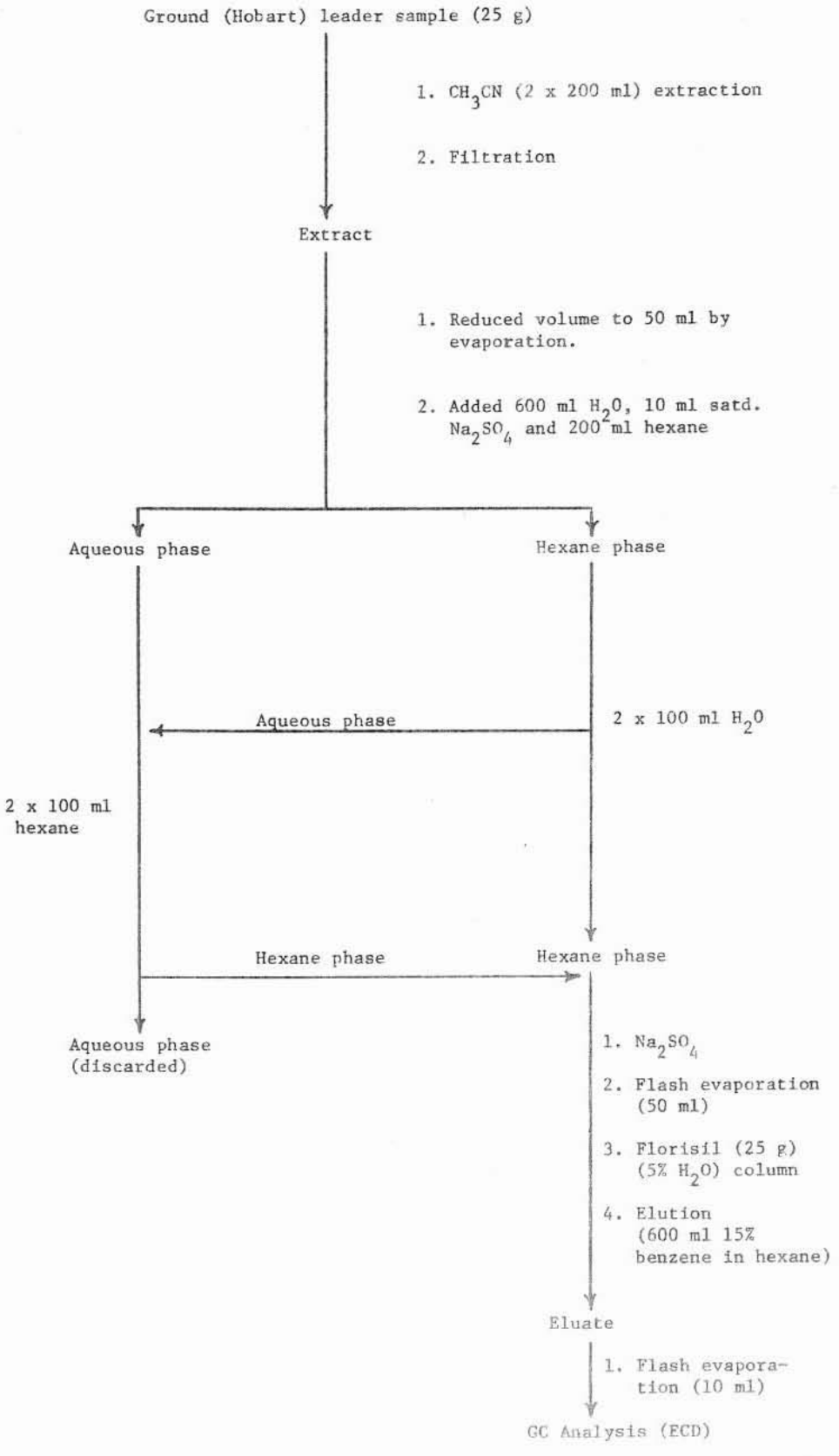

Fig. 1. Analysis of methoxychlor residues in white pine leaders.

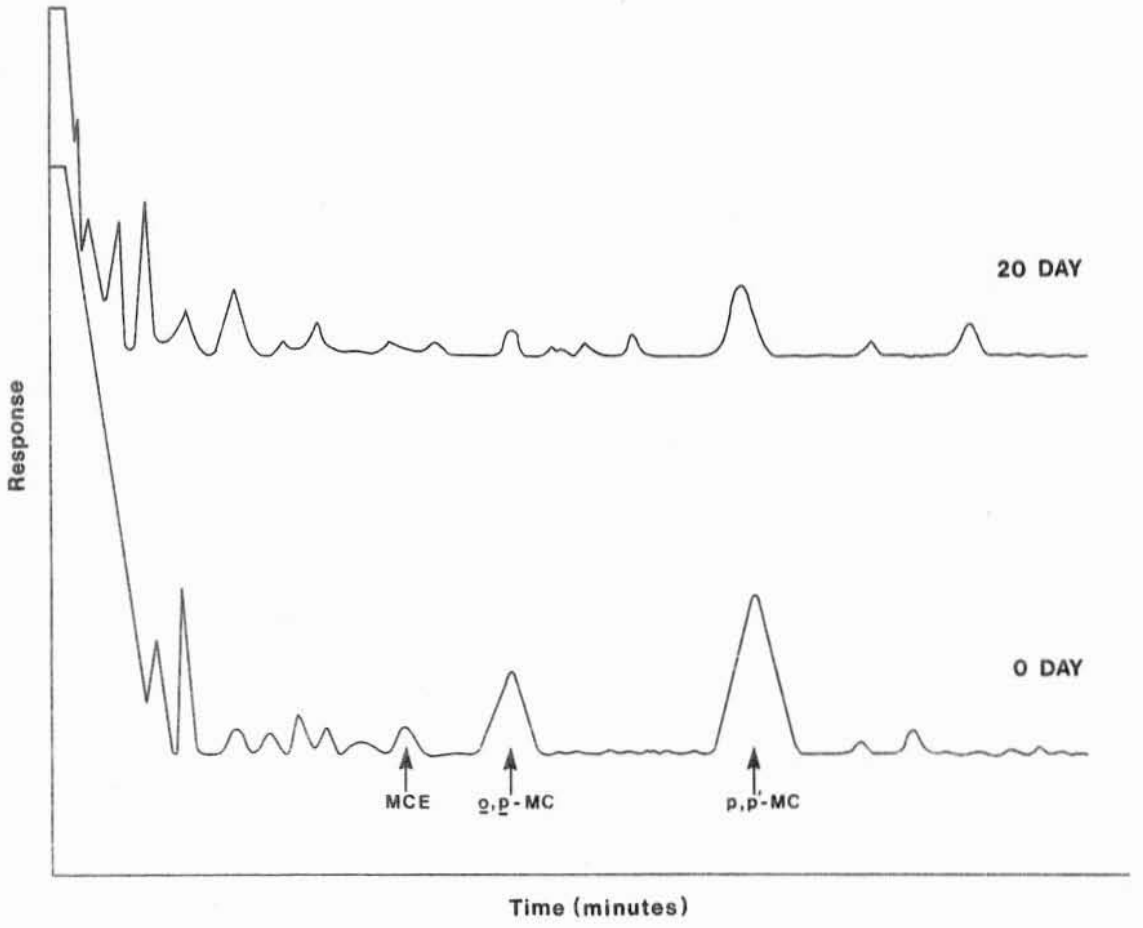

Fig. 2. Chromatogram of 0 and 20 day leader samples after cleanup. (Note the increase of interference with decrease in concentration of methoxychlor residues).

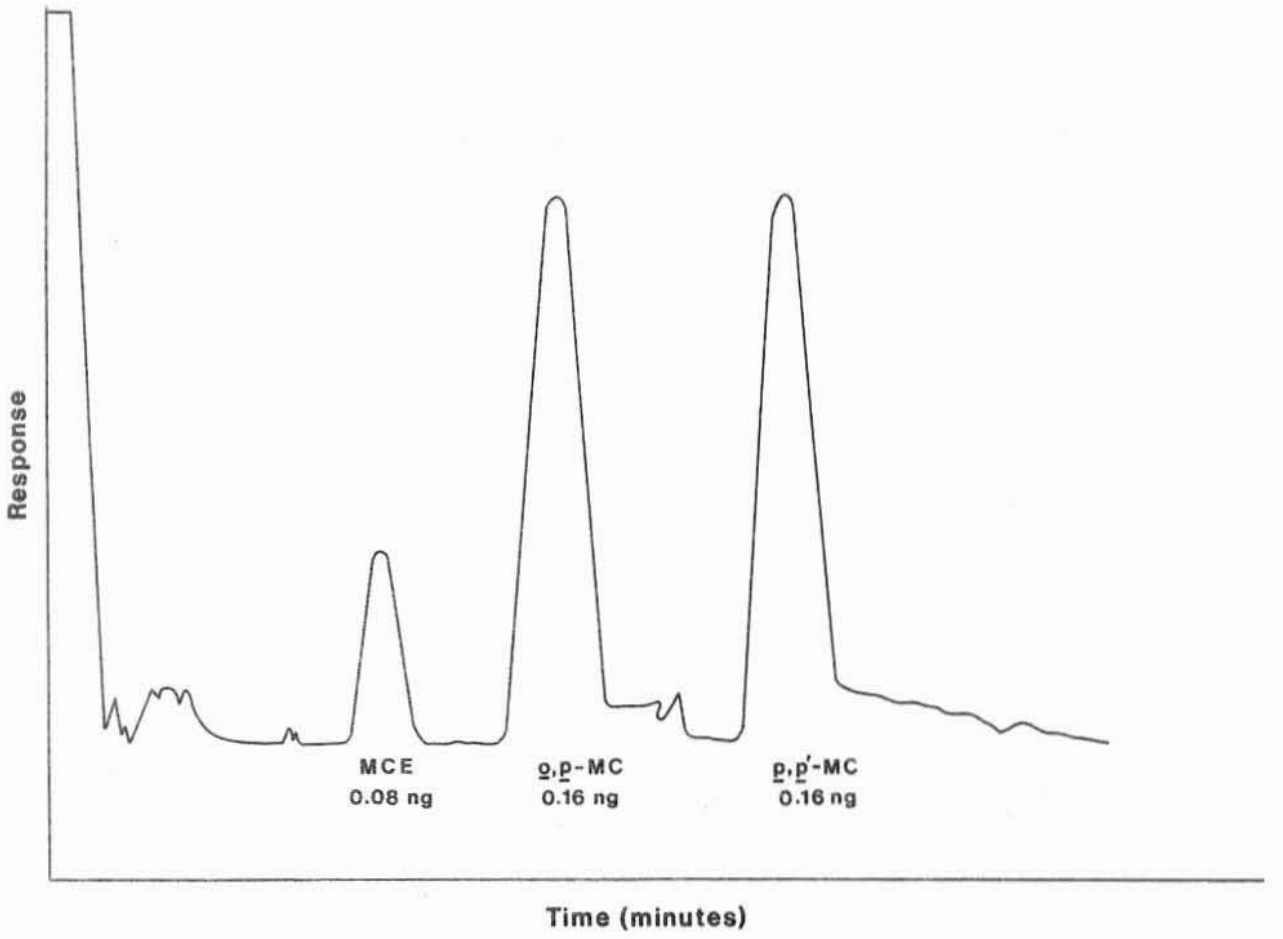

Fig. 3. Typical chromatogram of methoxychlor standards obtained from Chromosorb W column coated with 4% DC-200/6% QF-1.

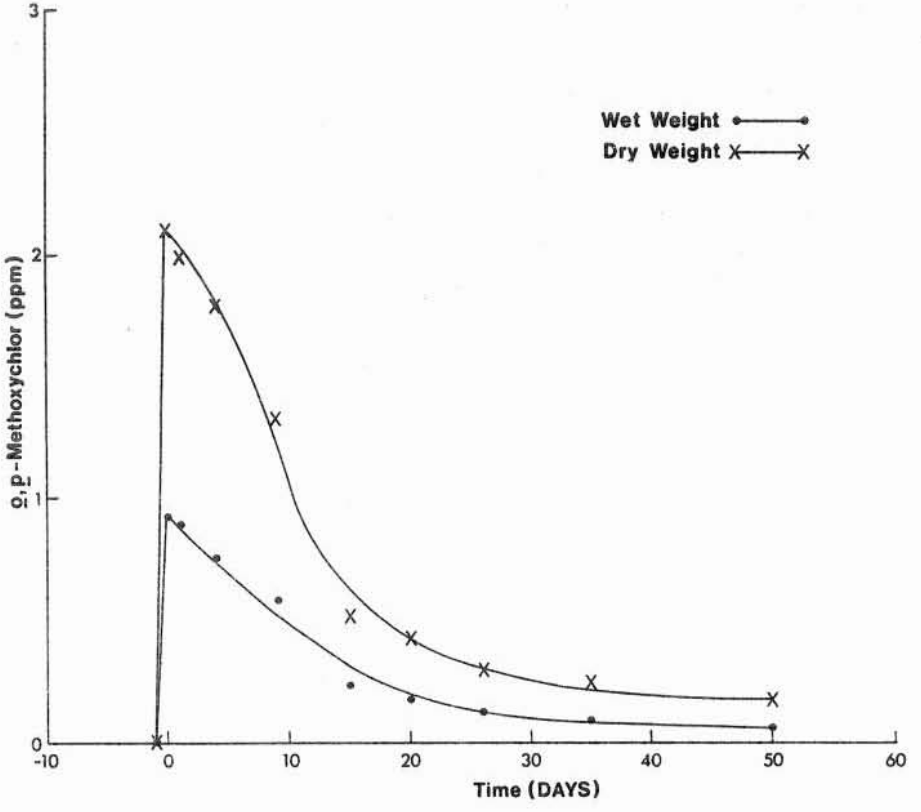

Fig. 4. Dissipation of o,p-methoxychlor from white pine leaders.

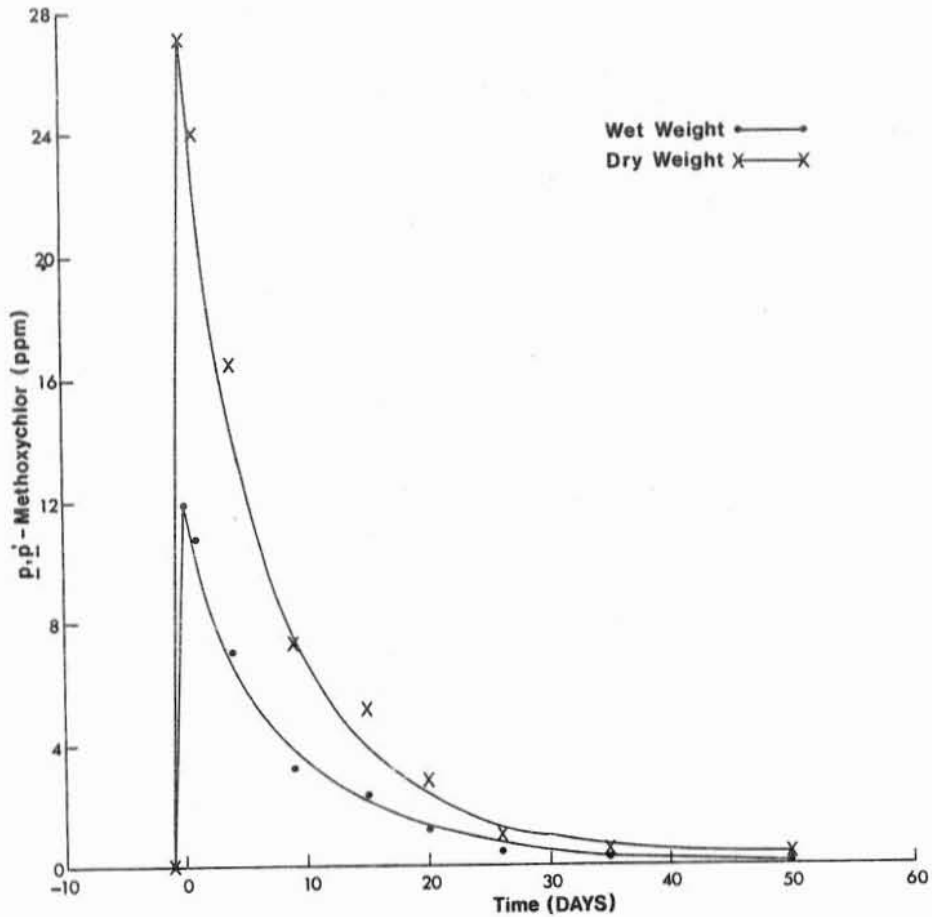

Fig. 5. Dissipation of p,p'-methoxychlor from white pine leaders.

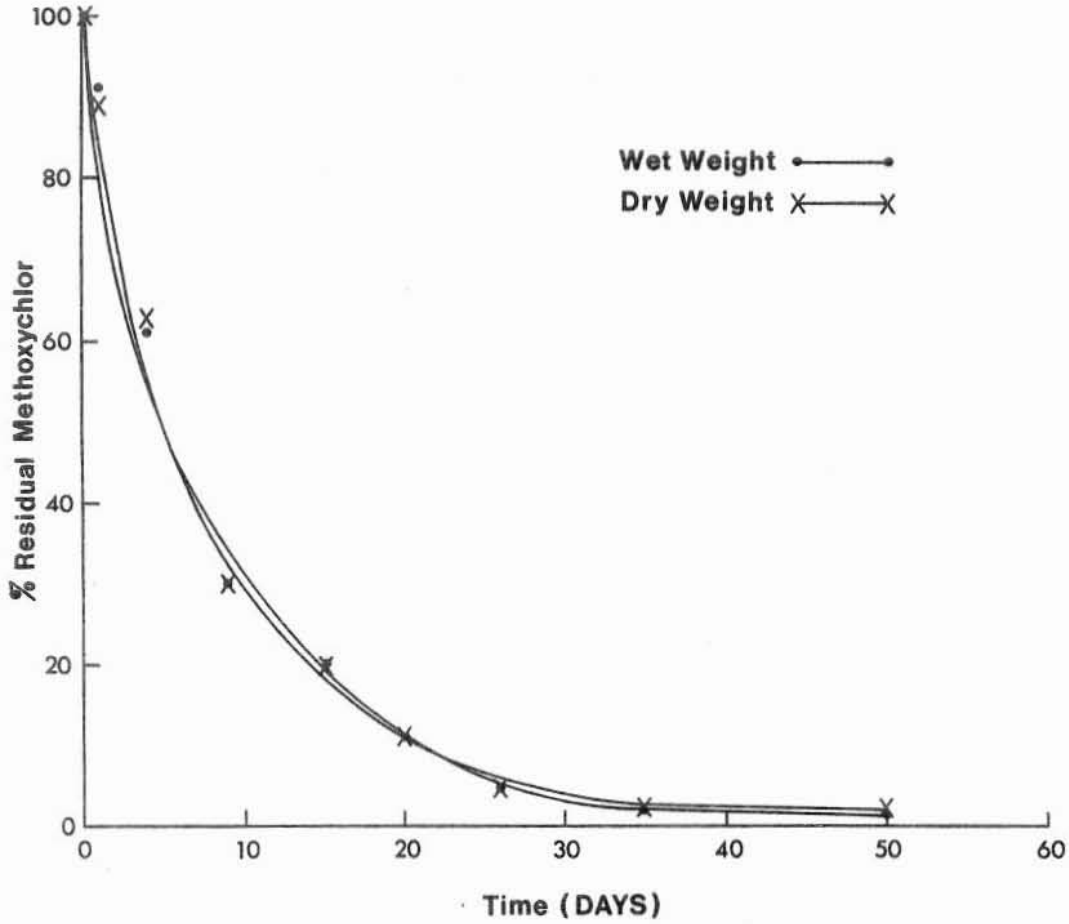

Fig. 6. Variation of percent residual methoxychlor with time.

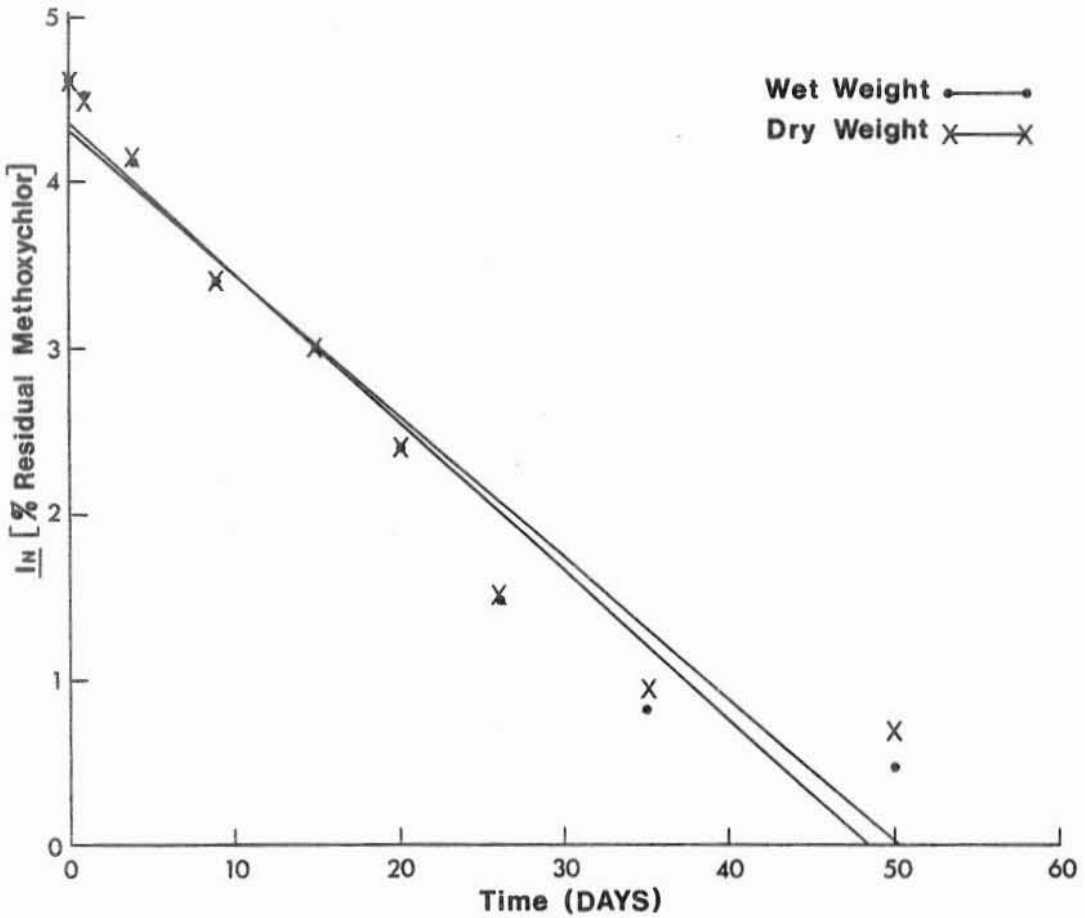

Fig. 7. Rate of variation of residual methoxychlor in white pine leaders.

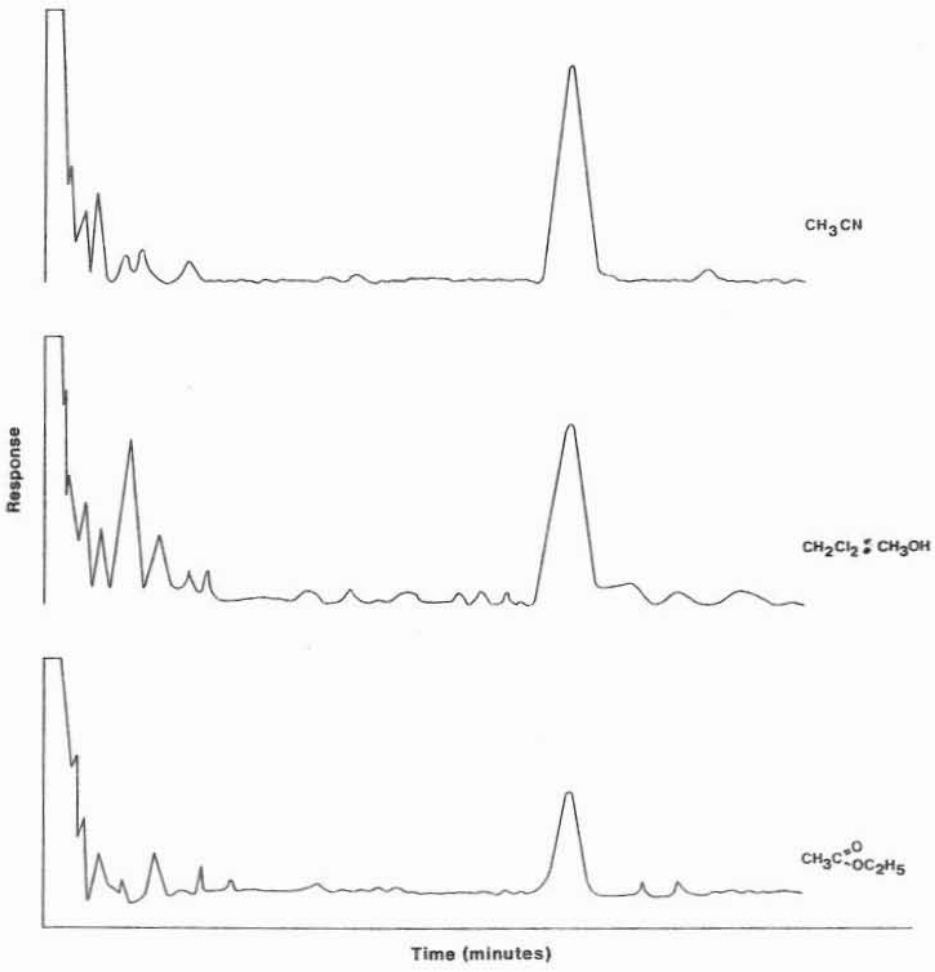

Fig. 8. Chromatograms of fortified leader extracts in different solvent media after cleanup.

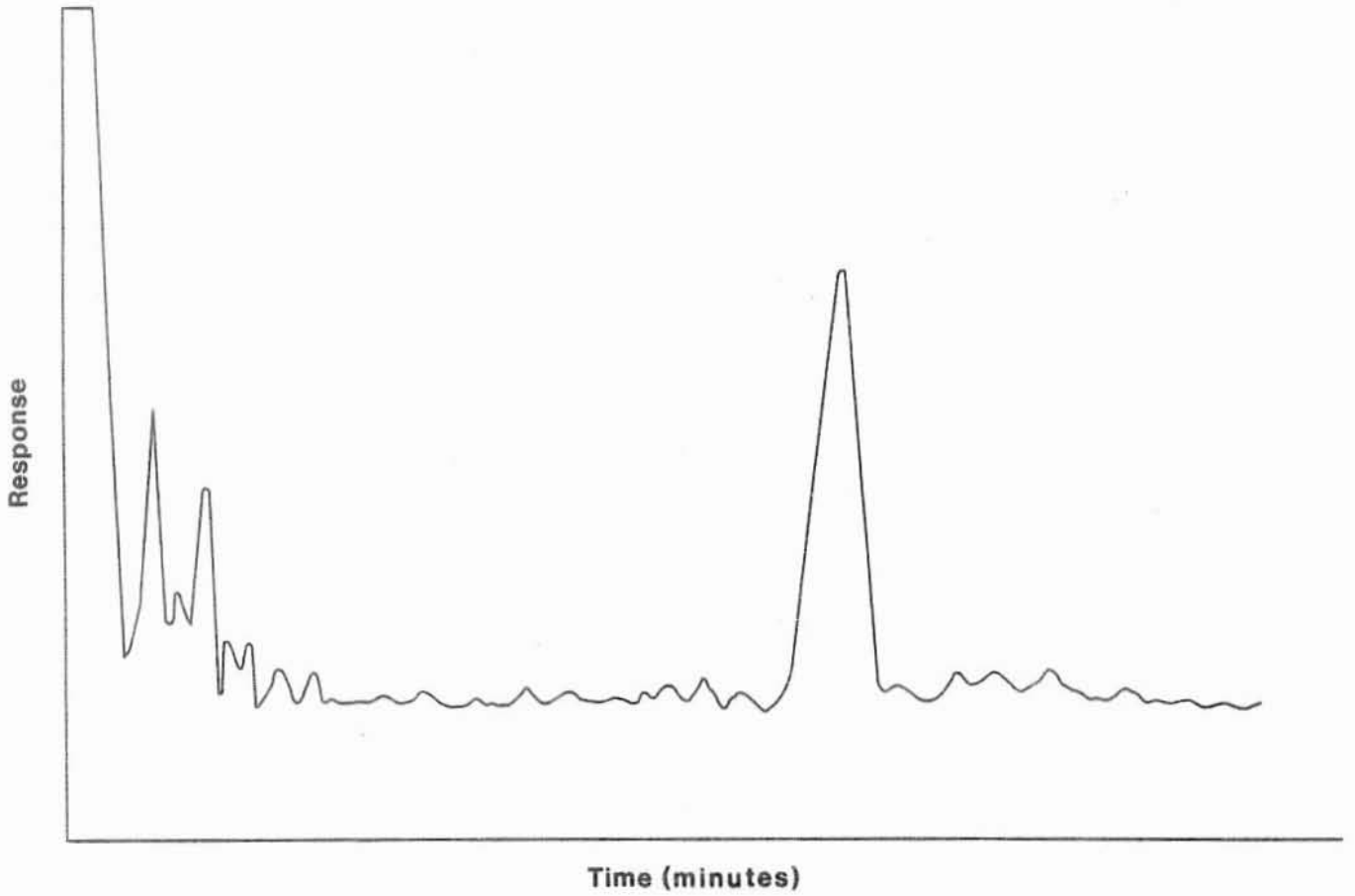

Fig. 9. Chromatogram of fortified leader sample (25 g) containing 5 mg of p,p'-methoxychlor after cleanup.

with time. The fall in concentration was rapid soon after spray; a fall of 3.05 ppm of *p,p'*-MC in one day, and the rate of decrease diminished rapidly with time. After 26 days the rate of fall was extremely small; a fall of only 0.60 ppm for the para isomer in 24 days. Similar decay patterns were observed when the percent residual insecticide,

i.e. $$\frac{\text{Residual MC } (o,p\text{-MC} + p,p'\text{-MC}) \text{ in ppm at time t (days)}}{\text{Initial concentration of MC } (o,p\text{-MC} + p,p'\text{-MC}) \text{ in ppm at time 0 (day)}} \times 100$$

or represented simply as ([A]/[Ao]) x 100 (Sundaram et al 1972) vs time (days) are plotted (Table 3, Fig. 6). In this case a decrease of 11 ppm from 0 to 1 day were observed compared to 2.5 ppm in 24 days from the 26 to 50 day interval. Logarithmic plots of percent residual insecticide, i.e., ln ([A]/[Ao] x 100) against time, t (days) is shown in Fig. 7 for wet and dry leader samples and are linear indicating that the dissipation of methoxychlor in leaders are linear, at least in the earlier parts, and obeyed nearly first-order kinetics as observed earlier (Sundaram et al 1972). The formation and disappearance of MCE did not follow a uniform pattern. Maximum concentration (0.40 ppm on wet mass basis) was noted on the ninth day after spraying and decreased to below 0.03 ppm within a period of eleven days. Afterwards no noticeable concentration of the olefin metabolite was found in the leaders.

DISCUSSION

Methodology Development

The four principal steps followed in the methodology

development for the analysis of methoxychlor residues from white pine leaders are given in Fig. 1. Comparing the several extraction methods and solvent systems employed (Table 1), near quantitative recovery (< 80%) of fortified *p,p,*-MC was obtained from chopped and homogenized leader samples using acetonitrile as extraction solvent. Extraction by ethyl acetate showed poor recovery (Fig. 8) of the spiked insecticide isomer. Although dichloromethane-methanol (1:1 V/V) solvent mixture was found adequate (ca 70 % recovery) for the extraction of fortified leader samples, a large part of resinous and pigment materials were coextracted which later led to column poisoning and increased background level (Fig. 2). After acetonitrile extraction, hexane partition and Florisil column cleanup removed nearly all the interfering impurities (see Fig. 9) except the more volatile and low boiling coextractives which partioned readily from the immobile solvent phase and responded to the EC dectector giving peaks in the chromatogram soon after the solvent front (Figs. 2 and 9). These peaks did not cause any interference in the quantitation of methoxychlor residues. The use of large volume (600 ml) of benzene in hexane (15%, V/V) solvent mixture to elute the adsorbed insecticide residues from Florisil column was not desirable; in future semimicro columns with other adsorbents such as alumina and silica should be tried to reduce the volume of the eluate. The Charcoal - Celite column was not useful (Table 1) in the cleanup procedure due to strong adsorption of MC-residues on carbon. At low concentrations of the insecticide residues, i.e., after 20 day interval of the spray operation, the eluate was concentrated < 2 ml for a good response in GC, consequently in spite of the cleanup treatment, noise

level of the EC detector increased appreciably (Fig. 2). Attempts to cleanup the eluate further, resulted in loss of the residues. Chromosorb W coated with DC-200 and QF-1 (10.0 : 0.4 : 0.6 g) column was found to be sensitive and responded well in separating the MC isomers and the olefin metabolite compared to SE-30 QF-1 and DC-200 columns (Table 2). Typical chromatograms obtained with DC-200 QF-1 column are shown in Figs. 2, 3 and 9.

Distribution of Methoxychlor Residues

The zero day leader samples contained 11.90 (92.1%), 0.92 (7.1%) and 0.10 (0.8%) ppm (Table 3 - wet mass) of *p,p'*-MC, *o,p*-MC and MCE respectively. Since the *o,p* and *p,p'*-insecticide isomers have high biological activity compared to the olefin metabolite, the total (ppm) or residual concentration (%) is expressed as the sum of the two isomers only ignoring the olefin (Table 3 - columns 7 and 8). The initial concentration of MC residues found in leaders (12.82 ppm) after the aerial spraying, was nearly 47 times lower than the concentration (600 ppm) obtained using a hydraulic sprayer (Sundaram et al 1972). The initial olefin concentration found (0.10 ppm) was low but rose to a maximum of 0.40 ppm after 9 days and decreased to traces (0.03 ppm) on 20th day leader samples. The formation, apart from the low amounts found in the spray mixture, and the disappearance of MCE in the substrate confirmed the earlier observation (Sundaram et al 1972) that the olefin is formed from the *p,p'*-isomer through bio- and phototransformations.

Persistence of Methoxychlor Residues

Methoxychlor, unlike DDT is readily biodegradable by plant enzymes (Sundaram et al 1972). Residue data (Table 3, column 7) show a rapid decline in residue levels from leaders. The initial concentration (*o,p* + *p,p'*-MC) of 12.82 ppm (wet mass) was reduced to 0.21 ppm within a period of 50 days. Initially the rate of decrease in concentration was high, a fall of 39% in 4 days after treatment, and the residue dissipation nearly followed first-order kinetics (Fig. 6). The decrease in concentration was ca 89%, i.e., 12.82 ppm to 1.40 ppm (wet mass) after 20 days. Beyond this period the dissipation was low and after 35 days, it nearly reached a constant level. A similar pattern was also observed for the oven dry leader samples.

The difference in the rates of dissipation of the *o,p* and *p,p'*-isomers of methoxychlor was significant. The zero day concentration of the *o,p*-isomer was found to be 0.92 ppm constituting only 7.2% of the total residue level but it decreased to 0.06 ppm after 50 days, i.e., a fall of 93.5%; whereas the initial concentration of the *p,p'*-isomer was 11.90 ppm constituting 92.8% of the total insecticide which diminished rapidly to 0.15 ppm within 50 days, i.e., a decrease of 98.7%. The relative ratio (percent) of the two isomers (*o,p* : *p,p'*) on zero day was 7.2 : 92.8 (0.72 ppm : 11.90 ppm) compared to 28.6 : 71.4 (0.06 ppm : 0.15 ppm) on the final day of analysis. It is possible from this limited study to suggest that the *p,p'*-isomer disappeared more rapidly, probably due to the larger deposit concentration in leaders, than the *o,p*-isomer. An approximate estimation of the deposit half-life from

Fig. 5 for the *p,p'*-isomer was found to be 4.75 days whereas for the *o,p*-isomer (Fig. 4), it was 10 days. A detailed investigation is necessary to evaluate and compare critically the decay rates and residue half-lives of these two isomers in pine leaders.

The graphical representation of the dissipation of *o,p*- plus *p,p'*-methoxychlor residues with time (Fig. 6) show that the process follows first-order kinetics at least during the early part of the study period. As noted earlier, the degradation curve falls rapidly but exponentially showing that the dissipation of the insecticide was very high initially but diminished to a lesser extent after the 20 day interval. The rapid decrease showed that the insecticide was deposited primarily on the surface of the leaders after spray application and held loosely by weak surface forces, which then degraded or dislodged easily by various physical processes such as weathering, volatilization, and abrasion, in addition, to a lesser extent by photo- and bio-degradations. This rapid dissipation of the insecticide from the leader samples followed nearly the first-order kinetics (Figs. 6 and 7). After awhile (ca 15 days), the surface deposit, being lipophilic dissolved gradually in terpene waxes present on the surface of the leaders forming a homogenous solid solution which penetrated and embedded below the surface tissues of the leaders, and was not readily dislodgable further by the various physical factors, outlined above, except probably by biodegradation. Since the major route of disappearance of the insecticide molecules was greatly inhibited by solution formation followed by penetration into leader cuticles, the residues persisted in small amounts up to 50 days and beyond.

The residue half-life obtained from the degradation curve (Fig. 6)

was found to be 5.0 days for both wet and dry leader samples confirming the rapid dissipation of methoxychlor. The value obtained was low compared to the one found (15.83 days) in 1972 using hydraulic sprayer. The formulation (aqueous emulsion) and the amount used in 1972 were very different, and the initial deposit concentration obtained (600 ppm) was very heavy. Consequently in such non-uniform spray conditions coupled with varying climatic parameters, comparison of the half-lives was not appropriate. A plot of ln [% residual MC] vs time (days) (Fig. 7) gave a linear relationship for both the wet and dry leader samples. The regression equations for the straight lines are

$$y = 4.359 - 0.090x \text{ (wet samples)}$$

$$y = 4.328 - 0.086x \text{ (dry samples)}$$

and deviations from regression are 0.99 and 1.15. Both lines have negative slopes equal to 0.090 and 0.086 respectively confirming the instability of the insecticide and its rapid disappearance from leader samples.

Efficacy of Methoxychlor Treatment

The results of methoxychlor treatment by using a hydraulic sprayer at the rate of 2 lbs AI /acre in 100 gal. of water at Orr Lake white pine plantations in 1972 and by using aircraft at the rate of 2.5 lb AI /acre in 1.75 gal. fuel oil and xylene at Thessalon in 1973 are shown in Table 4. From the results it is apparent that during the 1972 insecticidal application, although the reduction in weeviled trees was found to be relatively high i.e., 98% showing that methoxychlor treatment by hydraulic sprayer offered excellent protection for white pines against weevil attack, the initial deposit concentration

(600 ppm) and the residual half-life (15.8 days) were very high compared to the aerial application of the insecticide in 1973. Aerial spraying provided a low but uniform distribution (low variation from the mean residue values) of methoxychlor and the initial deposit concentration was only 12.82 ppm, nearly 46 times lower than the 1972 level. The half-life obtained by aerial application was 3.2 times lower (5 days) compared to the hydraulic sprayer (15.8 days). In addition to low half-life and low initial deposit concentration, the reduction in weeviled trees was reasonably high i.e. 80% in 1973 compared to the value of 98% obtained in 1972. Considering the low residue half-life and negligible environmental contamination, aerial application of methoxychlor for white pine weevil control seems to be favourable over the use of more difficult hydraulic sprayer application. Low mammalian toxicity (Metcalf 1955), rapid rate of disapperance, low half-life, high reduction in weevil population, etc., qualifies methoxychlor as one of the environmentally safe and effective insecticides and a suitable replacement for DDT for plantation pest control especially for the protection of white pines against weevil attack.

In conclusion, apart from requiring large amounts of methoxychlor (2.5 lb AI/acre) to obtain optimum level of protection (80% +), methoxychlor appears to be a suitable replacement for DDT in plantation weevil control. One concern, not evaluated and assessed is, the long term effects and immediate hazards of the toxicant on the plantation ecosystem. To accomplish this, additional experimentation is required which will stimulate increased research activity in weevil control and

consequently will assist in the overall evaluation and usefulness of the insecticide in plantation research. It is evident that the fate, persistence and efficacy of an insecticide is a function of the toxicant's properties, formulation used, mode of application and various environmental factors. It is recommended that sufficient emphasis be placed on formulation development, especially using emulsifiable concentrates containing various surfactants, adjuvants, stickers, spreaders, etc., to modify the properties of formulations used in spray operations and to increase the surface deposit concentration of the toxicant so as to span the activity of the compound against adult weevil attack, and at the same time reduce the dosage required. Aerial application is obviously a greater hazard than careful direct application to leaders by hydraulic sprayer. It is hoped that in future, more progress will be made to gain knowledge and insight into some of these areas outlined above to assess the significance and usefulness of methoxychlor for weevil control by aerial application.

SUMMARY

White pine trees (*Pinus strobus* L.) were sprayed with methoxychlor at the rate of 2.5 lbs AI/acre by aircraft. Leader samples were collected from sprayed trees at various time intervals for GLC assay. Homogenization of leaders and extraction by acetonitrile showed good recovery. The cleanup procedures involved hexane partition, concentration and column chromatography on deactivated Florisil. The initial deposit concentration in leaders was 12.82 ppm which decreased rapidly to 0.21 ppm

after 50 days. The dissipation rate of the insecticide was high with low persistance and residue half-life of only 5 days. The reduction in weeviled trees was 80% showing that methoxychlor treatment by aircraft provided sufficient protection to white pines against weevil attack and appears to be a suitable replacement for DDT in weevil control.

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