PERSISTENCE AND FATE OF METHOXYCHLOR USED FOR ELM BARK BEETLE CONTROL IN THE URBAN ENVIRONMENT OF THE NATIONAL CAPITAL AREA

by

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INTRODUCTION

Dutch elm disease (DED), caused by the fungus *Ceratocystis ulmi* [(Buism) C. Moreau] is the most serious disease problem of elm trees *Ulmus americana* L., in North America, threatening the very existence of these cherished shade trees (Fig. 1). It reached the continent from Europe about 1930 and was first observed in Canada in 1944. The disease is now widely distributed in the area stretching eastward from Lake Superior in Ontario to Nova Scotia. The vectors of the fungus are the native elm bark beetle, *Hylurgopinus rufipes* (Eichh) and the smaller European elm bark beetle, *Scolytus multistriatus* (Marsh) (Fig. 2). Contaminated beetles may inoculate healthy elms with fungal spores through egg-galleries or twig-crotch feeding scars depending on the species. The fungus grows in the water-conducting xylem vessels and other tissues of the tree which eventually lose their function, resulting in the death of the infected tree.

Although no economically feasible large-scale curative method is available as yet, the spread of the disease can be minimized and individual, high-value trees can be protected to a degree by rigorous application of quarantine, sanitation and chemical protection methods. In Ottawa, for example, the National Capital Commission (NCC) has taken special measures to protect the large number of stately elms present in the Ottawa-Hull area. In addition to a systematic program of sanitation to eliminate active or incipient beetle-breeding sites and diseased trees, regular spraying of healthy elms with insecticides is carried out in priority areas such as scenic driveways and around Parliament Hill to reduce chances of infection *via* normal feeding activities of the bark beetle vectors. The expensive chemotherapeutic method of trunk and root injection of fungicide solutions such as benomyl* [methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate] and its derivatives has been tested experimentally (Kondo *et al* 1973, Prasad 1974) as a control measure in some urban sectors of Ottawa for the protection of individual and high-value elms. For many years, the insecticide DDT [2,2-*bis*(p-chlorophenyl)-1,1,1-trichloroethane] was used to combat elm bark beetles, however, due to its environmental effects, the compound has been abandoned and currently the less hazardous and ecologically more acceptable chemical methoxychlor [2,2-*bis*(*p*-methoxyphenyl)-1,1,1-trichloroethane] is registered in Canada for this purpose and is used extensively by the NCC against the elm bark beetles.

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* Mention of trade names or commercial products in this report does not constitute endorsement or recommendation for use by the Canadian Forestry Service.

The material, somewhat more expensive than DDT, appears to be effective in controlling the feeding of elm bark beetles (Barger *et al* 1972, Cuthbert *et al* 1973). However, questions have been raised about its distribution, persistence and fate on the elms in the Ottawa-Hull environment, its residual properties in relation to application techniques and its overall ability to protect the trees against the disease. The present study was undertaken in conjunction with the current spray programs of the NCC with the full co-operation and assistance of that organization to find answers for some of the above questions. This report summarizes the findings of preliminary studies made in conjunction with the regular spray program carried out by the NCC in the Ottawa-Hull area in the fall and spring of 1974/75 under the following categories:

1. Methodology developed and used for the residue determination of methoxychlor isomers (*o,p*-MC and *p,p'*-MC and the degradation product methoxychlorethylene (MCE) in the bark of elm twigs.
2. Distribution, persistence and fate of the chemical in elm trees in the NCC area.
3. Evaluation of the deposit levels of the material in relation to spray equipment, *i.e.* mistblower *versus* hydraulic sprayer in order to find out which type of spraying was more effective.
4. Assessment of the efficacy of the compound as an insecticide in elm bark beetle control.

MATERIALS AND METHODS

1. Design of the Experiment

The experiment was conducted on plots located in three districts in the Ottawa-Hull area of the NCC: the Eastern District (ED) near the National Research Council (NRC) on Montreal Road; the Central District (CD) [at Strathcona Park (SP) in Ottawa and Printing Bureau (PB) in Hull]; and the Western District (WD) on Island Park Drive near the Central Experimental Farm (Fig. 3). In ED, three plots (P) were selected: in the first plot, one tree (# 333-345), designated ED-P1 served as the untreated "control" (Table 2), the second plot ED-P2 contained four trees which were sprayed with methoxychlor in the fall of 1974 (November 9) using a mistblower (Table 3). In the third plot ED-P3, the tree selected was sprayed with the insecticide on the last day of April in 1975 (Table 5) using a hydraulic sprayer. Two plots were chosen in the Central District, the plot CD-P1 was located in Strathcona Park and the selected tree was sprayed at the end of April 1975 using a hydraulic sprayer (Table 6). The tree in plot CD-P2 near the Printing Bureau in Hull was sprayed at the same time with a mistblower (Table 7). The tree in plot WD-P1 near the Experimental Farm was sprayed with the chemical in the spring of 1975 using a hydraulic sprayer (Table 8). Unfortunately, the trees selected by the NCC for this study were not of uniform height or shape. The average height was 18.3 m (60 ft)., range 6.1 to 27.4 m (20-80 ft) and mean d.b.h. 58.4 cm (23"), range 7.5 to 109.2 cm (3 to 43"). All the trees, including the control, had been exposed to methoxychlor spray in the past.

2. Spray Application

The spray application was done by commercial applicators hired by the NCC. The technical methoxychlor concentrate containing an emulsifier and xylene was diluted with water to prepare a 2% emulsion for use with hydraulic sprayers and 12.5% for mistblowers. The diluted material was applied as uniformly as possible to all four quadrants of the tree crown in late winter or early spring before the leaves appeared using either a truck mounted mistblower at an average rate of 9.2 ℓ/tree (2 gal/tree) or a mobile hydraulic sprayer at an average rate of 92 ℓ/tree (20 gal/tree). The amount of methoxychlor sprayed at a tree was estimated by either timing or metering the volume of spray applied.

3. Sampling

Sampling of elm twigs for the methoxychlor residue analysis was done by NCC personnel according to the instructions of the author. About twenty-five randomly selected twigs of uniform size (30 cm long) were cut with a hand-pruner from the mid-crown level of the four quadrants of each plot tree (9) using a personnel hoist. Prespray sampling was done first on April 23 followed by postspray samples on May 6, 23, June 17, July 30 and August 29, 1975 (Tables 2, 3, 5-7 and 8). The twigs collected from tree in plot ED-P2 on April 23 constituted the first postspray sample after the insecticide application in the fall of 1974. The twigs were enclosed in plastic bags and transported immediately to the Pesticide Laboratory at the Chemical Control Research Institute (CCRI) for residue analysis.

4. Analytical Methodology

a. Extraction

The analytical procedure developed by Sundaram (1973) for the analysis of methoxychlor isomers and MCE from pine leaders using gas-liquid chromatography was found to be sensitive, rapid and precise for analysing the insecticide residues on elm barks.

In the laboratory, the bark from each sample was stripped from the wood of twigs with a sharp knife, cut into small pieces and ground in a Hobart machine until a homogeneous powdery mixture was obtained. An aliquot (10 g) was taken for moisture determination (AOAC 1955). Three 10 g ground bark samples from each sampling period were homogenized in a Sorvall Omni-Mixer with 100 ml of acetonitrile for 5 min. at a speed setting of 7. The macerate was filtered under suction through "S and S Shark Skin" filter paper. An additional 10 ml of the solvent used to wash the residue, was added to the original extract and the total volume reduced to *ca* 10 ml by flash-evaporation and partitioned in a separatory funnel (500 ml) in presence of water (250 ml), saturated Na_2SO_4 (5 ml) and hexane (200 ml). After equilibration, the hexane phase containing the insecticide residues was separated and washed with 100 ml of water. The aqueous layer was discarded and the hexane was dried by passing through a column of anhydrous Na_2SO_4. The dried extract was reduced to *ca* 5 ml by flash-evaporation.

b. Cleanup Procedure

The cleanup to remove any electron capturing coextractives was achieved by passing the hexane concentrate through a Shell type liquid chromatographic column (1 x 30 cm) containing 12.5 g of Florisil (Fisher, F100, 60/100 mesh, equilibrated to contain 5% H_2O) sandwiched between 5 g Na_2SO_4 and prewashed with 25 ml of hexane. The column was eluted with 300 ml of 15% benzene in hexane (V/V). The eluate was flash evaporated to a small volume for GLC analysis.

c. Gas-liquid Chromatographic Analysis

The elm bark extracts containing the methoxychlor isomers (*o,p*-MC and *p,p'*-MC) and *p,p'*methoxychlor ethylene [2,2-*bis*(*p* - methoxyphenyl)-1,1-dichloroethylene, abbreviated here as MCE] were analysed with a Hewlett-Packard 5750 gas chromatograph fitted with a Ni-63 electron capture detector. Operating parameters were as follows:

Column:	180 cm x 4 mm Pyrex glass packed with 4% DC 200 + 6% QF1 on 60-80 mesh Gas Chrom Q, preconditioned 48 hrs at 230°C.	
Temperature (°C):	Injection ports	245
	Column oven	220
	Detector	280
Carrier gas:	Argon/methane (95/5%) pressure of 50 psi and flow rate of 50 ml/min.	

Instrument settings:	Attenuation and range 32 x 10, pulse 150, electrometer 4 x 10^9 amp. full scale with 1 mv recorder.	
Chart speed:	16 in/hr or 0.27 in/min.	
Retention times (min.):	MCE	7.7
	o,p-MC	8.9
	p,p'-MC	12.1
Relative retention times:	MCE	0.63
	o,p-MC	0.73
	p,p'-MC	1.00

The gas chromatograph was standardized on the same day as the bark samples were analysed by injecting aliquots (2-6 ul) of freshly prepared standard solutions in hexane containing MC isomers and MCE (Fig. 4), measuring the peak heights, and preparing a calibration curve by plotting peak heights (cm) *vs* weight (ng) (Fig. 5). The bark extracts were either diluted with hexane or concentrated to bring the amount of the insecticide injected within linear range of the detector. Quantitative results of the extracted samples were obtained by measuring each of the peak heights after injections (2 to 4 ul), under the same operating conditions, and reading the concentrations from the calibration curves (Fig. 5).

5. 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 of reagent grade, heated at *ca* 150°C overnight and stored in a glass-stoppered bottle.

TABLE 1

PERCENT RECOVERY OF METHOXYCHLOR ISOMERS AND METHOXYCHLOR ETHYLENE* FROM SPIKED BARK SAMPLES OF ELM TREES

SERIAL NO.	MASS OF ELM BARK (g)	FORTIFICATION LEVEL *(ug)*			AVERAGE PERCENT RECOVERY			COEFFICIENT OF VARIATION (%)		
		MCE	*o, p-MC*	*p, p'-MC*	*MCE*	*o, p-MC*	*p, p'-MC*	*MCE*	*o, p-MC*	*p, p'-MC*
1	20	10	10	10	82	80	88	6	7	4
2	20	20	20	20	85	82	92	4	5	4

* Each value represents the average of three analytical replicates.

TABLE 2

METHOXYCHLOR RESIDUES IN ELM TREE* (CONTROL) FROM NRC, MONTREAL ROAD (EASTERN DISTRICT)

SERIAL NO.	DATE OF SAMPLING	MOISTURE CONTENT (%)	METHOXYCHLOR RESIDUES AS SAMPLED - *ppm*			
			MCE	*o, p-MC*	*p, p'-MC*	*MC* - TOTAL
3	April 23	44	0.70	1.20	10.60	12.50
4	June 17	51	0.25	0.95	6.90	8.10
5	July 30	41	0.15	0.55	4.35	5.05
6	August 29	42	0.10	0.40	3.40	3.90

* Tree No. 333/345

TABLE 3

METHOXYCHLOR RESIDUES* IN FOUR ELM TREES FROM NRC, MONTREAL ROAD (EASTERN DISTRICT)

SPRAYED BY MIST BLOWER

		SAMPLING DATE: APRIL 23					JUNE 17					JULY 30					AUGUST 29				
SERIAL NO.	TREE NO.	Moisture Content (%)	*MCE*	*o,p-MC*	*p,p'-MC*	Total *MC*	Moisture Content (%)	*MCE*	*o,p-MC*	*p,p'-MC*	Total *MC*	Moisture Content (%)	*MCE*	*o,p-MC*	*p,p'-MC*	Total *MC*	Moisture Content (%)	*MCE*	*o,p-MC*	*p,p'-MC*	Total *MC*
7-10	333/347	46	5.50	15.60	251.20	272.30	52	5.10	3.75	55.00	63.85	42	15.75	17.70	275.65	309.10	45	11.50	7.25	70.85	89.60
11-14	333/348	44	9.50	28.40	283.00	320.90	51	4.20	4.70	45.85	54.75	46	3.05	1.25	45.70	50.00	44	2.05	1.10	15.45	18.60
15-18	333/350	46	2.00	14.00	138.90	154.90	43	11.20	10.00	117.50	138.70	38	15.80	59.00	880.25	955.05	-	-	-	-	-
19-22	333/353	45	12.50	22.50	684.90	719.90	49	7.80	18.15	178.15	204.10	40	10.85	15.75	465.00	491.60	-	-	-	-	-

* Concentrations are expressed in *ppm* "as sampled".

TABLE 4

AVERAGE LEVELS OF METHOXYCHLOR RESIDUES IN FOUR ELM TREES*

FROM NRC, MONTREAL ROAD (EASTERN DISTRICT) SPRAYED BY MIST BLOWER

DATE OF SAMPLING	AVERAGE MOISTURE CONTENT (%)	Methoxychlor Residues As Sampled - *ppm*			
		MCE	*o*, *p*-*MC*	*p*, *p*'-*MC*	TOTAL *MC*
April 23	45	7.40	20.10	339.50	367.00
June 17	49	7.10	9.15	99.10	115.35
July 30	42	11.40	23.40	416.65	451.45
August 29	45	6.80	4.20	43.15	54.10

* Tree Nos. 333/347, 333/348, 333/350, 333/353.

TABLE 5

METHOXYCHLOR RESIDUES IN ELM TREE* FROM NRC, MONTREAL ROAD (EASTERN DISTRICT)

SPRAYED BY HYDRAULIC SPRAYER

SERIAL NO.	DATE OF SAMPLING	MOISTURE CONTENT (%)	Methoxychlor Residues As Sampled - *ppm*			
			MCE	*o, p-MC*	*p, p'-MC*	*MC* - Total
23	May 6	45	7.80	13.50	179.20	200.50
24	May 23	47	5.40	12.80	132.40	150.60
25	June 17	45	2.20	3.00	31.70	36.90
26	July 30	38	4.45	5.25	68.80	78.50
27	August 29	46	3.30	3.95	29.25	36.50

* Tree No. 333-05

TABLE 6

METHOXYCHLOR RESIDUES IN ELM TREES FROM STRATHCONA PARK(CENTRAL DISTRICT)

SPRAYED BY HYDRAULIC SPRAYER

SERIAL NO.	DATE OF SAMPLING	MOISTURE CONTENT (%)	Methoxychlor Residues as Sampled - *ppm*			
			MCE	*o, p*-*MC*	*p, p'*-*MC*	*MC* - Total
28	April 23*	49	7.10	9.40	161.70	178.20
29	May 6**	49	15.70	9.50	197.90	223.10
30	May 23**	40	9.80	3.60	103.70	117.10
31	June 17**	44	5.20	6.20	88.70	100.10
32	July 30**	42	2.10	3.40	19.95	25.45
33	August 29**	45	1.05	2.15	15.05	18.25

* Tree No. 328-1 from Diplomatic Precinct

** Tree No. 124-5 from Strathcona Park

TABLE 7

METHOXYCHLOR RESIDUES IN ELM TREES* AT THE PRINTING BUREAU IN HULL (CENTRAL DISTRICT)

SPRAYED BY MIST BLOWER

SERIAL NO.	DATE OF SAMPLING	MOISTURE CONTENT (%)	Methoxychlor Residues as Sampled - *ppm*			
			MCE	*o, p-MC*	*p, p'-MC*	*MC* -Total
34	May 6	51	0.80	2.40	26.00	29.20
35	May 23	39	3.60	10.80	99.00	113.40
36	June 17	47	8.95	5.25	45.45	59.65
37	July 30	42	4.50	4.45	38.70	47.65
38	August 29	47	3.00	4.00	32.65	39.65

* Tree No. 306-6

TABLE 8

METHOXYCHLOR RESIDUES IN ELM TREES FROM ISLAND PARK DRIVE (WESTERN DISTRICT)

SPRAYED BY HYDRAULIC SPRAYER

SERIAL NO.	DATE OF SAMPLING	MOISTURE CONTENT (%)	Methoxychlor Residues as Sampled - *ppm*			
			MCE	*o, p-MC*	*p, p'-MC*	*MC* -Total
39	April 23*	47	2.90	1.60	15.30	19.80
40	May 6**	49	8.50	12.70	120.00	141.20
41	May 23**	46	9.50	14.20	141.90	165.60
42	June 17**	51	5.10	5.30	40.50	50.90
43	July 30**	43	3.50	2.25	20.75	26.50
44	August 29**	43	1.50	1.80	13.05	16.35

* Tree No. 202-160

** Tree No. 202-150

TABLE 9

AVERAGE LEVELS OF METHOXYCHLOR RESIDUES IN FIVE ELM TREES*

SPRAYED BY MIST BLOWER

DATE OF SAMPLING	AVERAGE MOISTURE CONTENT (%)	Methoxychlor Residues as Sampled - *ppm*			
		MCE	*o, p-MC*	*p, p'-MC*	TOTAL *MC*
April 23	45	7.40	20.10	339.50	367.00
May 6	51	0.80	2.40	26.00	29.20
May 23	39	3.60	10.80	99.00	113.40
June 17	48	7.45	8.40	88.40	104.25
July 30	42	10.00	19.60	341.10	370.70
August 29	45	5.50	4.10	39.70	49.30

* For tree numbers see Tables 3 and 7.

TABLE 10

AVERAGE LEVELS OF METHOXYCHLOR RESIDUES IN THREE ELM TREES*

SPRAYED BY HYDRAULIC SPRAYER

DATE OF SAMPLING	AVERAGE MOISTURE CONTENT (%)	Methoxychlor Residues as Sampled - *ppm*			
		MCE	*o, p-MC*	*p, p'-MC*	TOTAL *MC*
April 23	48	5.00	5.50	88.50	99.00
May 6	48	10.70	11.90	165.70	188.30
May 23	44	8.30	10.20	126.00	144.50
June 17	47	4.20	4.80	53.60	62.60
July 30	41	3.35	3.60	36.50	43.45
August 29	47	1.95	2.60	19.10	23.65

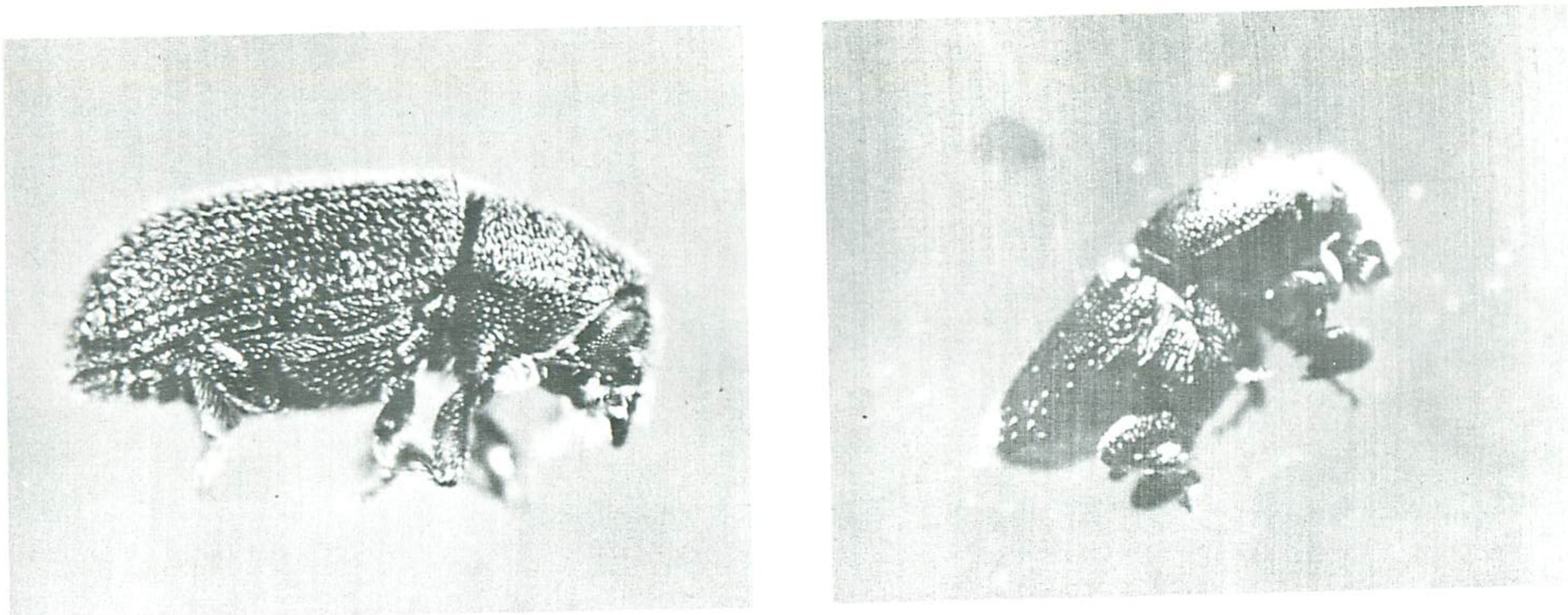
* For tree numbers see Tables 5, 6 and 8.

(a)

(b)

Fig. 1 (a) Stately elms on the Parliament Hill.

(b) Victim of DED near the National Arts Centre, Ottawa, July 1975.



(a) (b)

Fig. 2. Vectors of DED fungus. (a) Native elm bark beetle. (b) European elm bark beetle.

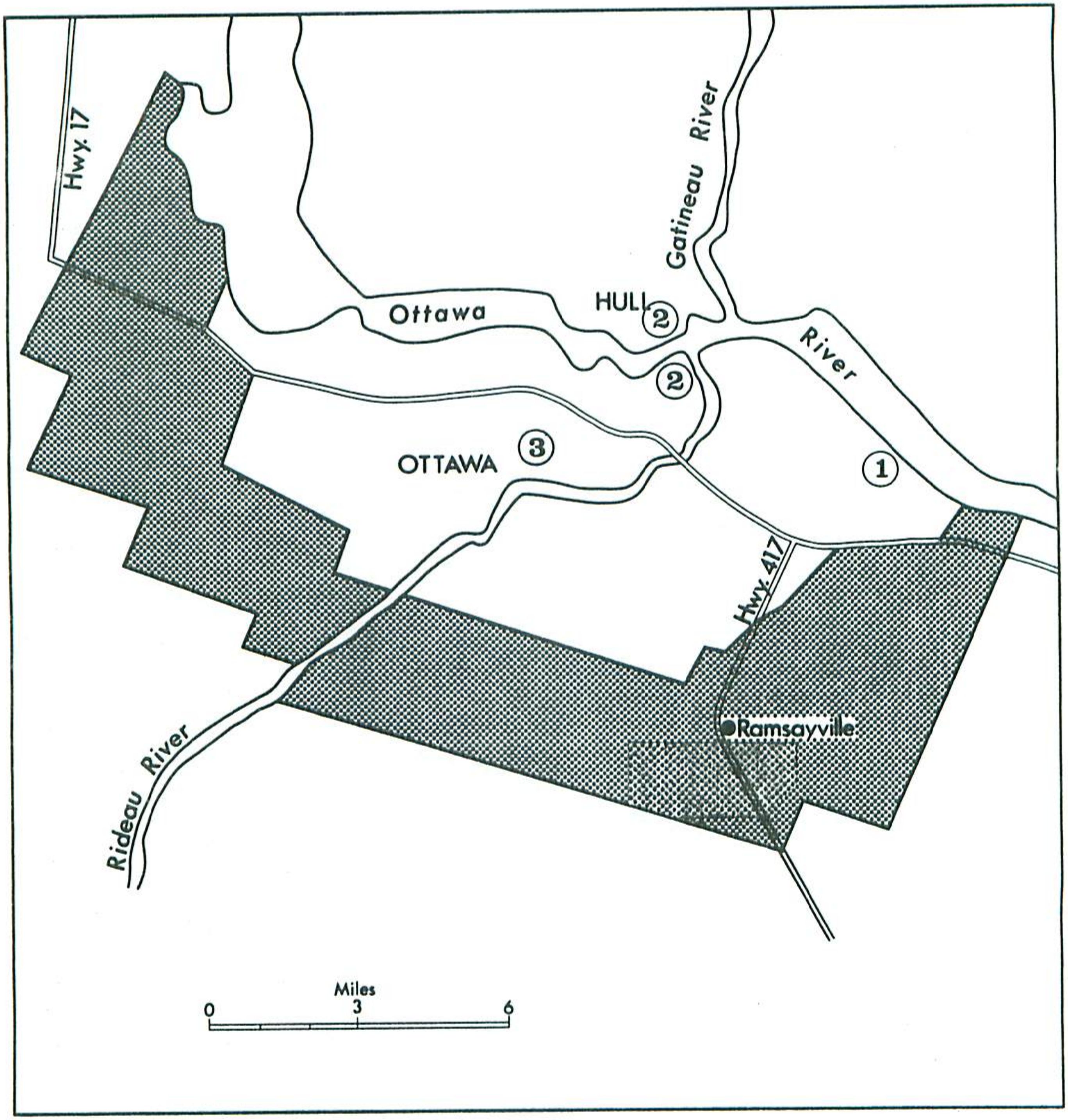


Fig. 3. Diagram showing the various sampling areas of elm trees in the NCC region for methoxychlor residues.

(1) Eastern District NRC, Montreal Road.

(2) Central District - Strathcona Park in Ottawa and Printing Bureau in Hull.

(3) Western District - Island Park Drive.

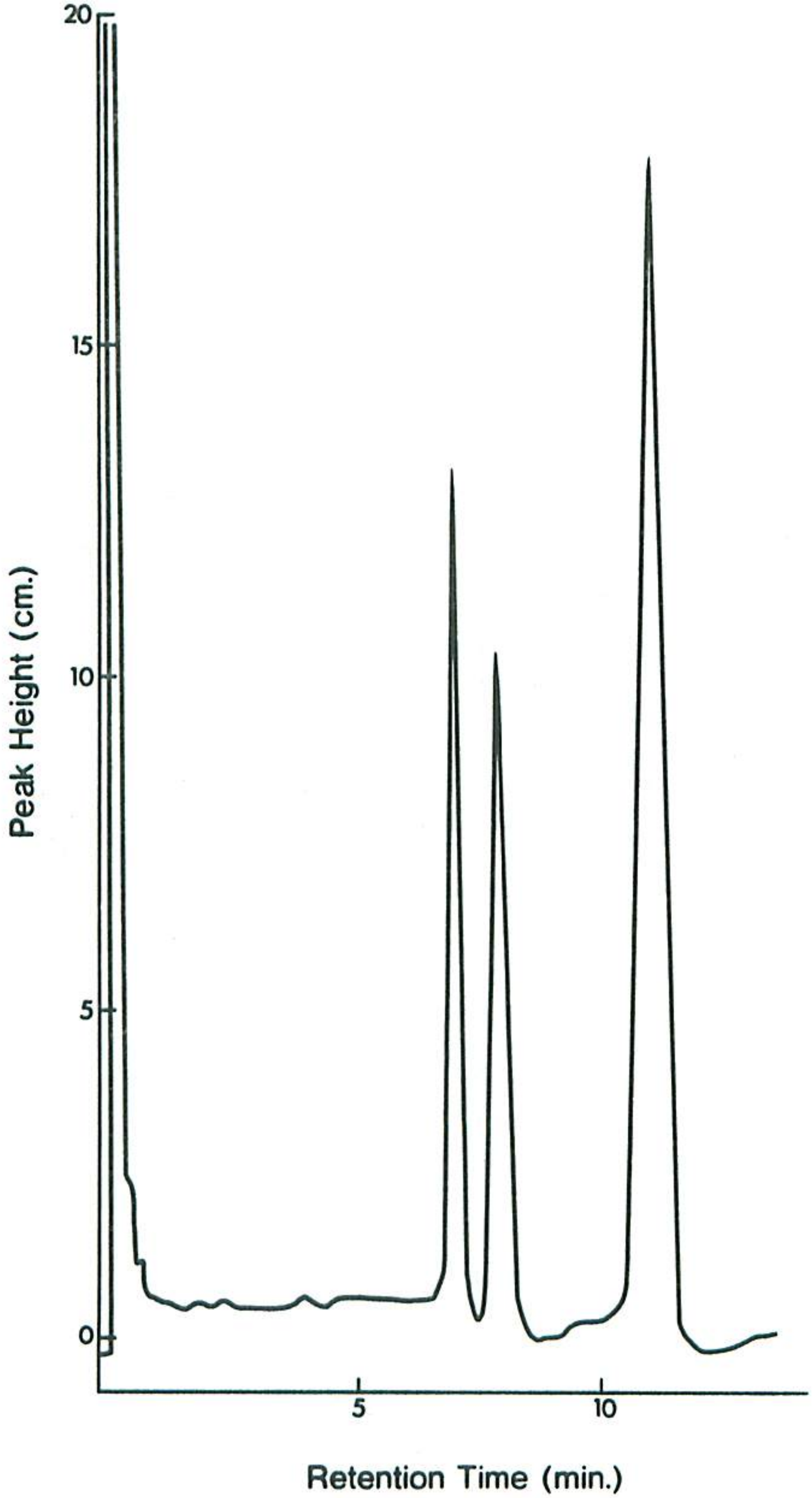


Fig. 4. Gas chromatogram of a standard solution (2 ul) containing 0.56 ng of MCE, 0.84 ng of *o,p*-MC and 1.40 ng of *p,p'*-MC. R.T. (min) MCE 7.7, *o,p*-MC 8.9 and *p,p'*-MC 12.1 R.R.T. MCE 0.6, *o,p*-MC 0.7, *p,p'*-MC 1.0.

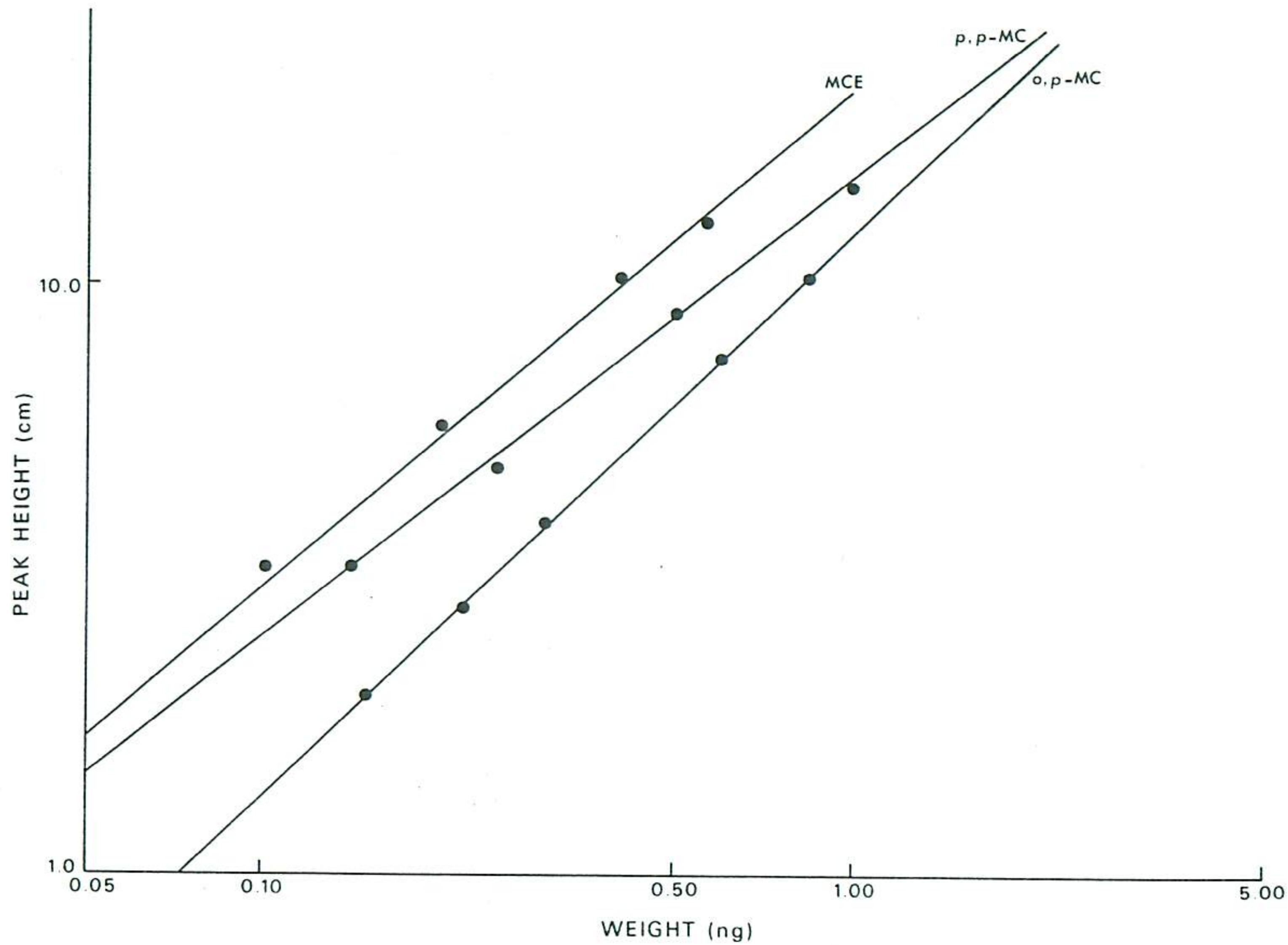


Fig. 5. Gas chromatographic calibration curves for methoxychlor isomers and methoxychlorethylene.

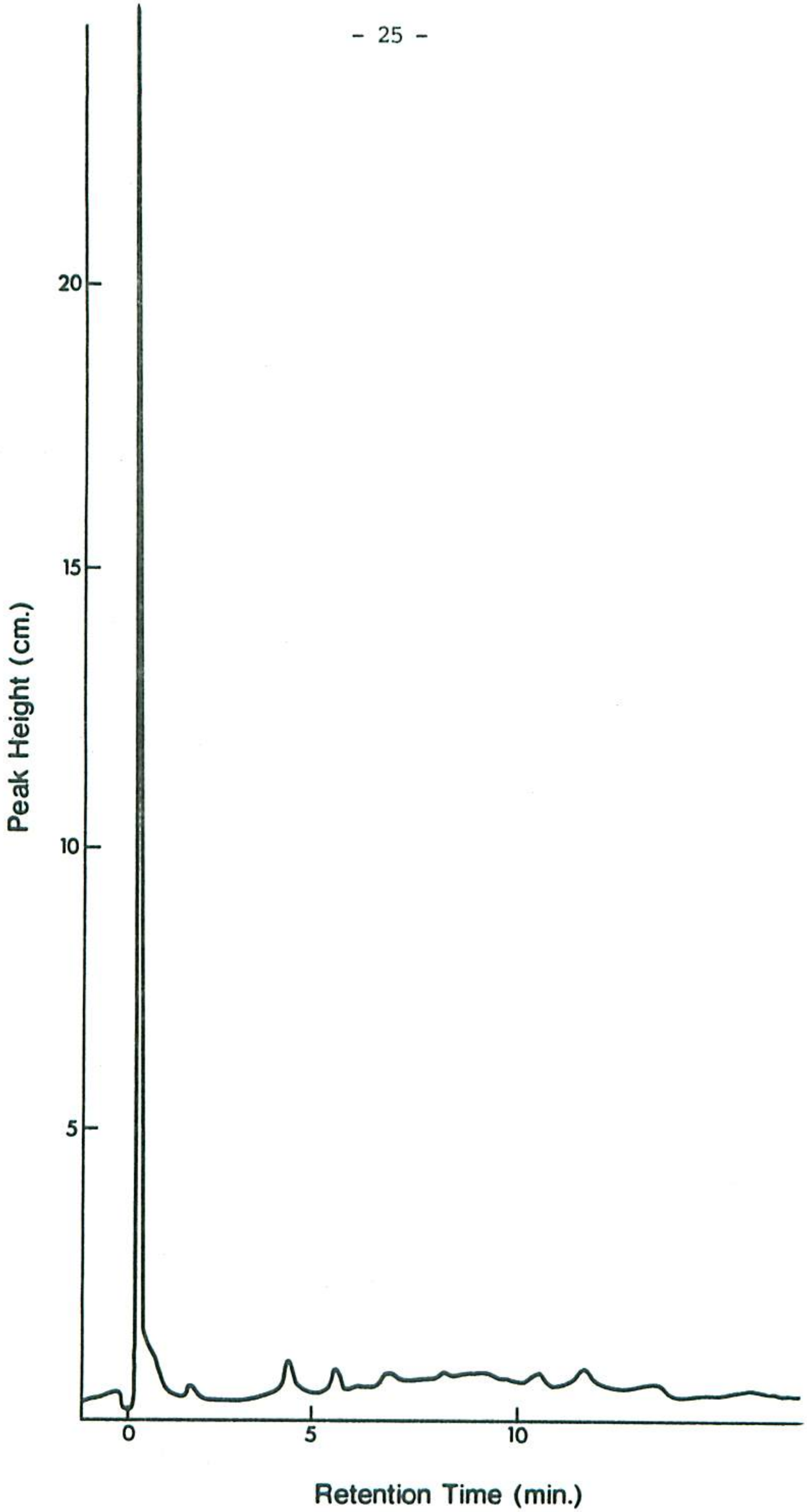


Fig. 6. Gas chromatogram of an extract of 200 ug of the bark of an elm tree free from methoxychlor residues.

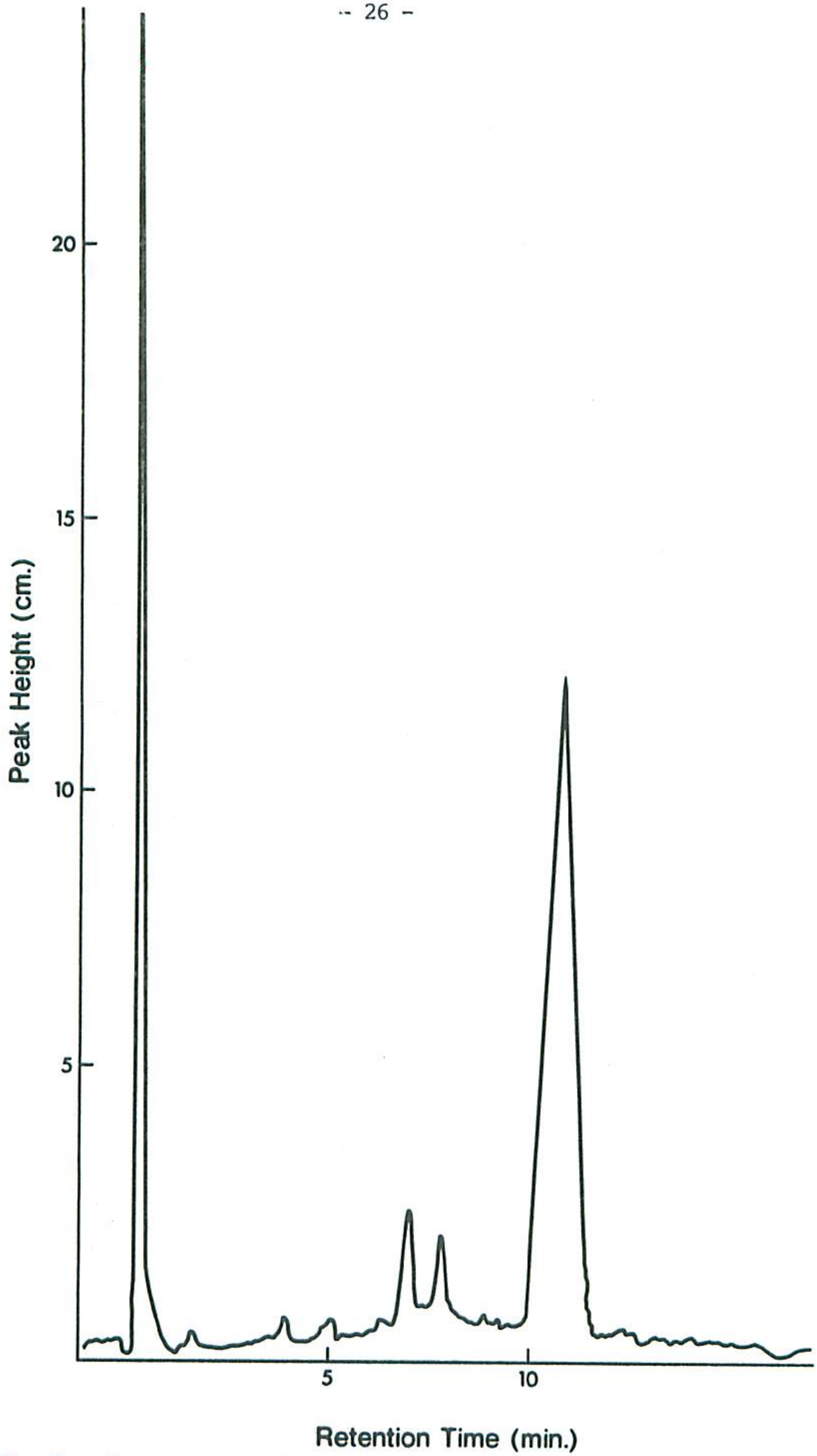


Fig. 7. Gas chromatogram of an extract of elm bark fortified with 0.5 ppm of MC-isomers and MCE before extraction.

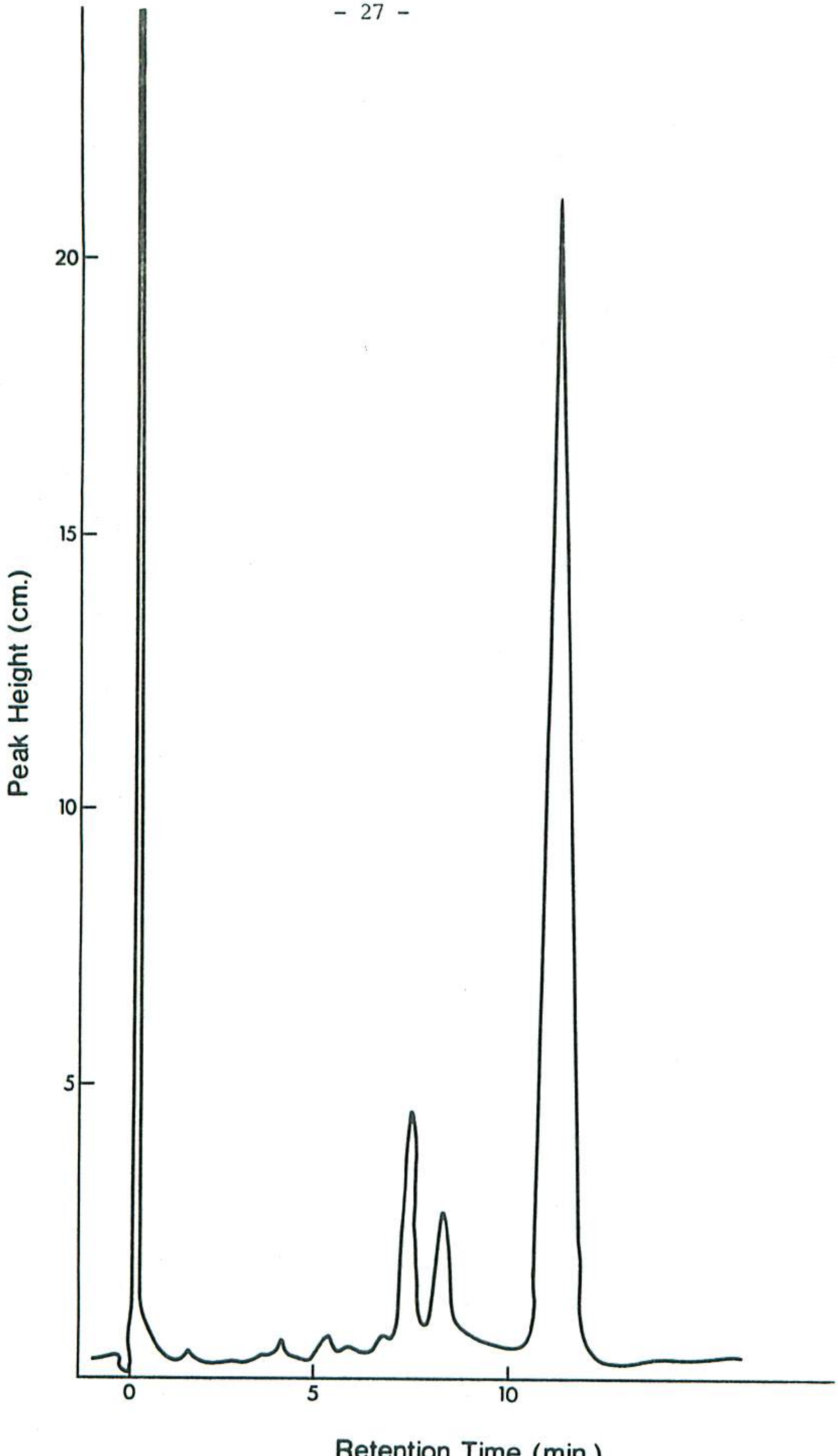


Fig. 8. Gas chromatogram of an extract of 400 ug of the bark of an untreated "control" tree (# 333-345) from the Eastern District. Note that the tree had been exposed earlier to the insecticide.

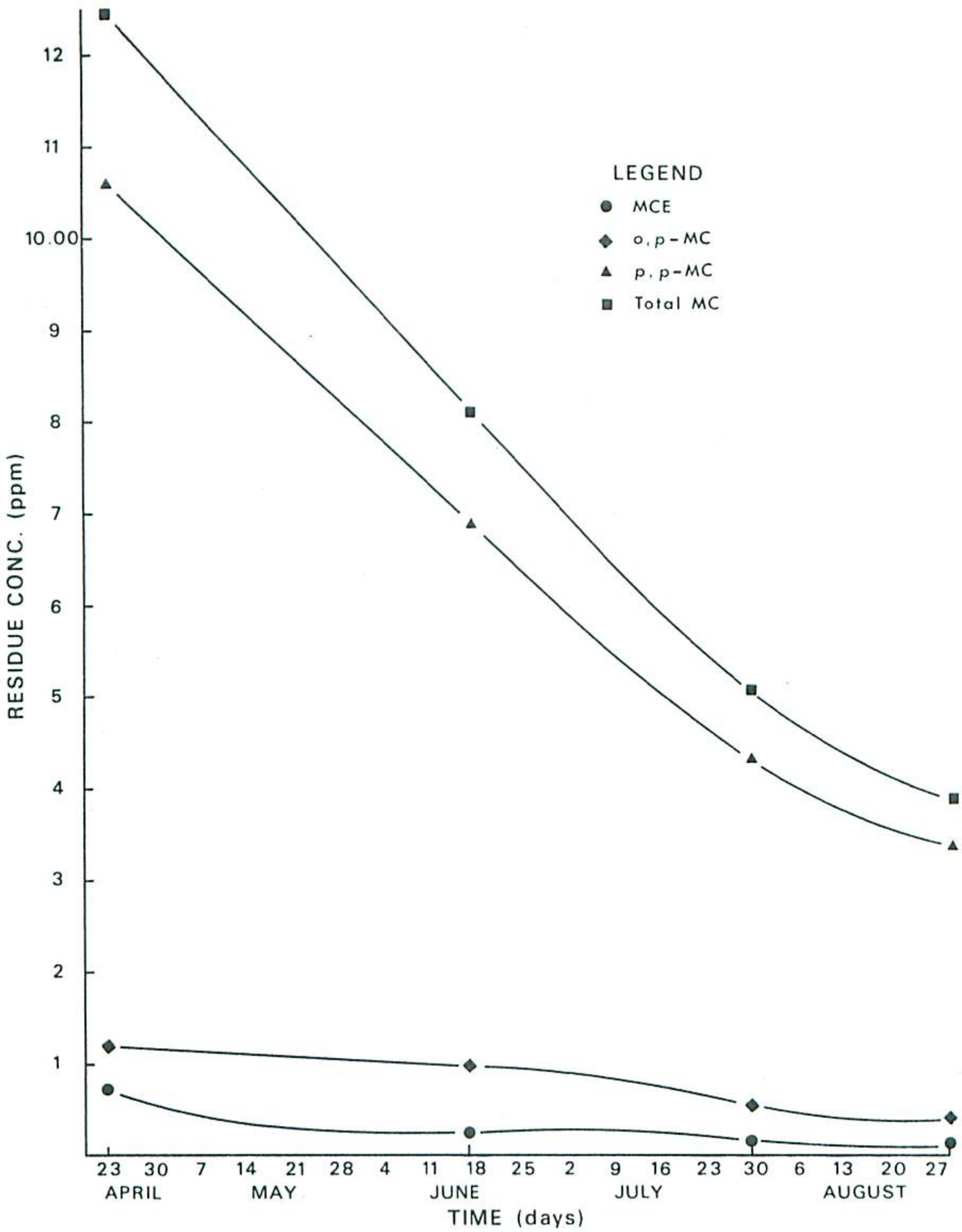


Fig. 9. Rate of dissipation of MC-isomers and MCE in the control tree (# 333-345) from the Eastern District.

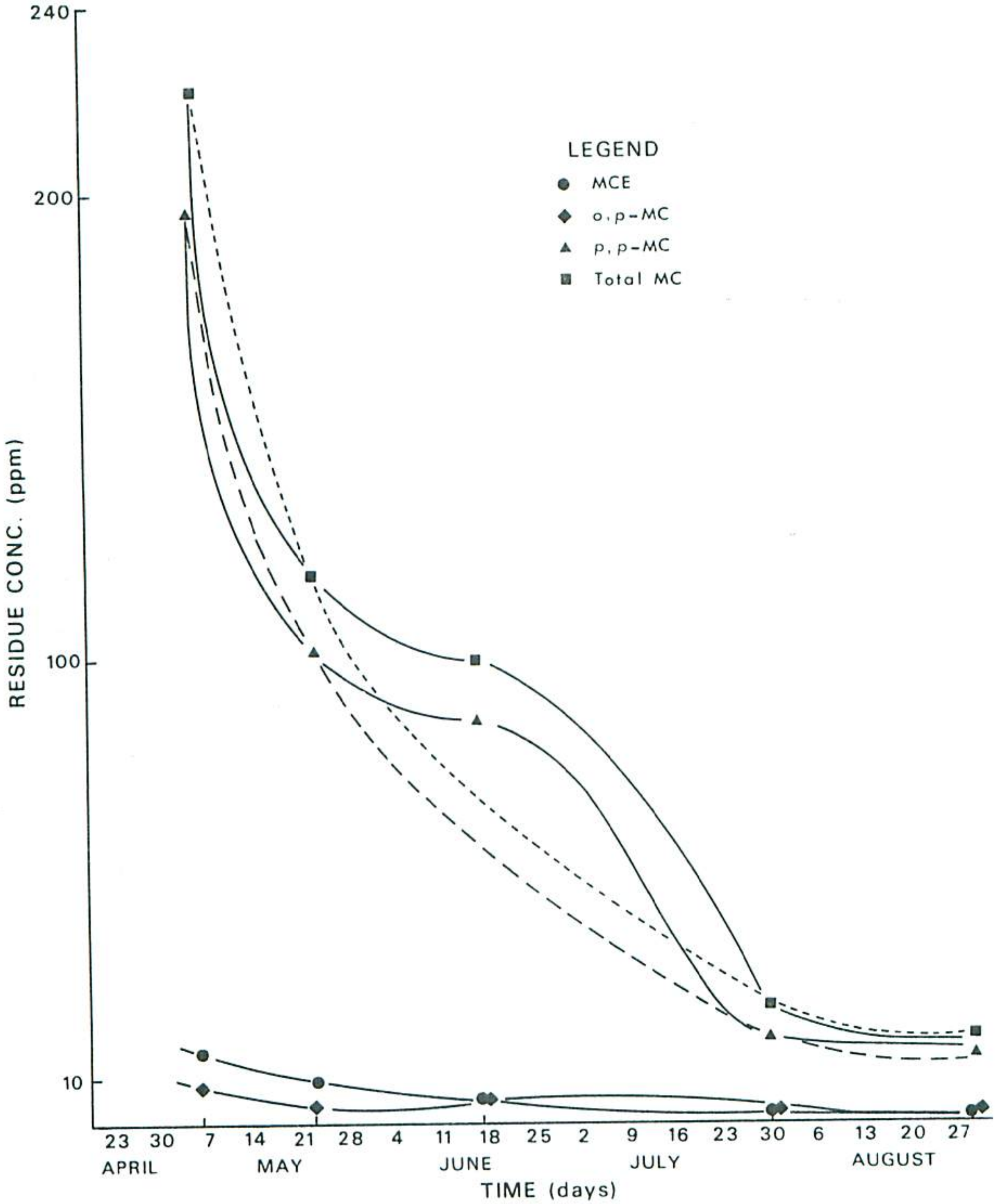


Fig. 10. Dissipation characteristics of methoxychlor from an elm tree in the Central District sprayed by hydraulic sprayer. Dotted lines show the overall degradation patterns for the *p,p'*-MC and total MC. The half-life for the latter is *ca* 25 days.

RESULTS AND DISCUSSION

1. Analytical Methodology

Recoveries of MC isomers and MCE in elm bark samples obtained from Larose Forest and fortified with 0.5 and 1.0 ppm levels are given in Table 1. Average percent recoveries for the *p,p'*-MC, *o,p*-MC and MCE were 90 ± 4, 81 ± 6 and 84 ± 5 respectively with a minimum detection limit of 0.05 ppm for all the three compounds showing that the analytical method described here is precise, reproducible, sensitive and suitable for estimating methoxychlor residues in elm bark. The GLC responses to the standards of these three compounds are shown in Fig. 4, and the retention times (RT) in minutes found were 7.7 for MCE, 8.9 for *o,p*-MC and 12.1 for *p,p'*-MC. Similarly, chromatographic profiles for the unspiked and spiked bark extracts after cleanup are illustrated in Figs. 6 and 7. The background interference in the chromatogram of the bark fortified with toxicants (Fig. 7) was small showing that the extraction, partition, column cleanup and final quantitation methods employed were satisfactory.

2. Distribution of Methoxychlor Residues

Amounts of methoxychlor deposits (*o,p*-MC, *p,p'*-MC and MCE) in ppm found in the barks of control and sprayed elm trees are recorded in Tables 2 to 10. The concentration levels are expressed on moist weight (as sampled) basis. If the percentages of MC on oven-dry weight basis are required, they may be calculated readily using the moisture content data in the tables. The overall recovery of the insecticide in terms of *p,p'*-MC was around 90%. The data presented in Tables 2 to 10 do not include any correction for % recovery from spiked sample.

The control sample of elm bark from ED-P1 had been exposed to methoxychlor sprays before and is evident from the results recorded in Table 2 and Fig. 8, probably during the 1974 fall spraying. The sample collected on April 23, 1975 contained 12.50 ppm of total methoxychlor (MCE, *o,p*-MC, *p,p'*-MC) which slowly degraded to 3.90 ppm on August 29, after 107 days with a half-life of *ca* 80 days (Fig. 9). The relative percentages of the olefin (MCE) and the two MC-isomers on the first sampling day were (MCE : *o,p*-MC : *p,p'*-MC) 5.6 : 9.6 : 84.8, changing to 2.6 : 10.3 : 87.2 by the last sampling date. The ratio between the two isomers (*o,p*-MC : *p,p'*-MC) found in the bark samples was nearly the same as that in commercial methoxychlor (tech.).

Table 3 shows the methoxychlor residues present in the bark of twigs of four elm trees (ED-P2) sprayed in the fall of 1974 *via* mistblower. The total deposit levels varied widely and erratically not only among the four trees on the same sampling day (July 30) (e.g. 50.00 to 955.05 ppm) but also between the four sampling periods (154.90 to 955.05 ppm). Enormous variations (> 220%) in the insecticide concentration were also observed within the four quadrants of the tree on the same sampling day. Some tree quadrants caught very little sprays whereas others received much. The average residue levels of methoxychlor found on April 23 was 367.00 ppm (Table 4) which decreased undulately to 54.10 ppm on August 29, 1975. The data of of July 30 are much out of line indicating that the trees had been contaminated in varying degrees in the course of an unrecorded summer spray application. Because of this uncertainty, no significant correlations can be derived from Tables 3 and 4. However, the high insecticide concentration found in the spring indicates that the material had weathered very little during the cold weather.

Methoxychlor residues on a tree (# 333-05) sprayed by hydraulic sprayer during the spring of 1975 are recorded in Table 5. The total deposit levels were moderate (maximum 200.50 ppm on May 6) and dissipated unevenly to 36.50 ppm after 15 weeks. Although significant differences in initial and final deposit levels were found in elm barks between the two methods of application and treatments at different seasons in the same area, no useful correlations could be derived from the data recorded.

Methoxychlor residues found in elm trees in the central district (Strathcona Park CD-P1 and Printing Bureau, Hull CD-P2) are given in Tables 6 and 7. The tree in Strathcona Park had been sprayed with the insecticide using a hydraulic sprayer whereas the tree in Hull area was sprayed with a mistblower. Ignoring the first value recorded in Table 6 (different tree and area), the maximum hydraulic spray deposit level was 223.10 ppm (Table 6) compared to 113.40 ppm with a mistblower (Table 7) and they dissipated to 18.25 (Fig. 10) and 39.65 ppm respectively after 14 weeks showing an approximate half-life of 3.5 weeks or 25 days. No significant differences in half-lives were found in spite of the differences in initial concentrations.

Residues of methoxychlor in elm trees collected from Island

Park Drive in the Western District (plot WD-P1) are given in Table 8. Tree 202-160 sampled on April 23, 1975 contained 19.80 ppm pre-spray MC residue concentration. The insecticide concentrations in the tree 202-150, after the spray application, ranged from 165.60 ppm on May 23 to 16.35 ppm on the last day of sampling.

The variability of coverage within and between trees was enormous as can be seen from the results recorded in Tables 3 to 8 showing that the chemical was not uniformly distributed on the tree to deter effectively the feeding of elm bark beetles. In general, beetle mortality depends on the concentration level of the methoxychlor deposited on or in the bark and its persistence and toxicity. The uneven coverage may be attributed to difference in tree size (range : d.b.h. 7.5 to 109.2 cm, height 6.1 to 27.4 m) non-uniform application (moving the spray equipment uniformly while spraying around the tree), type of spray equipment [high volume (92 ℓ/tree) spraying hydraulic sprayer *vs* high concentrate but low volume (9.2 ℓ/tree) spraying mistblower] used, amount of insecticide sprayed to each tree (1.84 kg/ tree using hydraulic sprayer *vs* 1.15 kg by mistblower) and to some extent meteorological conditions existing while spraying as well as the stability and adherent properties of the formulation used. If meaningful results are to be obtained from future experimental work, these variables must be controlled as closely as possible, and greater care taken to follow designated procedures for obtaining representative samples for residue analysis. The chemists' residue data may be precisely determined but may not be accurate because of inconsistency in field sampling by not conforming to defined procedures.

The residue levels found in the bark were very high, and accordingly in future it may be possible to simplify the complex analytical procedure used. Sorvall homogenization and Florisil column cleanup steps can probably be eliminated. Shaking the bark in hexane solvent followed by filtration through a column of Na_2SO_4, then concentrating the filtrate for GLC analysis should be adequate to give the required residue data for this project. The simplified procedure should adequately distinguish differences in amounts of methoxychlor found between trees at different times of the year.

3. Spray Equipment and Deposit Levels

The average total methoxychlor levels on elm barks resulting from using the mistblower and hydraulic sprayer are pooled and summarized in Tables 9 and 10 respectively. Considering the sampling periods of May 6 and 23 only, it is evident that the sample deposits from hydraulic spraying were heavier than mistblower sample deposits but the differences were inconsistent. More data gathered under rigid experimental conditions are necessary for a useful assessment on the advantages of one type of equipment over the other. The overall differences in deposit level observed throughout the year was not very significant, as observed earlier by Cuthbert *et al* (1973), and no correlation could be established. As explained earlier, the differences in deposit levels and their enormous variations are attributable to many variables (contamination, equipment, dosage, mode of application, tree size, formulation, meteorological conditions, sampling methods, etc.) and these should be considered carefully in future spray programs conducted by the NCC. Unless the bark is uniformly covered by a high level of insecticide residue ranging from 0.5 to 1.0 ug/mm^2 (Burger *et al* 1972) especially on tree top which is more vulnerable to beetle attack and where insecticide dissipation is high (Wolfenbarger and Buchanan 1939), prolonged protection of an elm tree by detering the beetle vectors is not to be expected. In addition to coverage of the bark, the compound should persist in active form long enough to be effective throughout the vectors' active period. Formulations with various adjuvants like surfactants, ultraviolet light protectants and stickers may prolong the activity of methoxychlor and increase its effectiveness as a protectant against the disease vectors.

4. <u>Persistence of Methoxychlor Residues</u>

Methoxychlor, unlike DDT is readily biodegradable by the enzymes present in plants and animals (Kapoor *et al* 1970, Reinbold *et al* 1971) and environmentally a safe insecticide. Since such enzymes are absent in the outer dead tissues of elm bark, the primary dissipation mechanism of the toxicant could only be through various physical processes such as volatilization, photodegradation and weathering.

The residue levels recorded in Table 2 on the control tree which had been sprayed, probably a couple of years earlier, but exposed to spray drift, were appreciable (12.50 ppm) showing a low level build-up of methoxychlor over the years of sporadic spraying. This accumulation pattern is also indicated in the residue data gathered on two other trees (Tree No. 328-1 in Table 6 and Tree No.

202-160 in Table 8) sampled before the spring 1975 spray operation.

Since the methoxychlor deposits varied very widely and erratically among the trees in different sampling areas, dissipation curves obtained by plotting residual insecticide concentrations (Tables 3 to 10) against time (not shown) did not show, because of uncontrolled variables and probable resprays, the uniform curvilinear decrease as in Fig. 10 and as observed elsewhere (Sundaram *et al* 1972) under nearly similar spray conditions. Consequently, no definite half-life for the insecticide deposits in elm barks could be established. It appears that the rate of disappearance initially was high and depended on the initial concentration levels on the bark and the varying physical and environmental factors. Usually after 4 to 7 weeks, depending on the season, half of the initial amounts present in the elm trees were lost. It is also evident that the methoxychlor deposit on the bark surfaces sprayed during the fall of 1974 (Table 3) did not deteriorate appreciably and the material overwintered intact to act as toxicant for beetles in the following spring. A systematic and intensive investigation, under controlled conditions, is necessary to evaluate quantitatively the decay rate and persistence of this material in elm trees.

5. Fate of the Applied Methoxychlor

The methoxychlor sprays were applied by mistblower (low volumes of concentrated sprays, 1.15 kg in 9.2 ℓ/tree) and hydraulic sprayer (large volumes of diluted sprays, 1.84 kg in 92.0 ℓ/tree sprayed to the dripping point). The compound is thus released in large amounts in the urban environment. The short and long-term effects of this compound on urban flora and fauna is still largely unknown and further study would be required to determine possible hazards arising from spray run-off to soil and aquatic organisms, and domestic animals, birds and humans in the spray area that are exposed to the toxicant spray.

Kapoor *et al* (1970) and Reinbold *et al* (1971) established that methoxychlor, unlike DDT, is rapidly degradable through attack by the multifunction oxygenase enzymes found in plant tissues. Since such active enzyme systems are not present in the dead outer bark tissues, the deposited insecticide probably can be dissipated only by various physical processes such as weathering by rain and wind, volatilization, hydrolysis and photo degradation. The apparent formation and disappearance of MCE in the bark (Tables 2, 3, 5 to 8) confirmed the observations of Li and Bradley (1969) that the olefin is formed from the *p,p'*-isomer through phototransformations. An indepth study is necessary to understand fully the mechanism of dissipation of methoxychlor from the elm trees sprayed with the material.

6. Efficacy of Methoxychlor Treatment

Extensive field studies (Barger *et al* 1972, Cuthbert *et al* 1973) in U.S. have shown that spraying elm trees in late fall or early winter with methoxychlor controlled the level of disease incidence considerably. The material has been available and used for Dutch elm disease control for a number of years in North America. A preliminary study made by Sadler (1971) for NCC on the efficacy of methoxychlor treatment showed that on the average about 5% of the sprayed elm trees contracted the disease. Considering the seriousness of the disease problem, the level of protection claimed by Sadler was more than satisfactory. The accurate field record of tree infestations for the fall of 1974 and the spring of 1975 are not available to date. When the data are gathered and evaluated statistically, the information will be valuable for predicting the infection pattern of the disease throughout the National Capital Region of Ottawa and Hull and the control measures necessary for protecting the stately elms in the nation's capital.

SUMMARY AND CONCLUSIONS

The National Capital Commission in Ottawa, as part of its regular control programs of Dutch elm disease, sprayed some of the elm trees in high priority areas around Ottawa-Hull area with methoxychlor using mistblower and hydraulic sprayer during the 1974/75 spray season.

Elm twigs from sprayed trees were collected from four different locations at different times for GLC assay. Homogenization of barks and extraction by acetonitrile yielded good recovery of the insecticide. The cleanup procedures involved hexane partitioning, concentration and column chromatography on deactivated Florisil.

Methoxychlor deposits varied widely and erratically among the trees due to poor experimental design, inconsistency in spraying and sampling of the trees. Although measured deposit levels appeared slightly higher in hydraulic sprayer, no significant differences in deposits were detected between the two application methods.

The initial deposit levels in bark samples decreased rapidly but unevenly. Consequently, plots of the residual insecticide *versus* time as linear co-ordinates did not yield curvilinear relationships; from the graphs the approximate time for 50% disappearance of the insecticide was found to be 4 to 7 weeks.

Although the dissipation mechanism of the insecticide from elm trees has not been fully studied, preliminary studies indicate that the toxicant is lost primarily by physical processes such as weathering, volatilization, decomposition by light and hydrolysis. Apart from requiring large amounts of methoxychlor to obtain protection against the vectors of the fungus, considerable evidence is still unavailable to confirm that the material is effective in elm bark beetle control. One concern, not evaluated and assessed is, the effects and hazards of the toxicant on the urban ecosystem. Additional experimentation is required which will stimulate increased research activity in elm bark beetle control and consequently will assist in the overall evaluation and usefulness of the insecticide in the control of Dutch elm disease in urban environments.

RESUME

La Commission de la Capitale Nationale, dans le cadre de son contrôle régulier de la maladie de l'orme liège, a arosé de méthoxychlore quelques ormes des secteurs manacés de la region d'Ottawa-Hull. Durant la saison propice de 1974-1975, elle a utilisé pour cela des atomiseurs et des vaporisateurs hydrauliques.

Des brindilles d'ormes vaporisés furent recueillis pour une analyse "GLC" en quatre endroits à des moments différents. Les techniques d'homogénéisation des écorces et d'extraction par acétonitrile permirent de récupérer une bonne quantité d'insecticide. Le nettoyage fit appel à une partion avec l'hexane, ainsi qu' à une chromatographie sur colonne, ou le florisil déactivé agit comme adsorbant.

Les dépots de méthoxychlore variaient grandement et irrégulièrment d'un arbre à l'autre à cause du mauvais concept initial de l'inconsistence de la vaporisation et de l'échantillonnage des arbres. Malgré qu'il semble que la quantité mesurée de dépots soit plus grande par vaporisation hydrolique, en réalité, la difference n'est pas significative, si on la compare au "mistblower".

Il a été decouvert que la quantité initiale de dépots dans les échantillons d'écorce diminuait rapidement mais également. Ainsi le tracé des restes d'insecticide par rapport au temps écoulé exprimé comme ordonné linéaire n'a pas fournit de rapport "curvilinear". D'aprés les graphiques nous savons que le temps nécessaire pour la disparition de 50% de l'insecticide est de 4 à 7 semaines environ.

Malgré que le mécanisme de dissipation de l'insecticide n'ait pas été étudié en profondeur, les études préliminaires indiquent que la substance

toxique se dissipe par des processus physique comme des intempéries, la volatisation, la décomposition par la lumière et l'hydro lyse. Non seulement une grande quantité de méthoxychlore est nécessaire pour fournir une protection contre les porteurs du fungus mais il y a un grand nombre de preuves indiquant que la substance contrôle efficacement le parasite de l'écorce.

Les conséquences et les risques qui n'ont pas été étudiés et évalués, de ce produit toxique sur l'écosystème urbain est un sujet d'inquiétude. D'autres expériences seront nécessaire pour stimuler une recherche plus poussée dans le contrôle du parasite de l'écorce de l'orme. Ces expériences serviront éventuellement à l'évaluation de l'utilité de cet insecticide dans le contrôle de la maladie de l'orme liège en milieu urbain.

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