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

by

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INTRODUCTION

Carbamate pesticides are becoming increasingly important in the field of insect control primarily due to their effectiveness combined with low mammalian toxicity and relatively short residual life in the environment. Because of these desirable properties, carbaryl (1-naphthyl methylcarbamate), a member of this class of compounds was tried as a substitute for methoxychlor* in white pine weevil (*Pissodes strobi* L.) plantation at Ramsayville near Ottawa, Ontario. This report describes the initial studies made during this research project under the following categories:

(1) Methodology developed and used for the residue determination of carbaryl present in and on white pine shoots,

(2) Persistence of carbaryl in pine shoots and

(3) Efficacy of carbaryl in weevil control.

MATERIALS AND METHODS

Plan of Operation

The pine plantation selected for the aerial application of carbaryl was located about 15 miles east of Ottawa near the village of Ramsayville (Fig. 1). The plot size (7.3 ha or 18 acres), design, stand types, white pine tree dimensions selected for sampling etc. are discussed in detail by DeBoo and Campbell (1974). An untreated check plot 2 miles away from the spray area and free from any insecticide drift served as a check to compare the damage levels in both plots and to

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* 1,1,1-Trichloro-2,2-bis (p-methoxyphenyl) ethane

obtain weevil population densities during the years of 1973 and 1974. The trees in both the control and spray plots suffered on average 31% and 9% leader mortality respectively during the year 1973.

Carbaryl Application

Carbaryl was supplied by Union Carbide in the Sevin 4-Oil® formulation at the concentration level of 0.48 kg AI/l (4 lb. AI/U.S. gal). The spray mixture was prepared by mixing thoroughly the Sevin formulation with fuel oil to give 0.121 kg AI/l (1 lb. AI/U.S. gal) and applied at the rate of 1.12 kg AI/ha (1 lb. AI/acre) on the morning of April 30, 1974 when the adult weevil feeding activity was maximum using CCRI's Cessna 185 (Skywagon) aircraft fitted with 4 Micronair AU3000 emission units (Fig. 2). The meteorological conditions while spraying were satisfactory with an average wind speed of 7.2 km/hr (4.5 miles/hr), temperature 12.2°C (54°F) and relative humidity 85%. Details of the spray application are discussed more fully by DeBoo and Campbell (1974).

Sampling of Pine Shoots

White pine shoots for residue analysis were taken from both the untreated and treated blocks one day before treatment on April 29, 1974 (prespray), 1 hour after on April 30 (0 day), then 2, 6, 10, 15, 24, 34, 49, 59 and 90 days later. Each sample consisted of 8 nearly uniform shoots taken at random throughout each plot. Samples were stored in polythene bags in a cooler containing ice cubes and transported immediately to the Institute's laboratory for analysis.

Analytical Methodology

The direct application of gas chromatography is generally unsatisfactory for the quantitation of carbaryl because of the on-column decomposition of the molecule and the weakness of detector response. These difficulties can be averted by converting the molecule to stable derivatives giving good response to electron capture or other specific detectors. Dorough and Thorstenson (1975) have reported some of the techniques currently utilized for the analysis of various carbamate insecticides. However, success has not been great enough for these procedures to have been generally adopted by the residue chemist.

In the present study, a colorimetric method based on the procedure described by Miskus *et al* (1959) was used to determine the residues of carbaryl after isolation from the pine shoots. The method depends on the hydrolysis of the insecticide to 1-naphthol by alcoholic sodium hydroxide followed by a coupling reaction with p-nitrobenzenediazonium fluoroborate to produce an intense colour.

Composite 20g samples of shoots in duplicate were cut into 1.27 cm (0.5") length pieces, placed in a Mason jar along with 200 ml of acetonitrile, tightly sealed and shaken for 10 min in a Fisher-Kendall mixer to remove the adsorbed surface deposits of the insecticide. After decanting the solvent, the pieces were homogenized in a Sorvall blender for 5 min at maximum speed with another 200 ml of acetonitrile to extract the absorbed insecticide molecules. The homogenate was filtered through a"S and S sharkskin"filter paper. Both the extracts were passed separately through columns of anhydrous sodium sulphate (50 g) for drying, partitioned with hexane (50 ml) to remove the plant lipids, terpene oils,

etc. and flash evaporated to dryness. The residues were taken in methylene chloride and subjected to Florisil (3.5% H_2O) column cleanup as described by Johnson *et al* (1963). The eluate, after partitioning with 50 ml of 0.25 M sodium hydroxide to remove the phenolic and naphthoic impurities present, was dried by passing through a Na_2SO_4 column and evaporated to dryness under vacuum. The residue containing carbaryl was hydrolysed by adding 2 ml of 0.5 M NaOH, the resulting solution left in a waterbath at 80°C for 5 min and the colorimetric reaction was produced by the addition of 1 ml of 0.10% methanolic solution (W/V) of p-nitrobenzenediazonium fluoborate. The solution was made up to 10 ml with methanol, allowed to stand for 30 min for maximum colour development and the absorbance read at 590 nm in a Beckman Acta CIII UV-visible spectrophotometer using the cleaned up and coupled prespray shoot extract as a reference to minimize and compensate for background interferences. The concentration of carbaryl was read from a calibration curve (absorbance *vs* concentration - ppm of carbaryl) prepared by carrying out the colorimetric measurements using the standard solutions of the insecticide at 3, 5, 10, 15 and 20 ppm levels (Fig. 3). The corresponding absorbances (10^3) read in the instrument were: 25, 36, 63, 87 and 115.

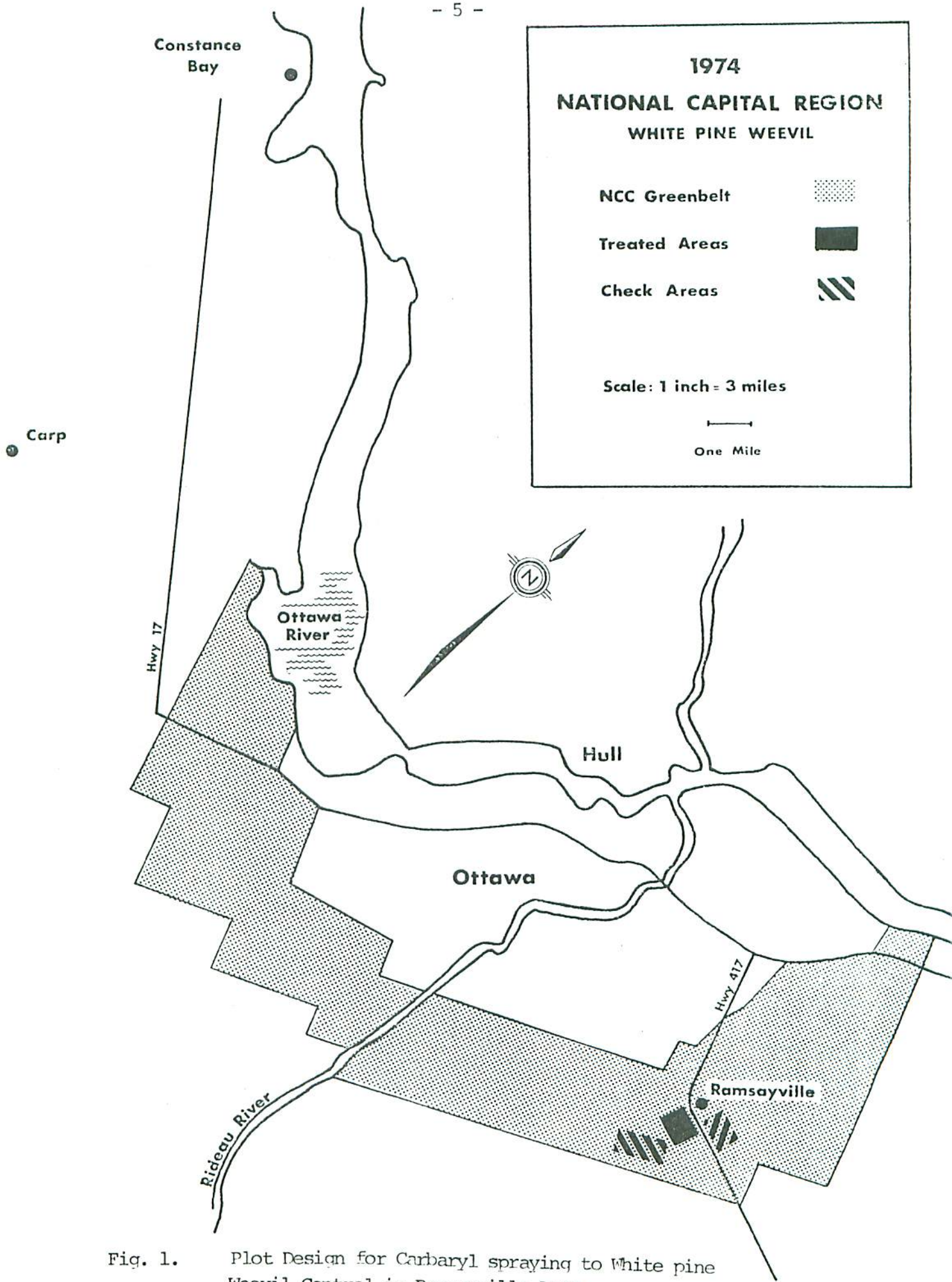

Fig. 1. Plot Design for Carbaryl spraying to White pine Weevil Control in Ramsayville Area.

Fig. 2. Cessna 185 Aircraft Equipped with 4 Micronair AU 3000 Emission Units for Aerial Spraying.

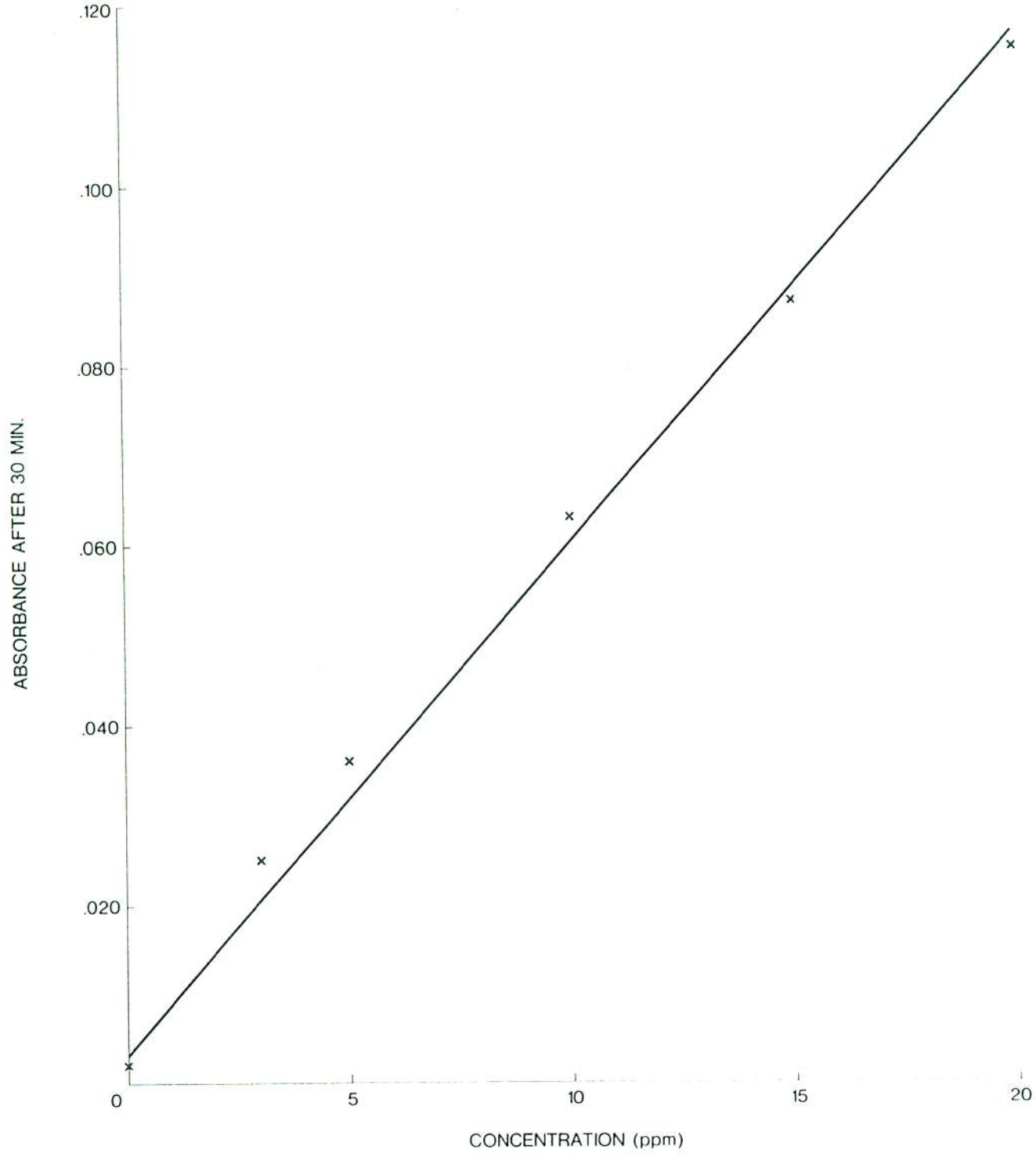

Fig. 3. Spectrophotometric Calibration Curve for Carbaryl

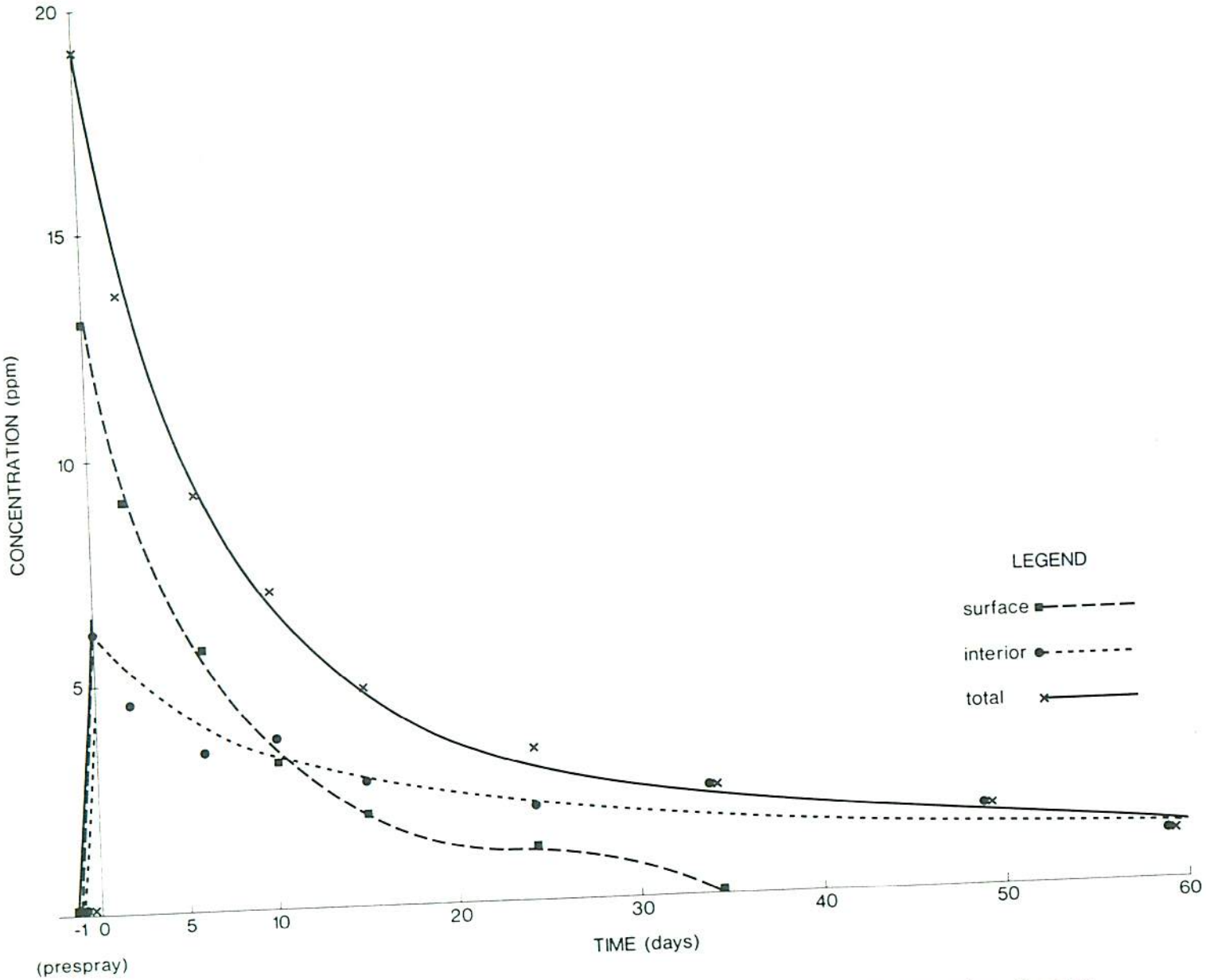

Fig. 4. Dissipation curves for Carbaryl Residues in White Pine Shoots.

RESULTS AND DISCUSSION

The results of the chemical assay of carbaryl residues are recorded in Table 1 in units of ppm (parts per million, i.e. microgram of the insecticide per gram of pine shoot) "as sampled" including the variables such as water and volatile components and are useful for ecological interpretations under actual field conditions.

The concentrations of carbaryl found on "surface" (Table 1) represent the readily dislodgable insecticide residues deposited on the bark surface of the shoots analysed, and the concentrations recorded as "interior" show the penetrated molecules of the compound that are imbedded below the cuticular layers of the bark and possibly in the woody parts of leaders.

Table 1

Carbaryl Residues on and in the Shoots of White Pine after Aerial Application - Summer 1974

Serial No	Date of Sampling	Days after Spraying	Carbaryl Residues, (ppm) *		
			Surface	Interior	Total
1	April 29	Prespray	0	0	0
2	30	0**	12.9	6.2	19.1
3	May 2	2	9.0	4.6	13.6
4	6	6	5.7	3.5	9.2
5	10	10	3.2	3.8	7.0
6	15	15	2.0	2.8	4.8
7	24	24	1.2	2.1	3.3
8	June 3	34	T	2.4	2.4
9	18	49	N.D.	1.8	1.8
10	28	59	N.D.	1.1	1.1
11	July 29	90	N.D.	T	T

T : Traces (< 1 ppm)

N.D. : Not Detected

* As sampled

** Taken one hour after application

Sensitivity of the Analytical Method

The method used in this study was evaluated by analysing 20 g samples of shoots containing known amounts (1 to 10 ug/g) of carbaryl. The percent recoveries of the insecticide ranged from 70 ± 15 at 2.5 ppm level to 85 ± 5 at 10 ppm levels of spiking. Evidently the method was not reliable at low levels of the insecticide concentration. Consequently deviations in the results recorded in Table 1 after May 10 sampling increased. In addition to the low and variable sensitivity, the method has been found to be less than satisfactory for analysis of carbaryl residues because of the varying interferences including variations in blank reading, instability of reagents and fading of the colour of diazonium salt produced. The method also was time-consuming, laborious and lacked sensitivity and specificity. However, the results may be accepted as giving a general indication of the insecticidal activity and persistence under the described conditions.

Persistence of Carbaryl in Pine Shoots

The results in Table 1 show that after 1 hour of spray, the shoots contained 19.1 ppm of carbaryl, nearly 68% of which was on the surface and the rest probably absorbed and imbedded below the cuticular layers of the shoots. It is interesting to note that within a short time (60 min), 32% of the total measured carbaryl deposited on the leaders had penetrated the outer cuticular layers and was found in the epidermis. The total and the surface concentrations of the insecticide recorded in this study, dissipated rapidly with half-lives of 6 and 5 days respectively whereas the absorbed residue levels found in the leaders decreased slowly with a half-life of ca 12 days and persisted in small amounts (1.1 ppm) up to

59 days (Fig. 4). The total residue level of carbaryl decreased 30% within 2 days of spraying, another 18% decrease was observed on the sixth day, but afterwards loss was more gradual probably due to the interior deposit levels being protected from various environmental factors contrary to the deposits on the surface. Compared with the carbaryl absorbed in the epidermis, the disappearance of the surface residue was rapid and within 24 days it had diminished to negligible amounts (1.2 ppm) probably due to various physical and metabolic processes.

The zero day deposit level (19.1 ppm) recorded in Table 1 is low considering the amount (1.12 kg AI/ha or 1 lb. AI/acre) of the material sprayed. However, this is the normal application rate and the actual deposit on the target area would undoubtedly be much lower, probably no more than 25% depending on meteorological conditions, drop size, mode of application, etc. The rapid dissipation also indicates that in addition to physical and metabolic degradations, much of the insecticide deposited initially could have dripped off due to the instability of the formulation (a fine suspension of carbaryl in oil) used in spraying.

Efficacy of Carbaryl in Weevil Control

Careful counting of weeviled trees and systematic observations on the fluctuations of insect populations were made by DeBoo and Campbell during the years 1973 (prespray) and 1974 (postspray) at the Ramsayville pine plantation to evaluate the efficacy of carbaryl for weevil control. The percent weeviling of the leaders during the test period was calculated (DeBoo and Campbell 1974) and Abbott's formula (1925) used to determine changes in leader injury for the two years 1973 and 1974.

The consolidated results (DeBoo and Campbell 1974) of the 1974

aerial application of carbaryl for control of white pine weevil in the Ottawa Valley showed that in 1973 the percent of untreated trees weeviled was 31 and in 1974, after the application, the percent decreased to 17, a fall of 14 per 31 weeviled trees, thus giving a 45% (14 x 100/31) reduction in injury between the two years 1973 and 1974. This is far below the accepted level of 85% protection (DeBoo and Campbell 1972) observed earlier by using methoxychlor. The unsatisfactory control indicates that the chemical was not present at the site of action in an active form in sufficient quantities and for a sufficient period of time, perhaps due to its rapid degradation (low half-life) to give effective control. In general, mortality depends on the magnitude of the concentration level deposited on leaders, the toxicity of the compound and the duration of persistence of the insecticide exposed to the target organism. The results of the present study indicate that carbaryl is neither intrinsically active against weevils nor persists for sufficient time to act as an acute toxin against the insects. Possibly large doses of the chemical with various adjuvants, e.g. surfactants, ultraviolet light protectors and stickers might prolong its activity and increase its effectiveness in weevil control operations. The long term effects of the compound, if released in higher doses in plantation ecosystems, is still largely unknown and further study would be required to determine possible hazards to the environment.

SUMMARY

Aerial application of carbaryl (1-naphthyl methylcarbamate) in an oil formulation applied at the rate of 1.12 kg AI/ha (1 lb. AI/acre)

did not provide adequate leader protection to eastern white pine plantations in the Ottawa Valley during the 1974 spray program. The reduction in weevil injury was found to be only 45% compared to the acceptable level of 85% established earlier using methoxychlor.

Leader samples were collected from sprayed trees at various time intervals for residue analysis. A modified colorimetric procedure was developed for determining adsorbed and absorbed carbaryl residues in pine leaders. The acetonitrile extract of the leaders, after partitioning with hexane was flash evaporated to dryness. The residue in dichloromethane was partitioned with dilute aqueous sodium hydroxide to eliminate phenolic impurities and the organic phase was purified by a Florisil column. Alkaline hydrolysis of the carbaryl residue present in the eluate produced 1-naphthol which was reacted with *p*-nitrobenzene-diazonium fluoborate to produce a colour with maximum absorption at 590 nm which was measured spectrophotometrically. Recoveries were generally low and the method was reliable and sensitive only in the high concentration levels of carbaryl hence the method is not recommended for routine residue analysis.

The zero day deposit concentration of carbaryl in leaders was 19.1 ppm and nearly 68% was found on the surface. The residue level decreased rapidly at the beginning and thereafter gradually to 1.1 ppm after 59 days. The dissipation rate of the absorbed carbaryl residues was low ($T_{\frac{1}{2}}$ = 12.5 days) but the overall decrease in concentration of the insecticide was high with a half-life of only 6 days.

The insecticide, at the aerially applied rate of 1.12 kg AI/ha (1 lb. AI/acre), was not sufficiently active to the white pine weevil for effective control.

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