PERSISTENCE AND DEGRADATION OF DIFLUBENZURON IN CONIFER FOLIAGE, FOREST LITTER AND SOIL, FOLLOWING SIMULATED AERIAL APPLICATION

INFORMATION REPORT FPM-X-74

K.M.S. SUNDARAM

GOVERNMENT OF CANADA
FOREST PEST MANAGEMENT INSTITUTE
CANADIAN FORESTRY SERVICE
1219 QUEEN STREET EAST, P.O. BOX 490
SAULT STE. MARIE, ONTARIO
P6A 5M7

1986

ABSTRACT

Persistence and degradation of diflubenzuron [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl) urea] in spruce foliage, forest litter and soil were studied under forestry conditions by applying the chemical as a simulated aerial spray in acetone (DAc) and in fuel oil:Arotex® 3470 mixture (DFAr), each at 90 g AI (active ingredient) in 18 L/ha. The residues of diflubenzuron in the substrates were determined by gas-liquid chromatography, after derivatization as its dimethyl analog. The highest concentrations of the chemical in foliage, litter and soil were 30.6, 4.60 and 3.20 µg/g (fresh weight), detected at 1 h after application of the DFAr formulation. The corresponding concentrations in the three substrates were comparatively low for the DAc formulation. With both formulations, residues found in the substrates correlated well with the droplet density and deposit levels observed on the Kromekote® card/glass plate units placed at ground level. In soil and litter, the residues decreased more rapidly with time than those in foliage. The half-lives (in days) for the chemical in foliage, litter and soil (fresh weight) for the DAc formulation were respectively 9.30, 8.36 and 7.49; and for the DFAr formulation, 12.8, 7.34 and 6.52. Forty-five days after application, the residue levels in foliage were 3.9 and 0.80 µg/g respectively for DFAr and DFAc formulations. The soil and litter samples did not contain detectable levels of the chemical.

RÉSUMÉ

La persistance et la dégradation du diflubenzuron [(chloro-4 phényl)-1 (difluoro-2, 6 benzoyl)-3urée] dans le feuillage de l'épinette ainsi que dans la litière et le sol forestiers ont été étudiées dans des conditions réelles, après application de l'antiparasitaire simulant un traitement aérien, à la concentration de 90 g de matière active à raison de 18 L/ha dans l'acétone (DAc) et dans un mélange de fuel et d'Arotex® 3470 (DFAr). Les résidus ont été déterminés par chromatographie en phase gazeuse, après synthèse d'un dérivé diméthylique. Les plus fortes concentrations dans le feuillage, la litière et le sol étaient de 30,6, de 4,60 et de 3,20 µg/g (de poids frais), et elles ont été décelées 1 h après l'application de la préparation DFAr. Dans le cas de la préparation DAc, les concentrations correspondantes étaient relativement faibles. Dans les deux cas, les résidus retrouvés dans les substrats étaient bien corrélés à la densité des goutelettes et aux dépôts observés sur des surfaces de verre et de cartes Kromekote® disposées au niveau du sol. Dans le sol et la litière, la concentration des résidus a diminué plus rapidement que dans le feuillage. La période de persistance de la préparation DAc dans le feuillage, la litière et le sol (en poids frais) était respectivement de 9,30, de 8,36 et de 7,49j; celle de la préparation DFAr, de 12,8; 7,34 et 6,52 jours, respectivement. 45 jours après le traitement, les résidus des préparations DFAr et DFAc étaient respectivement de 3,9 et de 0,80 µg/g. Les échantillons de sol et de litière ne contenaiet aucune quantité décelable de la substance.

INTRODUCTION

Diflubenzuron [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl) urea], a novel insecticidal compound, was first discovered by Duphar B.V. in Holland, and was introduced commercially in 1976 under the trade name Dimilin (Rabenort et al. 1978). It is a stomach poison and acts *in vivo* by interfering with the deposition of chitin, one of the main components of the insect cuticle, thus inhibiting the moulting process and causing death (Mulder and Gijswijt 1973; Post et al. 1974; Verloop and Ferrell 1977; Deul et al. 1978).

As an insecticide, the chemical has been shown to have many desirable properties, such as low toxicity to mammals, birds, fish, and bees (Hartley and Kidd 1983; Worthing and Walker 1983), short environmental persistence, little impact on non-target species, except some aquatic arthropods (Apperson et al. 1978), and good storage and thermal stabilities (Duphar 1985). Recent studies at this institute [Forest Pest Management Institute (FPMI), Canadian Forestry Service] and elsewhere, have shown that diflubenzuron is effective against a number of leaf-feeding forest pests such as gypsy moth, *Lymantria dispar* (L.) (Granett and Dunbar 1975), Douglas-fir tussock moth, *Orgyia pseudotsugata* (McD.) (Hard et al. 1978), forest tent caterpillar, *Malacosoma disstria* (Hbn.) (Retnakaran et al. 1979), pine sawfly, *Diprion similis* (Htg.) (Fogal 1977) and oak leaf shredder, *Croesia semipurpurana* (Kft) (Retnakaran and Grant 1985). Retnakaran et al. (1985) reviewed the importance of this class of chemicals in insect control programs. Efficacy on hemlock looper, *Lambdina fiscellaria* (Guen), has recently been demonstrated (Raske et al. 1986). Because of these many favourable properties, the chemical is currently undergoing field trials in eastern Canada as a candidate material for large scale control programs of forest insects against which it is reported to be effective.

Prior to marketing the chemical for broadcast application to control forest pests in Canada, it must be field-tested and assessed for its environmental safety, persistence and fate under Canadian conditions. The data generated should meet the requirements of the Pest Control Products Act, which is a federal regulatory law that ensures the safe use of pesticides and is administered by Agriculture Canada. Development of such a data base is not only essential for registering the chemical for forestry use, but is also required in addressing provincial and public concerns relating to the use of such pest management tools.

Persistence and fate of diflubenzuron in agricultural crops, pasture, soils, water and animals have been reported in literature (Metcalf et al. 1975; Schaefer and Dupras Jr. 1976; Bull and Ivie 1978; Mansager et al. 1979; Maas et al. 1980; Mian and Mulla 1982; Nimmo et al. 1984; Duphar 1985). However, no such data are available for diflubenzuron in conifer foliage, forest litter and soil samples. The present study was undertaken specifically to elucidate the behavior and fate of the chemical in these three substrates using a simulated aerial spray application technique developed by Hopewell (1974). The use of this technique has already provided quantitative and definite information on the persistence and fate of currently used forestry insecticides, viz., aminocarb (4-dimethylamino-m-tolyl methylcarbamate) (Sundaram and Sundaram 1981), and fenitrothion (O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate) (Sundaram and Sundaram 1982).

MATERIALS AND METHODS

Experimental design

The study was carried out on a privately owned tree farm (8 ha) near Shawville, Quebec (76°30'W; 45°36'N) about 60 km northwest of Ottawa, Ont. during the months

of May and June, 1976. The area contained white spruce trees [*Picea glauca* (Moench) Voss] of uneven height, ranging from 2 to 7 m, planted at intervals during the past 30 years. The forest floor was flat and covered with grass and moss patches.

In the test area, measuring approximately 500 m^2, nine spruce trees, including one control, of nearly uniform size and shape (2.3 to 2.7 m in height and 8.5 to 9.5 cm d.b.h.) and with abundant foliage were selected, tagged with colored plastic ribbon and numbered D_1 to D_9. Trees D_1 to D_4 were sprayed, each separately with a solution of diflubenzuron in acetone (DAc) and similarly, trees D_5 to D_8 were sprayed with the insecticide solution in fuel oil no. 2 and Arotex® 3470 mixture (DFAr) (Table 1). The tree D_9 served as the untreated control. The ground vegetation under each tree was removed, and the area around each test tree was cleared by trimming interfering foliage from adjacent trees.

In open areas of the test site, litter and soil plots, each measuring about 5 m^2, were established and flagged. All small objects such as fallen branches, twigs and small stones were cleared from the litter plot. The overlying litter, moss and the organic detritus were removed from the soil plot to a depth of about 10 cm (primarily histisol) to fully expose the underlying soil layer to the spray droplets. Small objects such as fallen branches, twigs, roots, stones, etc., were also removed from it. Similar plots a few meters away served as untreated check plots.

Spray solutions

The ingredients used in the two spray solutions, the amounts present in each, and the names of the suppliers are given in Table 1. The spray formulations were made in amber-colored volumetric flasks a few hours prior to application and stored in the dark.

Sampling units and deposit collection

For spray deposit collection, the conventional Kromekote card (supplier, Kruger Paper Co., Montreal, Que.) - glass plate units (collection units) (Randall 1980) (the card, 10 x 10 cm; and the two glass plates, each 5.0 x 7.5 cm), mounted on aluminum sheets fastened together, were used. The number of collection units used per plot (4 units/tree and 4 units/litter or soil plot) is given in Table 2. The collection units were placed on the ground equally spaced around each tree and away from the overhanging foliage (Figure 1). Four collection units were also placed in the centre of each quadrant in soil and litter plots. They were placed about 10 min prior to spray application and removed 20 min postspray.

Spray application

The spray solutions were applied using the technique and device developed by Hopewell (1974) for producing simulated aerial spray droplets that are observed in ULV applications, i.e., droplets of NMD and VMD of about 80 and 160 µm respectively (Sundaram and Sundaram 1982). A portable shelter (heavy-duty polyethylene sheet fixed on wooden frames) enclosing an area of 2.1 x 2.1 m, and a height of 3.0 m (Figure 1) was placed around each tree during application. Prior to treatment, 8.0 mL of the spray mix was taken into the syringe of the droplet producing device (Figure 2). The device was fixed to the end of a 2.2 m horizontal arm on a 2.5 m vertical shaft. The operator raised the unit over the tree in the shelter and switched on the spinning disc and the speed motor. Power to the spinning disc and the feed mechanism was supplied from a variable voltage source (2 to 6 V). The unit was moved systematically over the enclosure during an emission period of 2.5 min, in order to allow a uniform emission over the entire enclosed area. In each treatment, 8.0 mL of the spray solution was emitted over the 4.41 m^2, giving dosage and applica-

Table 1. Percentage composition of ingredients used in spray formulations

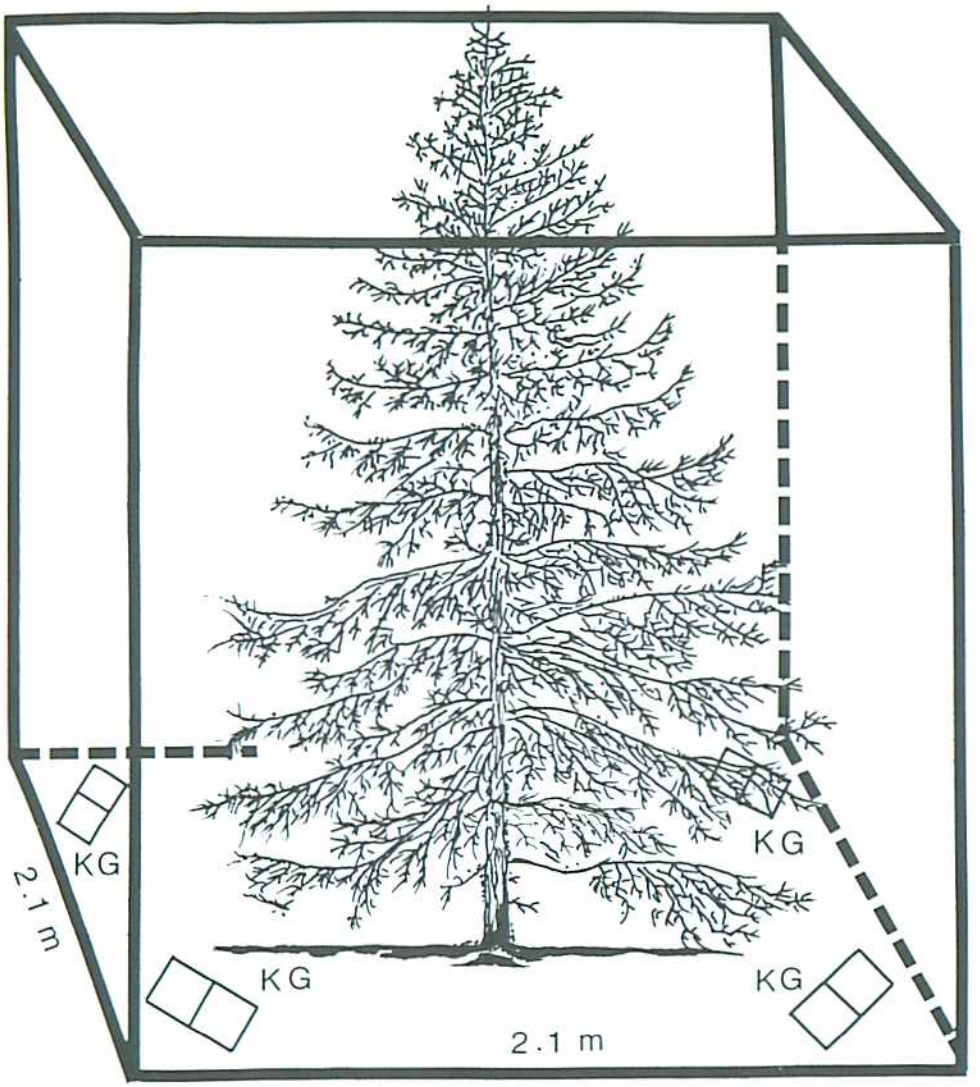
Formulation abbreviation	Percentage composition		Volume applied per 4.41 sq. m[a]	Dosage and application rates
DAc	Diflubenzuron (tech)[b]	0.5 g	8.0 mL	90 g AI in 18 L/ha
	Acetone	98.7 mL		
	Automate Red B (tracer dye)[c]	1.0 mL		
		100.0 mL		
DFAr	Diflubenzuron (tech	0.5 g	8.0 mL	90 g AI in 18 L/ha
	Fuel oil No. 2[d]	18.8 mL		
	Arotex 3470[d]	80.0 mL		
	Automate Red B	1.0 mL		
		100.0 mL		

[a] The area covered by the portable spray enclosure.
[b] Technical material was supplied by Thompson-Hayward Chemical Co., Kansas City, Kansas, USA.
[c] Supplied by Morton Williams Ltd., Ajax, Ontario, as a 20% solution in ethanol.
[d] Supplied by Texaco Oil Co., Toronto, Ontario.

Table 2. Droplet characteristics and deposit levels of diflubenzuron formulations on Kromekote® card glass plate units at ground level, following single tree application at 90 g A.I. in 18.0 L/ha

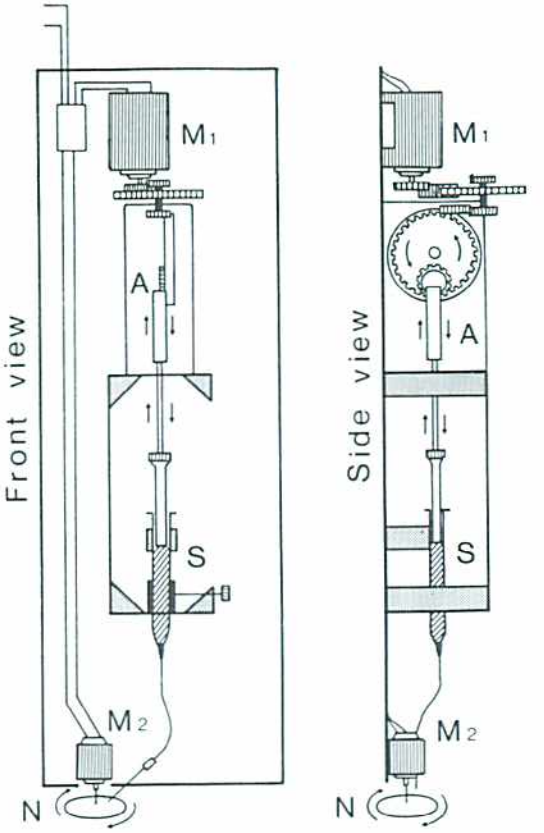
Parameters	DAc			DFAr		
	Tree plot	Litter plot	Soil plot	Tree plot	Litter plot	Soil plot
Sampling units	16	4	4	16	4	4
Droplet density (droplets/cm^2)	45 ± 8	55 ± 9	58 ± 6	60 ± 11	75 ± 8	71 ± 6
Droplet size range (µm)	15 - 135	15 - 145	15 - 145	17 - 147	17 - 189	17 - 174
NMD (µm)	48 ± 10	58 ± 9	61 ± 5	61 ± 8	81 ± 7	76 ± 5
VMD (µm)	105 ± 8	115 ± 11	112 ± 5	122 ± 6	156 ± 11	141 ± 9
Deposit on glass plate (g A.I./ha)	32.8	39.0	45.3	57.6	68.4	64.8
Percent of A.I. deposited*	36	43	50	64	76	72

* Determined by GLC analysis.



KG : Kromekote® Card / Glass Plate Units

FIGURE 1. POLYETHYLENE ENCLOSURE
(2.1 m x 2.1 m)



A Moving axle

M_1 Pump motor

M_2 Nozzle motor

N Spinning disc nozzle

S Syringe with spray mix

FIGURE 2. SPRAY APPLICATION
EQUIPMENT

tion rates of 90 g A.I. (active ingredient) in 18 L/ha (Table 1).

Spray application was carried out during the 2nd week of May, before the new shoots had begun to open and while they were still covered with bud caps. During the application, the average temperature, relative humidity (RH), wind speed and cloud cover were respectively 21°C, 81%, 2 km/h and 3/10. There was no precipitation. Detailed monitoring of the weather conditions which existed during the 45 d postspray sampling period, was not possible, although the amount of precipitation and the days on which it occurred, were both recorded. Appreciable precipitation occurred on 3, 5, 7, 10, 13, 19 and 45 day post-treatment, prior to sampling.

Sampling

Samples of foliage, litter and soil were taken at 1.0 h prior to treatment (prespray), and 0 (1 h post-treatment), 1, 3, 5, 7, 10, 13, 16, 19, 22, 25, 30, 35, 40 and 45 days after treatment. Foliar samples were collected from each quadrant of the tree crown at midcrown level (7-cm branch tips excluding the new growth and buds). Samples from D_1 to D_4 trees were pooled, and those from D_5 to D_8 were pooled to provide 16 branch tips per sample per spray solution. All sixteen branch tips corresponding to the same spray solution were cut into small pieces, mixed well, put into labelled plastic bags, stored in coolers containing dry ice, and brought to the residue laboratory in Ottawa where they were stored at -20°C until analysis.

Litter and soil samples were taken randomly from the top 1 cm layer as 5.0 cm diameter cores (10 cores per sample) using an auger. The sampling and pooling procedures and the time intervals of sampling were the same as for the foliage samples. Each composite sample corresponding to a specific spray solution was wrapped in aluminum foil and processed as described for foliage.

The deposits on the glass plates of the collection units were removed by washing each with 3 x 5 ml of pesticide grade ethyl acetate. The eluates were stored in tightly sealed amber-coloured bottles, transported to the laboratory in coolers packed with dry ice and stored at -20°C until analysis. The Kromekote cards were stored in the dark in slotted wooden boxes until evaluation of the size spectra of the impact droplets.

Analytical procedures

Residues of diflubenzuron in foliage, litter and soil samples were analyzed following extraction and necessary column cleanup by electron capture gas chromatography (EC-GLC) after converting the insecticide to its N,N'-dimethyl analog. The methylation was accomplished in DMSO with sodium hydride and methyl iodide. The method used was already published elsewhere (Lawrence and Sundaram 1976). Therefore, only a brief outline is given below.

Foliage

Ten gram aliquots of Hobart-chopped foliage in triplicate were homogenized twice in a Sorvall blender for 5 min at speed 6 with 100 mL acetonitrile as extractant each time. Each homogenate was filtered under suction using "S and S Sharkskin" filter paper. After being washed twice with 20 mL portions of the extractant, the filter cake was discarded. The extract was passed through a column of 50 g Na_2SO_4 and concentrated to 60 mL under a vacuum. An aliquot was partitioned twice with 20 mL of hexane. The hexane layers were discarded and the polar acetonitrile layer was flash evapor-

ated at 30°C to dryness. The residue was taken in four 1 mL portions of acetone: hexane 1:4 mixture for adsorption column chromatography.

For column cleanup, a glass column (35 cm x 14 mm i.d.) was packed from bottom to top in sequence with a silanized glass wool plug, 5 g Na_2SO_4, 10 g of partly deactivated Florisil (5.5% water) and 5 g Na_2SO_4. The column was prewashed with 75 mL of dry petroleum ether. The concentrated crude extract was transferred quantitatively to the column and eluted in succession with 45 mL hexane, 30 mL acetone-hexane (1 + 9) and 10 ml acetone-hexane (1 + 4). The eluates were discarded. Finally, the adsorbed diflubenzuron was eluted with 50 mL of acetone-hexane (1 + 4) mixture. The eluate was flash evaporated at 30°C to a small volume and the content was transferred quantitatively to a stoppered test tube and evaporated to dryness under nitrogen. The residue was mixed with 0.5 mL of DMSO, followed by 0.3 mL of CH_3I and about 20 mg of NaH. The tube was stoppered and shaken gently for about 15 min in a mechanical shaker for the methylation reaction to complete. The mixture was treated gradually while shaking with 3 mL of hexane followed by 1 mL of distilled water in drops to destroy the excess NaH, indicated by the cessation of effervescence. The resulting liquid mixture was shaken vigorously with 9 mL of distilled water and centrifuged to separate the layers. The hexane phase was transferred quantitatively to a stoppered tube using a Pasteur pipet and washed further with 3 x 5 mL of distilled water to remove the electron capturing impurities. The hexane layer was passed through a narrow column of Na_2SO_4 to remove the moisture and the column was rinsed with 2 mL of hexane. The combined hexane was evaporated to dryness in a current of dry N_2 and the residue was volumetrically adjusted with hexane for EC-GLC analysis.

Soil and litter

The soil and litter samples were passed successively first through a 1.25 cm mesh screen to remove stones and debris, and then through a 4 mm mesh sieve. The sieved samples were mixed thoroughly and chopped in a Hobart food processor. Three 10 g aliquots in each sample were used in the extraction, column cleanup, derivatization and analysis, using the procedure as described under foliage.

Moisture and pH determinations

Two 10 g quantities each of foliage, soil and litter sample were used to measure moisture (AOAC 1955) (drying at 105°C in a thermostatic oven to constant weight) content. The pH of the soil and litter was determined by using the method of Atkinson et al. (1958). The values were 5.9 for the litter and 6.1 for the soil samples respectively.

Glass plate rinses from collection units

The ethyl acetate rinses, after passing through Na_2SO_4, were flash evaporated to dryness, the residues were derivatized and quantified as discussed under foliage.

Kromekote cards

The cards were read using a micro-opaque card reader (National Cash Register Company, West Salem, Wisconsin, U.S.A.) and the stains were recorded. They were grouped according to size. These stain diameters were converted into their corresponding droplet diameters by using the spread factor values for the spray solutions (Rayner and Haliburton 1955). From these data, the number and volume median diameters (NMD and

VMD respectively), maximum and minimum diameters (D_{max} and D_{min} respectively), and droplet densities (droplets/cm^2) were calculated (Haliburton et al. 1975).

Gas-liquid chromatographic analysis

The residues of diflubenzuron present in the samples were analyzed by using a Hewlett-Packard HP-5750 gas chromatograph fitted with a Ni-63 E.C. detector. The operating parameters were as follows:

Column: 2 m x 6 mm o.d. Pyrex glass packed with 3% OV-210 coated on 80-100 mesh chromosorb W (HP).

Temp. (°C):		
	injection port	250
	column	235
	detector	250

Gas flow: carrier gas (Ar + CH_4; 95 + 5) 60 mL/min

Instrument settings: 6 x atten., 1 x 10^{-10} A 1 mV recorder (Linear Instruments)

Retention time (R.T.): 2.8 min

The GLC was standardized on the same day as the samples were analyzed by injecting aliquots of freshly prepared dimethyl derivatives of diflubenzuron (analytical grade of 99.4% purity, supplied by Thompson-Hayward Chem. Co., P.O. Box 2383, Kansas City, KN 66110, USA), measuring the peak heights and preparing the calibration curve by plotting peak heights *versus* concentration. The calibration was checked intermittently. Quantitative results of the extracted and derivatized samples were obtained by measuring each of the peak heights after injection (2 to 5 L), under the same operating conditions and reading the concentrations from the calibration curve.

Recovery levels and detection limits

For recovery, the prespray samples of foliage, litter and soil were fortified with diflubenzuron separately in triplicate at 1.0, 0.7, 0.4, 0.1 and 0.05 ppm levels, extracted, derivatized and analyzed according to the above-described method. The recoveries for foliage, soil and litter at the first four fortification levels were on average 85 ± 6%. At 0.05 ppm level, the recoveries were not satisfactory due to interference from coextracted impurities.

The analytical limit of detection for the insecticide was 0.1 µg/mL of the final extract for injection. This in turn was equivalent to 0.1 µg/g of the substrate on fresh weight basis.

The values recorded in this report (Tables 3 to 5) are the mean of three replicate measurements for each sample. The average error, $\Sigma[x_1 - \bar{x}]/n$ ($n = 3$), in them was less than 10%. Values reported here have not been corrected for recoveries.

None of the pre-spray and check samples (spruce foliage, forest soil and litter) contained any detectable levels of diflubenzuron.

All solvents used were pesticide grade or distilled in glass. The petroleum ether and hexane were dried by using the Dean-Stark apparatus. Anhydrous Na_2SO_4 was heated overnight at 260°C prior to use. Sodium hydride (50% oil dispersion) and Florisil were supplied by Fisher. Laboratory sources of contamination were monitored by conducting periodic blank checks. Contamination of apparatus, glassware, etc. was found to be negligible during the period of the study.

Table 3. Concentrations of Diflubenzuron (µg/g) in spruce foliage, following simulated aerial application at 90 g A.I. in 18 L/ha

Time after application (days)	DAc		DFAr	
	Fresh wt.	Oven-dry wt.[a]	Fresh wt.	Oven-dry wt.
0	23.8 (100)[b]	32.1 (100)	30.6 (100)	41.3 (100)
1	20.9 (87.9)	28.2 (87.9)	26.9 (87.9)	36.3 (87.9)
3	18.8 (79.1)	24.4 (76.0)	23.2 (75.8)	30.1 (72.9)
5	15.6 (65.5)	20.1 (62.6)	20.7 (67.6)	26.7 (64.6)
7	13.6 (57.4)	17.2 (53.6)	18.8 (61.4)	23.7 (57.4)
10	10.6 (44.7)	14.0 (43.6)	16.4 (53.6)	21.6 (52.3)
13	9.5 (39.8)	12.7 (39.6)	14.1 (46.1)	18.9 (45.8)
16	7.7 (32.5)	9.8 (30.5)	12.3 (40.2)	15.6 (37.8)
19	6.2 (26.0)	7.8 (24.3)	10.4 (34.0)	13.1 (31.7)
22	4.7 (19.9)	5.8 (18.1)	8.5 (27.8)	10.4 (25.2)
25	4.0 (16.7)	4.8 (15.0)	7.6 (24.8)	9.2 (22.3)
30	3.0 (12.4)	4.0 (12.5)	6.2 (20.3)	8.4 (20.3)
35	2.4 (9.9)	3.1 (9.7)	5.4 (17.6)	7.1 (17.2)
40	1.5 (6.4)	2.0 (6.2)	4.7 (15.4)	6.2 (15.0)
45	0.8 (3.2)	1.0 (3.1)	3.9 (12.7)	5.2 (12.6)

[a] Average moisture content of foliage = 30% (range = 21 - 39%).
[b] Values in parentheses represent residue levels in percentage.

Table 4. Concentrations of Diflubenzuron (µg/g) in forest litter, following simulated aerial application at 90 g A.I. in 18 L/ha

Time after application (days)	DAc		DFAr	
	Fresh wt.	Oven-dry wt.[a]	Fresh wt.	Oven-dry wt.
0	3.08 (100)[b]	3.62 (100)	4.60 (100)	5.38 (100)
1	2.67 (86.2)	3.25 (89.9)	3.78 (82.2)	4.62 (85.8)
3	2.23 (72.2)	2.67 (73.7)	3.15 (68.5)	3.77 (70.0)
5	1.70 (54.9)	2.17 (59.9)	2.47 (53.6)	3.15 (58.5)
7	1.37 (44.4)	1.82 (50.2)	1.85 (40.2)	2.45 (45.5)
10	1.18 (38.1)	1.33 (36.9)	1.63 (35.5)	1.85 (34.4)
13	0.88 (28.6)	1.10 (30.4)	0.88 (19.2)	1.10 (20.4)
16	0.78 (25.2)	0.97 (26.7)	0.77 (16.7)	0.95 (17.6)
19	0.73 (23.9)	0.80 (22.1)	0.62 (13.4)	0.67 (12.4)
22	0.60 (19.6)	0.67 (18.4)	0.50 (10.9)	0.55 (10.2)
25	0.43 (14.0)	0.50 (13.8)	0.43 (9.4)	0.50 (9.3)
30	0.23 (7.4)	0.25 (6.9)	0.33 (7.2)	0.37 (6.8)
35	0.13 (4.4)	0.17 (4.6)	0.23 (5.1)	0.28 (5.3)
40	0.10 (3.5)	0.13 (3.7)	0.13 (2.9)	0.17 (3.1)
45	N.D.[c]	N.D.	0.10 (2.2)	0.13 (2.5)

[a] Average moisture content of litter = 20% (range = 8 - 33%).
[b] Values in parentheses represent residue levels in percentage.
[c] N.D. Not detected (detection limit 0.1 µg/g on fresh weight basis).

Table 5. Concentrations of Diflubenzuron (µg/g) in forest soil samples, following simulated aerial application at 90 g AI. in 18 L/ha

Time after application (days)	DAc		DFAr	
	Fresh wt.	Oven-dry wt.[a]	Fresh wt.	Oven-dry wt.
0	1.87 (100)[b]	2.70 (100)	3.20 (100)	4.62 (100)
1	1.48 (79.5)	2.17 (80.2)	2.68 (83.9)	3.90 (84.5)
3	1.15 (61.6)	1.75 (64.8)	2.28 (71.4)	3.48 (75.5)
5	0.78 (42.0)	1.25 (46.3)	1.80 (56.3)	2.87 (62.1)
7	0.60 (32.1)	0.90 (33.3)	1.38 (43.2)	2.10 (45.5)
10	0.55 (39.5)	0.75 (27.8)	1.12 (34.9)	1.52 (32.9)
13	0.45 (24.1)	0.67 (24.7)	0.72 (22.4)	1.07 (23.1)
16	0.43 (23.2)	0.55 (20.4)	0.48 (15.1)	0.62 (13.4)
19	0.28 (15.2)	0.42 (15.4)	0.30 (9.4)	0.43 (9.4)
22	0.18 (9.8)	0.25 (9.3)	0.18 (5.7)	0.25 (5.4)
25	0.13 (7.1)	0.17 (6.2)	0.13 (4.2)	0.17 (3.6)
30	0.10 (5.4)	0.13 (4.9)	0.10 (3.1)	0.13 (2.9)
35	N.D.[c]	N.D.	N.D.	N.D.
40	N.D.	N.D.	N.D.	N.D.
45	N.D.	N.D.	N.D.	N.D.

[a] Average moisture content of soil = 41% (range = 25 - 59%).
[b] Values in parentheses represent residue levels in percentage.
[c] N.D. - Not detected (detection limit = 0.1 µg/g fresh wt.)

RESULTS AND DISCUSSION

Spray deposits and droplet size spectra

Table 2 gives the spray deposit levels and droplet characteristics of the two spray solutions of diflubenzuron. It is apparent from the data that droplet characteristics (droplet density, NMD and VMD) varied according to the type of formulation used. The high-volatility spray solution (based on acetone) gave an average low droplet density (53 droplets/cm^2), NMD (56 µm) and VMD (111 µm) compared to the formulation based on the low-volatility fuel oil:Arotex mixture. The average droplet parameters of the latter were: droplet density 69, NMD 73 µm and VMD 140 µm. This is because of the lower evaporation of the droplets in flight, resulting in larger droplets on the sampling units at the ground level. Since these larger droplets have a higher impaction efficiency on the flat sampling units, more droplets/cm^2 were observed on the sampling cards. Correspondingly, the average deposit on glass plates and the percentage of A.I. deposited were higher (63.6 g A.I./ha, 71%) for the DFAr formulation as compared to the DAc formulation (39.0 g A.I./ha, 43%). It is understandable that relatively lower deposit levels, observed in the tree plots (32.8 and 57.6 g A.I./ha) with both formulations, compared to those observed in the soil plot (45.3 and 64.8 g A.I./ha) and in the litter plot (39.0 and 68.4 g A.I./ha) were due to the filtration of the spray droplets by the tree canopy, in spite of the efforts taken to place the collection units away from the overhanging foliage. This indicates that the droplet deposition process was predominantly by inertial impaction rather than by gravitational sedimentation, which is valid for the fine droplet spectra obtained in the present study.

Residues of diflubenzuron in terrestrial components

The residue levels of diflubenzuron found in spruce foliage, litter and forest soil are given respectively in Tables 3, 4 and 5. The values are expressed in terms of 'µg/g (ppm) fresh weight' (as sampled) for the ecological interpretation, and 'µg/g oven-dry weight' for more standardized comparison of residues among the substrates studied with time. The concentration based on the fresh weight basis is used throughout the following discussion.

Residues in spruce foliage

The initial concentrations (µg/g) of the insecticide in spruce foliage were respectively 23.8 and 30.6 for the two formulations, DAc and DFAr. The increased foliar concentration observed for the DFAr is in agreement with the higher droplet density and deposit levels found on the Kromekote card/glass plate units (Table 2), confirming the earlier observations (Sundaram and Sundaram 1982) that formulations based on low-volatility diluent oils enhanced foliar deposition.

The percent residue levels that remained in the foliage (Table 3) showed that the chemical was lost rapidly during the early stages (Figure 3). There was little difference in the ratio of the amount lost between the two formulations. From day 7 on the decrease was slow and gradual for both the formulations. However, on a comparative basis, the rate of decrease was lower for the DFAr formulation than for the DAc formulation ($T_{\frac{1}{2}}$ for DFAr = 9.3 d, as opposed to the $T_{\frac{1}{2}}$ of DAc = 12.8 d) (Table 6 and Figure 3). The residue levels observed on the 45th day of the experiment (0.8 µg/g for DAc *versus* 3.9 µg/g for DFAr) also confirmed this observation. Measurable residue levels found on the 45th day indicate that the chemical has a tendency to persist in conifer needles. Residues of this compound were also found to persist for an appreciable period of time in aquatic plants (Booth and Ferrell 1977), in grasses (Schaefer and Dupras 1977) and cotton foliage (Bull and Ivie 1978; Mansager et al. 1979).

The dissipation of diflubenzuron in the foliage, litter and soil samples followed an exponential decay pattern, according to equations (1) to (5):

$$Y = A + B\, e^{-Ct} \qquad (1)$$

$$\log (Y - A) = \log B - (C/2.303)\, t \qquad (2)$$

$$Y = A + B \text{ (when } t = 0) \qquad (3)$$

$$Y = A \quad (\text{when } t = \infty) \qquad (4)$$

Non-linear regression analysis of the data in Tables 3, 4 and 5, yielded the numerical values for the three constants A, B and C (Table 6) for the two formulations. The half-lives ($T_{\frac{1}{2}}$, the time required for 50% of the decayed amount 'B' to reach half of its initial value) of the exponential decay were calculated from the equation (5):

$$T_{\frac{1}{2}} = (2.303 \log 2)/C \qquad (5)$$

In the above equations, constant 'A' represents the percent of residual concentrations of the A.I. that remained undecayed for an extended period of time; 'B' represents the percent of A.I. concentrations decayed; and 'C', the rate constant of the dissipation process. The rate constant 'C' represents the rapidity with which the residues were lost from the foliage, i.e., the greater the value of 'C', the faster the decay. The data indicate that there was a faster rate of loss of A.I. when DAc was sprayed (Table 6) than when DFAr was sprayed. This is in fact clearly reflected in the $T_{\frac{1}{2}}$ values, indicating the role of the additives in the rate of dissipation of the A.I. from conifer needles.

The rapid loss of the chemical during the initial stages of the postspray period was probably due to various physical factors (climatic parameters such as light, humidity, temperature, rain, and wind conditions) rather than to metabolic factors, as observed in other forestry insecticides (fenitrothion) (Sundaram 1984). Under field conditions, the combined action of all the weather factors would have played major roles in the dissipation of the diflubenzuron surface deposits. The residues may have been gradually absorbed by the polar lipophilic terpenoids of the foliage, and degraded at a slower rate (Figure 3), through chemical, biological and/or physical means as observed for aminocarb insecticide (Sundaram and Szeto 1984).

Residues in forest litter

Residues of diflubenzuron present in forest litter following application of the two formulations are given in Table 4. The maximum levels (fresh wt.) ranged from 3.08 µg/g for DAc to 4.6 µg/g for DFAr. These values correlated well with the deposits at the ground level (Table 2). The dissipation of the chemical was rapid and more than 50% of the initial concentration was lost from both sample types within 7 d. Beyond the 7 d interval, the dissipation was slow and curvilinear (Figure 3) and the residues persisted in detectable amounts up to 45 d (DFAr), probably due to adsorption onto the lipophilic matrix. However, calculations showed that the chemical will be lost in about 65 d post-treatment. It is apparent from the degradation pattern (Figure 3) that the chemical does not have any long-term persistence in the litter matrix.

The half-life of the chemical in litter (Table 6) obtained from the regression equations, shows a slightly higher value for the DAc formulation (8.36 d for fresh wt.) compared to the half-life of the DFAr formulation (7.34 d for fresh wt.). However, the two values are not significantly different.

Residues in forest soil

Concentrations of diflubenzuron in forest soil at various time intervals after application are given in Table 5. The initial residue levels (as sampled) of

Table 6. Decay characteristics of foliar, litter and soil residues of diflubenzuron formulations, following ground application at 90 g A.I. in 18.0 L/ha; and regression coefficients A, B and C of the exponential decay

Equation $Y = A + B\ e^{-Ct}$

Formulation abbreviation	Fresh wt. or oven-dry wt.	Sample type	A (% residual concn. of AI undecayed)	B (% of AI concn. decayed	C (rate constant of decay)	$T_{\frac{1}{2}}$ (d) (time for 50% of B to decay)	R^2 (%) (coefficient of determination
DAc	Fresh wt.	Foliage	0.8	99.2	0.0746	9.30	98.6
		Litter	0.0	100	0.0829	8.36	98.8
		Soil	0.0	100	0.0926	7.49	98.5
	Oven-dry wt.	Foliage	1.6	98.4	0.0806	8.60	97.4
		Litter	0.0	100	0.0827	8.38	99.3
		Soil	0.0	100	0.1002	6.92	98.6
DFAr	Fresh wt.	Foliage	4.9	95.1	0.0544	12.8	99.4
		Litter	1.1	98.9	0.0944	7.34	98.8
		Soil	0.0	100	0.1064	6.52	98.2
	Oven-dry wt.	Foliage	6.8	93.2	0.0599	11.6	99.0
		Litter	1.5	98.5	0.0986	7.03	99.0
		Soil	0.0	100	0.1089	6.37	97.5

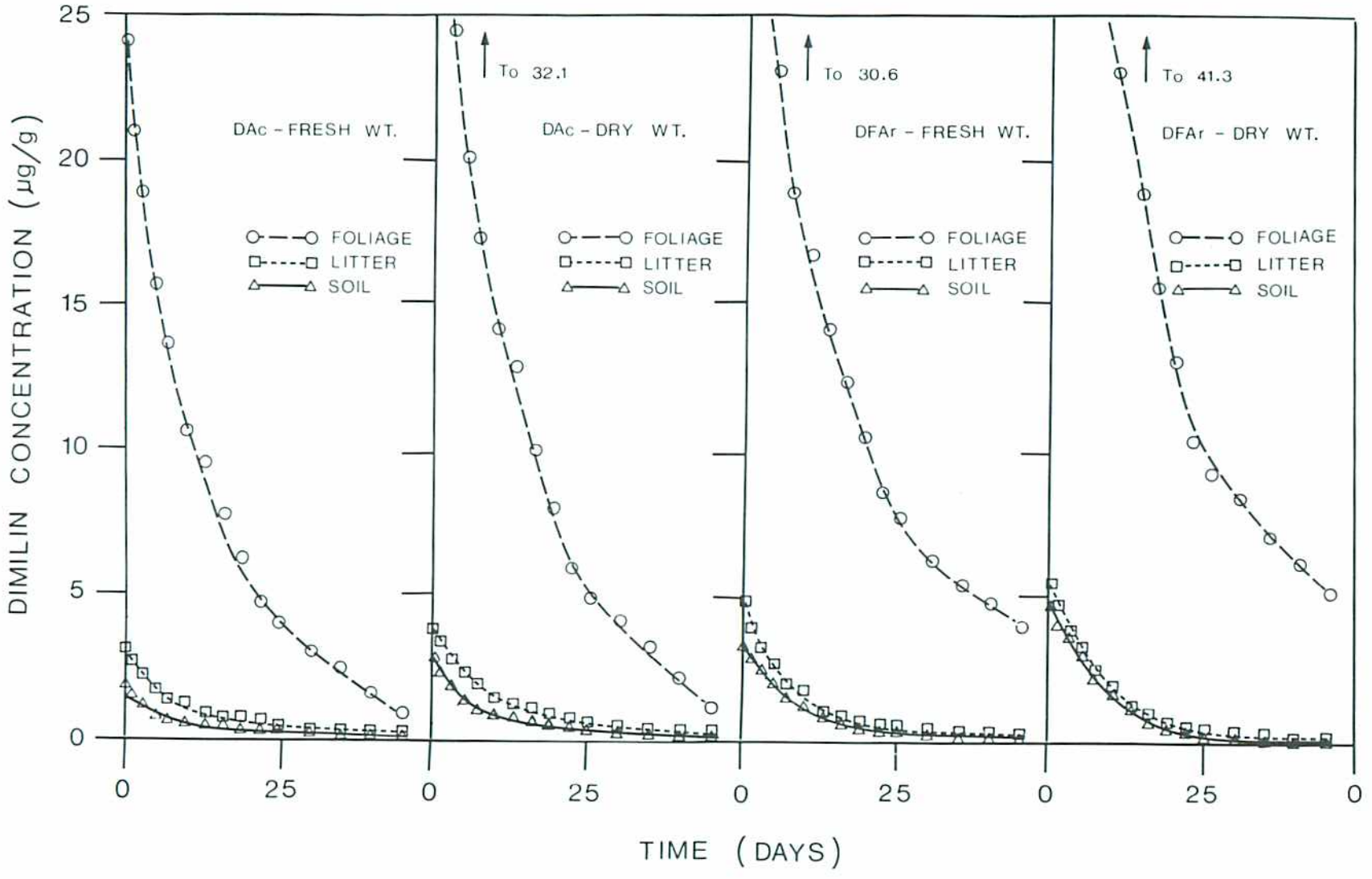


FIGURE 3. EXPONENTIAL DECAY OF DIFLUBENZURON IN SPRUCE FOLIAGE, FOREST LITTER AND SOIL SAMPLES.

1.87 µg/g and 3.20 µg/g obtained respectively for DAc and DFAr, correlated well with the spray deposits at the ground level (Table 2). The residue levels in soil were generally low compared to the litter samples (Table 4), and degraded rather rapidly. Within 7 d post-treatment, more than 50% of the initial concentration was lost with both formulations; and no detectable residues were present 35 d after treatment.

Literature findings on the persistence of diflubenzuron in soils were based on laboratory studies and are somewhat contradictory. Metcalf et al. (1975), Booth and Ferrell (1977), Bull and Ivie (1978) and Mansager et al. (1979) reported moderate stability of the chemical in soil, and with the passage of time degradation occurred slowly. On the other hand, Nimmo et al. (1984) reported rapid loss of the chemical in various agricultural soils and in hydrosoil. They also demonstrated that the breakdown of the chemical was dependent on the particle size of the chemical. Chapman et al. (1985) reported that about 2 to 12% remained in the soil after 12 weeks. Hartley and Kidd (1983) suggested that the half-life of the chemical in soil depended upon soil type, moisture content and organic matter content. Schaefer and Dupras (1977) reported a maximum soil concentration of 0.7 ppm, following aerial application of the chemical at 43 g A.I./ha. Neither liquid nor granular formulations produced long-lasting residues.

In the present study, which was conducted under the environmental conditions of the actual forest, the $T_{\frac{1}{2}}$ of the chemical in soil (as sampled) ranged from 6.52 to 7.49 d (Table 5), depending upon the type of formulation sprayed. However, these two values are not significantly different from each other. Therefore, it is not possible to comment on the crystallization potential of the A.I. from the acetone medium during the time the droplets were falling before impaction at ground level; and on the subsequent influence of particle size on the rate of degradation, especially when the study was conducted in a dynamic forest ecosystem. At this juncture, it is worth pointing out that, considering the initial concentrations of the chemical in soil (1.87 and 3.80 µg/g) (Table 5), the half-lives are relatively low. Both soil microbes and various physicochemical factors may be involved in the breakdown of diflubenzuron in the forest soil matrix as reported from other studies by Mian and Mulla (1982).

CONCLUSIONS

The simulated aerial spray trials carried out in the present investigation showed that, on average, about 43 and 72% of the sprayed material deposited on the forest floor for the two formulations, DAc (acetone-based) and DFAr (fuel oil:Arotex-based) respectively. The droplet density and size range also varied considerably, depending on the formulation. Generally, the fuel oil:Arotex-based formulation provided larger droplets and higher droplet density than the acetone-based formulation. The initial residue levels (fresh wt.) varied from 23.8 (DAc) to 30.6 (DFAr) µg/g in foliage, from 3.08 (DAc) to 4.60 (DFAr) µg/g in litter, and from 1.87 (DAc) to 3.20 (DFAr) µg/g in soil. The half-lives of the chemical in these substrates also varied depending on the type of substrate and formulation used. Generally the $T_{\frac{1}{2}}$ was higher in foliage than in litter and soil and ranged from 9.3 d (fresh wt.) for DAc to 12.8 d for DFAr in foliage, from 8.36 d for DAc to 7.34 d for DFAr in litter, and from 7.49 d for DAc to 6.52 d for DFAr in soil. The relatively high dosage and volume rates applied (90 g A.I. in 18 L/ha), combined with the application technique of using a spinning disc nozzle, resulted in deposit and residue levels much higher than those which are normally encountered ($\leq$1 ppm) in aerial spray operations involving dosage and application rates of 40-70 g A.I. in 1.5 to

5 L/ha (Schaefer and Dupras 1977; Sundaram and Szeto 1984; Sundaram and Nott 1985). Consequently the initial residue levels in the different substrates, and the corresponding half-lives, persistence etc., would be very much lower in aerial applications using the ULV technique, than those observed in the present study.

ACKNOWLEDGEMENTS

The author has drawn the help and cooperation of many people during this study. Mr. G. Eades was very generous in allowing the use of his tree farm near Shawville, Que., where this study was conducted. The enthusiastic support given by Mr. W.W. Hopewell in lending the spray applicator he had devised and the assistance of Mr. W. Haliburton in spread factor determination and droplet analysis, are acknowledged with thanks. Messers. P.E. LeCompte, G. Lafrance, Y. Volpe and M. Bryan have contributed greatly to this work by their technical skill, dedication and perserverance. The Thompson-Hayward Chemical Co., Kansas City, Kansas, has provided the analytical and technical grade samples of diflubenzuron used in this study.

REFERENCES

A.O.A.C. 1955. Official Methods of Analysis (8th ed.), Assoc. Official Anal. Chem., Washington, D.C., 1008 p.

Apperson, C.S.; Schaefer, C.H.; Colewell, A.E.; Werner, G.H.; Anderson, N.L.; Dupras, E.F., Jr.; Longanecker, D.R. 1978. Effects of diflubenzuron on *Chaoborus astictopus* and nontarget organism and persistence of diflubenzuron in lentic habitats. Jour. Econ. Entomol. 71:521-527.

Atkinson, H.J.; Giles, G.R.; MacLean, A.J.; Wright, J.R. 1958. Chemical Methods of Soil Analysis, Contribn. No. 169 (rev.), Chem., Div., Soil Serv., Agric., Canada, Ottawa, Ont., 90 p.

Booth, G.M.; Ferrell, D. 1977. Degradation of Dimilin® by aquatic foodwebs, p. 221-243. *In:* Khan, M.A.Q. (ed.), Pesticides in Aquatic Environments., Plenum Press, New York, N.Y.

Bull, D.L.; Ivie, G.W. 1978. Fate of diflubenzuron in cotton, soil and rotational crops. Jour Agric. Food Chem. 26:515-520.

Chapman, R.A.; Tu, C.M.; Harris, C.R.; Harris, C. 1985. Persistence of diflubenzuron and BAY SIR® 8514 in natural and sterile sandy loam and organic soils. Jour. Environ. Sci. Health B20:489-497.

Deul, D.H.; De Jong, B.J.; Kortenbach, J.A.M. 1978. Inhibition of chitin synthesis by two 1-(2,6-disubstituted benzoyl)-3-phenylurea insecticides, Pestic. Biochem. Physiol. 8:98-105.

Duphar. 1985. Dimilin : An Insecticide Interfering with Chitin Deposition. Tech. Inform., 9th edn., Duphar B.V., Weesp., Holland, 36 p.

Fogal, W.H. 1977. Effect of a phenylbenzoylurea [1-(4-clorophenyl)-3-(2,6-difluorobenzoyl) urea] on *Diprion similis* (Hymenoptera: Diprionidae), Can. Ent. 109:981-986.

Granett, J.; Dunbar, D.M. 1975. TH 60-40®: Laboratory and field trials for control of gypsy moths. Jour. Econ. Entomol. 68:99-102.

Haliburton, W.; Hopewell, W.W.; Yule, W.N. 1975. Deposit Assessment, Chemical Insecticides, p. 59-67 *In:* Prebble, M.L. (ed.), Aerial Control of Forest Insects in Canada. Inform. Canada Publication, Ottawa, Ont., K1A 0S9, 329 p.

Hard, J.S.; Ward, H.D.; Ilnytzky, K. 1978. Control of Douglas-fir tussock moth by aerially applied Dimilin (TH 60-40). USDA For. Serv. Res. Paper PSW-130, 6 p.

Hartley, D.; Kidd, H. 1983. The Agrochemicals Handbook, Royal Soc. Chem., The University, Nottingham, NG7 2RD, England.

Hopewell, W.W. 1974. Evaluation of commercial preparation of *Bacillus thuringiensis* with and without chitinase against spruce budworm. Env. Canada, For. Serv., Chem. Cont. Res. Inst., Inf. Rept., CC-X-59, Sect B, 14 p.

Lawrence, J.F.; Sundaram, K.M.S. 1976. Gas-liquid chromatographic analysis of N-(4-chlorophenyl-N'-2,6-diflurobenzoyl) urea insecticide after chemical derivatization. Jour. Assoc. Official Anal. Chem. 59:938-941.

Maas, W.; van Hes, R.; Grosscurt, A.C.; Deul, D.H. 1980. Benzoylphenyl Urea Insecticides, Vol. 6, p. 423-470, *In:* Wegler, R. (ed.), Chemie der Pflanzenschutz und Schadlingsbekampfungsmittel. Springer-Verlag, Berlin, Heidelberg and New York, N.Y.

Mansager, E.R.; Still, G.G.; Frear, D.S. 1979. Fate of [^{14}C]-diflubenzuron on cotton and in soil. Pestic. Biochem. Physiol. 12:172-182.

Metcalf, R.L.; Lu, P-Y.; Bowlus, S. 1975. Degradation and environmental fate of 1-(2,6-diflurobenzoyl)-3-(4-chlorophenyl) urea. Jour. Agric. Food Chem. 23:359-364.

Mian, L.S.; Mulla, M.S. 1982. Biological and environmental dynamics of insect growth regulators (IGRs) as used against Diptera of public health importance, Vol. 84, p. 27-112. *In;* Gunther, F.A. and Gunther, J.D. (eds.), Residue Reviews. Springer-Verlag, New York, Heidelberg and Berlin.

Mulder, R.; Gijswijt, M.J. 1973. The laboratory evaluation of two promising new insecticides which interfere with cuticle deposition. Pestic. Sci. 4:737-745.

Nimmo, W.B.; de Wilde, P.C.; Verloop, A. 1984. The degradation of diflubenzuron and its chief metabolites in soils: Part I: Hydrolytic cleavage of diflubenzuron. Pestic. Sci. 15:574-585.

Post, L.C.; de Jong, B.J.; Vincent, W.R. 1974. 1-(2,6-disubstituted benzoyl)-3-phenylurea insecticides: Inhibitors of chitin synthesis. Pestic. Biochem. Physiol. 4:473-483.

Rabenort, B.; de Wilde, P.C.; de Boer, F.G.; Korver, P.K.; DiPrima, S.J.; Cannizzaro, R.D. 1978. Diflubenzuron, Vol. 10, p. 57-72. *In:* Zweig, G. and Sherma, J. (eds.), Analytical Methods for Pesticides and Plant Growth Regulators. Academic Press, New York, N.Y.

Randall, A.P. 1980. A simple device for collecting aerial spray deposits from calibration trials and spray operations. Env. Canada, Can. For. Serv., Bimonthly Res. Notes, 36(5):23.

Raske, A.G.; Retnakaran, A.; Hudak, R.J.; Lim, K.P. 1986. The Experimental Spray Program Against the Hemlock Looper in Newfoundland in 1985, p. 79-88. *In:* Taylor, R.G. (ed.), Rept. of the XIII Ann. For. Pest Cont. Forum. Govt. Canada, Can. For. Serv., Ottawa, Ont., 465 p.

Rayner, A.C.; Haliburton, W. 1955. A rotary device for producing a stream of uniform drops. Rev. Sci. Instrum., 26:1124-1127.

Retnakaran, A.; Grant, G.G. 1985. Control of the oak-leaf shredder, *Croesia semipurpurana* (Kearfott) (Lepidoptera: Tortricidae), by aerial application of diflubenzuron. Can. Ent. 117:363-369.

Retnakaran, A.; Granett, J.; Ennis, T. 1985. Insect Growth Regulators, 12, p. 529-601 *In:* Kerkut, G.A. and Gilbert, L.I. (eds.), Comprehensive Insect Physiology, Biochemistry and Pharmacology, Pergamon Press, Oxford, England.

Retnakaran, A.; Smith, L.; Tomkins, W.; Granett, J. 1979. Control of forest tent caterpillar, *Malacosoma disstria* (Lepidoptera: Lasiocampidae), with Dimilin . Can. Ent. 111:841-846.

Schaefer, C.H.; Dupras, E.F., Jr. 1976. Factors affecting the stability of Dimilin in water and the persistence of Dimilin in field waters. Jour. Agric. Food Chem. 24:733-379.

Schaefer, C.H.; Dupras, E.F. Jr. 1977. Residues of diflubenzuron [1-(4-chlorophenyl)-3-(2,6-diflurobenzoyl) urea] in pasture, soil, vegetation and water following aerial applications. Jour. Agric. Food Chem. 25:1026-1030.

Sundaram, K.M.S. 1984. Fenitrothion residues in some forestry samples from a plantation forest following experimental spray application for five consecutive years. Env. Canada, Can. For. Serv., For. Pest Mngmt. Inst., Inf. Rept. FPM-X-66, 16 p.

Sundaram, K.M.S. Sundaram, A. 1981. Effect of additives on the persistence of aminocarb in conifer foliage. Env. Canada, Can. For. Serv. Res. Notes, 1(3):18-21.

Sundaram, K.M.S.; Sundaram, A. 1982. Influence of formulation on droplet size, deposit concentration and persistence of fenitrothion in conifers following a simulated aerial application. Env. Canada, Can. For. Serv. Res. Notes, 2(1):2-5.

Sundaram, K.M.S.; Szeto, S..Y. 1984. Persistence of aminocarb in balsam fir foliage, forest litter and soil after aerial application of three formulations. Jour. Agric. Food Chem. 32: 1138-1141.

Sundaram, K.M.S.; Nott, R. 1985. Mexacarbate residues in selected components of a conifer forest following aerial applications of oil-based and aqueous spray formulations. Jour. Environ. Sci. Health, B20:425-444.

Verloop, A.; Ferrell, C.F. 1977. Benzoylphenyl Ureas - A New Group of Larvicides Interfering with Chitin Deposition, p. 237-270. *In:* Plimmer, J.R. (ed.), Pesticide Chemistry in the 20th Century. ACS Symp. Series, No. 37, Amer. Chem. Soc., Washington, D.C. 310 p.

Worthing, C.R.; Walker, S.B. 1983. The Pesticide Manual, 7th edn., The British Crop Protection Council, 144-150 London Rd., Croydon, England, CRO 2TD, 693 p.