THE DISTRIBUTION AND FATE OF MEXACARBATE IN A FOREST AQUATIC ECOSYSTEM

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ABSTRACT

The distribution and persistence of aerially applied mexacarbate were studied in a New Brunswick aquatic forest environment after spraying twice at a dosage of 70 g A.I./ha using a fixed-wing aircraft. Average droplet density (drops/cm^2) and ground deposition (g A.I./ha) between the two applications differed considerably. The values for the first and second applications were respectively 1.7 and 0.73 and 5.2 and 2.0. But the average NMD (20 µm) and VMD (36 µm) for both applications were nearly the same. The maximum 1 h post spray concentrations of mexacarbate in the stream and pond waters were respectively 0.73 ppb and 18.74 ppb. Concentrations fell rapidly to below detection limits within 12 h in stream and within 3 d in pond water. Cattails *(Typha latifolia)*, manna grass *(Glyceria borealis)* and bog moss *(Sphagnum* sp.) collected from the pond contained peak 1-h post-spray concentrations of 720 ppb, 482 ppb and 81 ppb respectively. The concentration levels decreased rapidly and the average half-lives of the chemical in them were about 3.9, 8.5 and 2.0 h. Bog moss, stream moss *(Fontinalis* sp.), watercress *(Nasturtium officinalis)*, buttercup *(Ranunculus aquatilis)* and green alga *(Draparnaldia* sp.) sampled from the stream sites did not contain measurable levels of mexacarbate. Also, caged and wild tadpoles *(Rana clamitans melanota)* from the pond, brook trout *(Salvenilus fontinalis)* (caged and wild), Atlantic salmon *(Salmo salar)* (wild) and mayfly nymphs *(Ephemerella sp.)* collected from the stream did not contain any of the material. Mexacarbate was not detected in stream and pond sediments. The demelthylated products, 4-methylamino and 4-amino-3,5-xylyl methylcarbamates and the phenol, 4-dimethylamino-3,5-xylenol as transformation products were frequently detected in water and in the aquatic plants which had accumulated the insecticide. The presence of these compounds showed that demethylation and hydrolytic routes are the major metabolic pathways for the dissipation of mexacarbate from these substrates.

RÉSUMÉ

La distribution et la persistance du méxacarbate one été étudiées dans un environnement forestier aquatique au Nouveau-Brunswick après deux arrosages à la dose de 70 g/ha d'ingrédient actif effectués à l'aide d'un avion. Une différence considérable a été observée entre les deux arrosages pour la densité moyenne des gouttelettes (gouttes/cm^2) et le dépôt au sol (g/ha d'ingrédient actif). Les valeurs obtenues pour le premier et le deuxième arrosages sont respectivement de 1,7 et 0,73 et de 5,2 et 2,0. Cependant, les diamètres médians en fonction du nombre (20µm) et du volume (36µm) pour les deux arrosages étaient pratiquement les mêmes. Une heure après l'arrosage, les concentrations maximales de méxacarbate dans le cours d'eau et l'étang s'élevaient respectivement à 0,73 et 18,74 parties par milliard. Les concentrations sont descendues rapidement au-dessous de la limite de détection, en moins de 12 h dans le cours d'eau et en moins de 3 jours dans l'étang. Les quenouilles *(Typha latifolia)*, les glycéries *(Glyceria borealis)* et les sphaignes *(Sphagnum* sp) recueillies dans l'étang une heure après l'arrosage présentaient des concentrations maximales de 720, 482 et 81 parties par milliard respectivement. Les concentrations ont diminué rapidement, et les périodes (demi-vies) moyennes du méxacarbate dans ces plantes ont été d'environ 3,9, 3,4 et 2,0 h. Dans le cours d'eau, les sphaignes, les fontinalis *(Fontinalis* sp.), les cressons *(Nasturtium officinalis)*, les renoncules *(Ranunculus aquatilis)* et les algues vertes *(Draparnaldia* sp.) qui ont été recueillis à divers endroits ne renfermaient pas de méxacarbate en concentrations mesurables. Il en est de même pour les têtards de grenouille *(Rana clamitans melanota)* en cage et libres qui se trouvaient dans l'étang ainsi que pour les ombles de fontaine *(Salvenilus fontinalis)* (en cage et libres), les saumons de l'Atlantique *(Salmo salar)* (libres) et les éphémères *(Ephemerella* sp.) qui ont été prélevés dans le cours

d'eau. On n'a pas décelé de méxacarbate dans les sédiments de l'étang et du cours d'eau. Certains produits de transformation du méxacarbate ont été décelés fréquemment dans l'eau et les plantes aquatiques où s'était accumulé l'insecticide; il s'agit de deux produits déméthylés, le méthylcarbamate de méthylamino-4 xylyle-3,5 et le méthylcarbamate d'amino-4 xylyle-3,5, ainsi que d'un phénol, le diméthylamino-4 xylénol-3,5. La présence de ces composés indique que la déméthylation et l'hydrolyse sont les deux principales voies métaboliques de transformation du méxacarbate dans ces plantes.

ACKNOWLEDGMENTS

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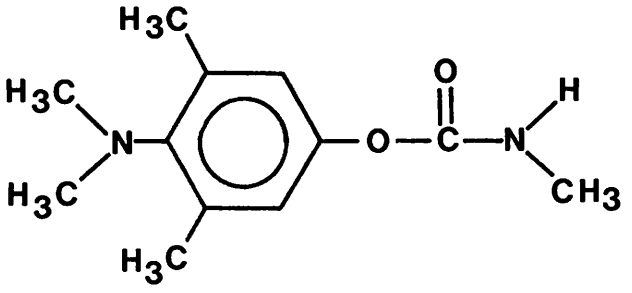
INTRODUCTION

Mexacarbate is the ISO (International Standardization Organization) common name for 4-dimethylamino-3,5-xylyl methylcarbamate (IUPAC).



Mexacarbate was first introduced by the Dow Chemical Company in 1961 under the code number "Dowco 139", trade mark ZECTRAN® (Martin and Worthing 1974). It is currently marketed by Union Carbide Agricultural Products Company, Inc. in the form of an emulsifiable concentrate UCZF-19 with an active ingredient (A.I.) content of 21.2% (wt/v).

Numerous field tests of mexacarbate conducted against the eastern spruce budworm, *Choristoneura fumiferana* (Clemens), a widely distributed and destructive defoliator of spruce-fir forests in Canada, have shown that the chemical is quick acting and toxic to the insect pest (Prebble 1975; Schmitt *et al.* 1984). The other desired characteristics of the chemical are its acceptable acute oral toxicity (LD_{50} for rats, mice, guinea-pigs and dogs: 15-63 mg/kg) (Wiswesser 1976) and low sub-acute and dermal toxicity to mammals (no effect level: rat 100-300 ppm; dog 300-600 ppm, skin-rat LD_{50} 1500 mg/kg) (Spencer 1973; Martin and Worthing 1974; Fairchild 1977). The insecticide is nonpersistent and is degraded rapidly by sunlight and biological systems (Crosby *et al.* 1965; Silk and Unger 1973; Spencer 1973; Benezet and Matsumura 1974; Sundaram *et al.* 1985a). In addition, the spray treatments showed that the chemical had a high degree of selectivity to budworm with negligible direct effects on various nontarget species and other resource values (USDA 1971; Haugen 1972; Dimond *et al.* 1972). Because of these desirable properties, the chemical is being field tested extensively at present in Canada as a prospective insecticide for the suppression of spruce budworm. Before the mexacarbate formulation UCZF-19 can be registered for operational use against the spruce budworm, it must first be field tested and thoroughly assessed for its environmental safety. The data generated must meet the rigid requirements of the Pest Control Products Act - a federal regulatory law, administered by Agriculture Canada, which ensures the safe use of pesticides.

In 1984, a broad research program was launched by the Forest Pest Management Institute (FPMI), Canadian Forestry Service in Sault Ste. Marie, Ontario. Its goal was to generate sufficient data on the efficacy of the chemical to the budworm, its persistence and fate in various terrestrial and aquatic forestry substrates and its potential adverse effects on nontarget organisms and other resource values. The environmental chemical studies conducted in 1984 after

a double application of the chemical, each time at 70 g A.I./ha at an interval of 5 d, showed that the chemical had very little persistence in various terrestrial components of the forest environment (Sundaram and Nott 1985). A similar study was conducted in June 1985, in the Little Forks Stream area of Kent County (coordinates 46°28'21"N; 65°28'15"W) 46 km SW of Rexton in northeastern New Brunswick, and was designed specifically to determine the distribution, deposition, fate and impact of mexacarbate in aquatic components of a forest environment and to evaluate its safety. This paper describes the distribution and dissipation of mexacarbate residues in natural waters and in various aquatic flora and fauna after a double application of ZECTRAN formulation (UCZF-19) at 70 g A.I./ha. The results on impact will be published elsewhere.

MATERIALS AND METHODS

Site description

The 300 ha experimental spray block (Fig. 1) was located in Kent County in the northeastern part of New Brunswick, 46 km southwest of the village of Rexton. The spray area consisted of a mixed boreal forest type, predominantly rich in black spruce, *Picea mariana* (Mill.) B.S.P. and balsam fir, *Abies balsamea* (L.) Mill. occasionally interspersed with sections of trembling aspen, *Populus tremuloides* Michx., balsam poplar, *Populus balsamifera* L., cedar, *Thuja* L., white birch, *Betula papyrifera* Marsh., pin cherry, *Prunus pensylvanica* L.f., red maple *Acer rubrum* L. and speckled alder *Alnus rugosa* (Du Roi) Spreng *[Alnus incana* (L.) Moench]. The canopy cover throughout the block ranged from 15 to 75% with occasional clearcut areas containing wetland grasses, bracken and moss patches often intruded with stunted conifer species, alder and poplar bushes with little or no canopy cover. The mean canopy height of the block was 12 ± 2 m.

Stream studies

The east branch of the Little Forks Stream originates north of the spray block in the Richibucto River valley and flows in a southwest direction through the spray block (Fig. 1). Three sampling stations, SS 1 (upper), SS 2 (middle) and SS 3 (bottom) were established on portions of the stream flowing through the spray block. Within the study area and in the absence of rainfall the stream was 1-3 m wide, 10-50 cm deep and was characterized by small, fast-flowing riffle areas (SS 1) with rubble-gravel substrates divided by a large beaver pond (SS 2) with little current and sandy/silt substrates. The downstream sampling station (SS 3) was just outside the spray block where the current of water, after passing through a narrow culvert, was fast due to large volume and high gradient and contained numerous riffles. The streambed at this station was comprised of small to large pebbles with a few cobbles and gravel substrates interspersed with silt sections. Instream cover was abundant (especially at SS 1 and 2) consisting of fallen logs, brush piles, instream boulders and undercut banks. Undercut banks, beaver ponds and brush piles provided substantial cover for different types of aquatic flora and fauna. The stream contained viable populations of brook trout, *Salvelinus fontinalis* (Mitchill) and juvenile Atlantic salmon, *Salmo salar*. Alder bushes, poplar and cedar shrubs, black spruce, fir, and birch trees lined the banks of the stream and provided a varying canopy cover of about 75% at SS 1, 65% at SS 2 and 45% at SS 3.

A sampling area in the unsprayed west branch of the Little Forks Stream, about 4 km west of the spray block (Fig. 1), served as the control station and the samples were collected only from a single station. The stream had a low gradient compared to the experimental one with average deciduous/conifer mixed canopy and dense shoreline bracken.

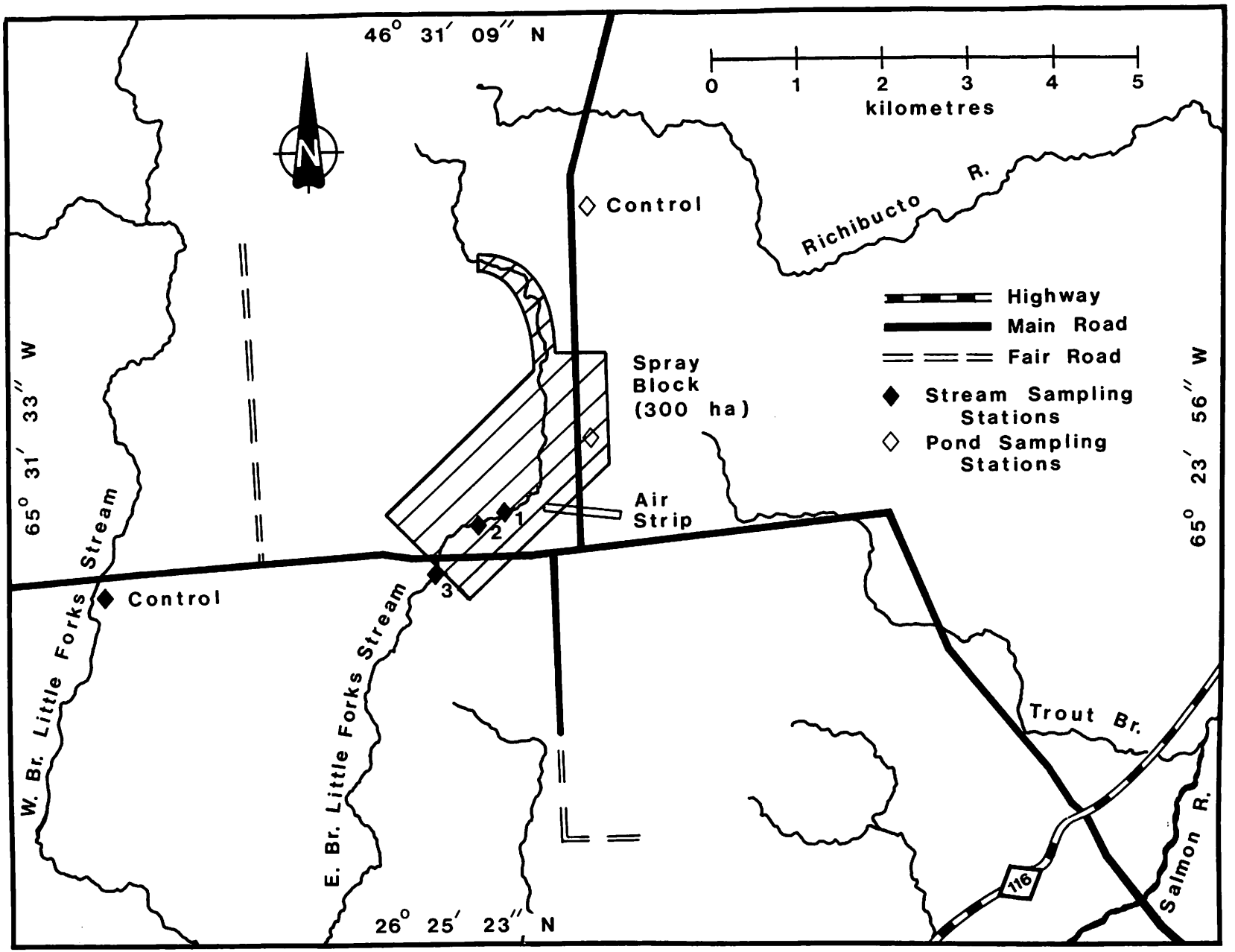


Figure 1.

Plot Location And Sampling Sites For The Mexacarbate Study In N.B. - 1985

Pond studies

One well-exposed and centrally located pond (Fig. 1) with irregular shape, average surface area 200 m^2 and depth 0.5 m was chosen for studying the uptake, dissipation and fate of mexacarbate in the forest lentic system. The pond was surrounded by spruce, *Picea* A. Dietr., alder, *Alnus* sp., willow, *Salix.*, sp., birch, *Betula* sp., and aspen, *Populus* sp., shrubs and the shoreline was covered with bracken [sweet fern, *Comptonia perignina* (L.) Coulter], rasberry, *Rubus idaeus* (L.) shrubs and wetland grasses providing very little canopy cover to the water surface. The pond water was brownish and murky during the entire study period. The bottom consisted of sand and silt heavily littered with detritus and organic debris which provided substantial cover for the growth of different species of aquatic flora and fauna.

Criteria for site and sample selections

The pond and stream used in the present study were selected on the basis of sampling accessibility, scientific relevance according to the established objectives and apparent capability of supporting viable populations of aquatic flora and fauna. Other factors such as surrounding forest type, exposure levels in relation to canopy density and suitability for aerial application were also considered. Similarly the selection of substrates and organisms to study the uptake, persistence and fate was largely based on their importance, availability, vulnerability to sprayed material and existing analytical capability in the laboratory.

Physical and chemical characteristics of the pond and stream

Average stream discharge and velocity, sampling site mean width, depth, pond dimensions, stream and pond water chemistry (pH, temp, sp. conductance, alkalinity, hardness, turbidity, major ionic contents, etc.) were measured using standard methods and are recorded in Table 1.

Mexacarbate tank mix

The spray formulation used in the study consisted of (V%) Zectran UCZF-19 22, Triton® X-114 emulsifier (P-tert-octylphenoxy heptaethoxyethanol, a nonionic surfactant manufactured by Rohm and Haas Canada Inc., West Hill, Ontario) 3, water 74 and Rhodamine B (a tracer dye manufactured by Allied Chemicals, Morristown, New Jersey, USA) 1.

Aerial application

Aerial applications were conducted by Forest Protection Ltd. (FPL), the crown corporation responsible for budworm spraying in New Brunswick. Both applications were carried out by two Cessna 188 Ag-truck aircrafts, mounted with four Micronair® AU 3000 atomizers with blade angles set at 30°, flying 50 m swath intervals with a speed of 160 km/h at 20 m above the canopy. The dosage rate each time was 70 g A.I./ha in 1.5L. Spraying for the first application commenced at 0725 ADT on June 2 with the planes flying in a north-south direction progressing from east to west. The last pass was completed at 0745 ADT. The second application began at 0840 ADT on June 8 and was terminated at 0900 h. Spotter planes were used to ensure that spray lines were followed and that the streams and pond sampling sites received adequate coverage. Meteorological instruments (Mechanical Weather Station-model 1072 and Rainfall Collector and Rain Gauge-model 303 by Meteorology Research Inc., 464 Woodbury Road West, Altadena, Calif., 91001, USA) to record the weather conditions during the time of applications were positioned within the vicinity of sampling sites. Details of spray application parameters, relevant meteorological data gathered and the composition of spray mix are summarized in Table 2.

Table 1

Physical measurements of the sampling sites and water chemistry

Parameters	Stream		Pond
	SS 1	SS 3	
Site width (Av.) (m)	4.7	9.4	Area (Av.) 200 m^2
Site depth (Av.) (m)	0.2	0.16	Depth (Av.) 0.5 m
Velocity of water (Av.) (cm/s)	42.0	50.4	-
Discharge (Av.) (L/s)	600	830	-
Temp (Av.) (°C)	9.3	9.5	8.2
Turbidity (JTU)	-	0.9	26.8
pH	-	6.7	6.2
sp. conductance (μmhos/cm)	-	25.6	15.8
Alkalinity (mg/L $CaCO_3$)	-	9.7	5.6
Hardness (mg/L $CaCO_3$)	-	-	11.22
SO_4^{2-} (mg/L)	-	5.38	3.53
Cl^- (mg/L)	-	<5	-
Total N (mL/L as N)	-	0.02	0.01
Cu^{++} (mg/L)	-	< 0.01	-
Fe^{++} (mg/L)	-	0.32	-
F^- (mg/L)	-	< 0.1	-
Mn^{++} (mg/L)	-	0.03	-
Zn^{++} (mg/L)	-	0.01	-
Pb^{++} (mg/L)	-	$< 2 \times 10^{-3}$	-
Al^{3+} (mg/L)	-	0.07	-

Ground spray deposit assessment

Folding aluminum plates known as collection units (Randall 1980), each containing two glass slides (7.5 cm x 5.0 cm) and a Kromekote® card (10 cm x 10 cm) mounted onto a 30 cm metal stand, were placed randomly on the banks of the pond and stream near the water surface 0.5 h prior to spray. Eighteen such units were placed in the clearings around the pond area (six at the water's edge and twelve on the open forest floor) and an equal number (six per site) along the stream banks. The collection units were useful (1) to determine the amount of A.I. deposited on the water surface and (2) to evaluate the droplet density (droplets/cm^2) and size spectra (NMD, VMD, D_{max}, etc.) of droplets. These units were collected 1 h after the spray application and transported immediately to the field laboratory. The deposits on the glass plates were removed by washing them with 3 x 5 mL of pesticide grade ethyl acetate. The eluates were stored in tightly sealed amber colored bottles at -20°C until analysis. The Kromekote cards were stored under dark, dry conditions in slotted wooden boxes until evaluation of the size spectra of droplets.

Sampling procedures

Water, sediment and various types of aquatic flora and fauna were collected from the sampling sites in the control and spray area prior to spraying to confirm the absence of mexacarbate and to check for the presence of naturally occurring compounds

TABLE 2

Weather conditions, aircraft parameters and formulation composition during the 1985 aquatic study in New Brunswick

Parameter	1st Application	2nd Application
Date of application	June 2	June 8
Time of application (ADT)	0725	0840
Windspeed (km/h) (Av.)	2.7	4.8
Wind direction	W	S-SW
Temp. (°C) (Av.)	13	13
R.H. (%)	90	80
Cloud cover	1/10	0/10
Precipitation	NIL	NIL
Spray block size (ha)	300	
Aircraft type	Two Cessna 188 AG trucks	
Atomizer units	Four Micronair AU3000	
Blade angle setting	30°	
Aircraft speed	160 km/h	
Spray height above canopy	20 m	
Swath width	50 m	
Dosage rate	2 x 70 g AI/ha	
Volume rate of application	1.5 L/ha	
Emission rate	18.3 L/min	
Composition of tank mix (V%)	Mexacarbate (tech.)	22
	Triton X-114	3
	Water	74
	Rhodamine B dye	1

which might interfere with the analysis of mexacarbate. Following spray application, post spray samples of water, sediment, aquatic flora and fauna were collected at 1, 3, 6, 12 h, 1, 2, 3 and 4 d and processed according to the set procedures discussed below.

Water

From each stream site, water was sampled by dipping a clean wide-mouthed open 1-L Teflon® bottle against the direction of stream flow to a depth of about 1 cm, without entraining the bottom sediment and organic debris. The surface water was allowed to flow in and when the bottle was about 95% full it was sealed tight with a Teflon screw cap, labelled and stored at 0°C in a cooler and shipped to the field laboratory for further storage at -20°C. Pond water was collected similarly from the mid-section of the pond without disturbing the bottom material and stored as described above.

Sediment:

Sediment samples were taken from the same locations as the water samples. Samples were taken by scooping bottom sediment to a depth of 1 cm, using a clean wide-mouthed amber colored glass jar of 0.5 L capacity fitted with a Teflon -lined screw cap. At each sampling site, the jar was gently lowered to the bottom, the lid was unscrewed and 1-cm of surface sediment was scooped by gently moving the jar around so that it became about half filled with sediment. The bottle was tightly sealed, brought to the surface and decanted to remove all the water. The samples were labelled, sealed, taken to the field laboratory in coolers at 0°C and kept frozen until analysis.

Aquatic plants:

From the pond, whole aquatic plant samples such as cattails *(Typha latifolia)*, manna grass *(Glyceria borealis)* and bog moss *(Sphagnum* sp.) were collected at intervals of time. The plant samples were rinsed with water to remove mud and other adhering debris. The adsorbed water was squeezed out. Each cattail and manna grass sample was clipped into two segments - one submerged under water and the other above the water. Each sample was then wrapped separately in aluminum foil, packed in labelled polyethylene bags, chilled immediately and transported to the field laboratory for storage at -20°C.

From the stream sites, bog moss *(Sphagnum* sp.), stream moss *(Fontinalis* sp.), green algae *(Draparnaldia* sp.), watercress *(Nasturtium officinalis)* and buttercup (a grass) *(Ranunculus aquatilis)* samples were collected at intervals of time. The dead tissues and other adhering organisms were removed and each individual sample which also included the submerged part was processed and stored as described above.

Aquatic insects:

Mayfly nymphs *(Ephemerella* sp.) were collected throughout the sampling period from randomly selected stones (approximately 15 cm in diameter) in the streambed at each sampling site. Debris and associated organisms were removed, rinsed with water and stored in clean stoppered bottles at -20°C until analysed.

Fish samples:

Indigenous populations of brook trout *(Salvelinus fontinalis)* and Atlantic salmon *(Salmo salar)* in the stream were sampled and taken out randomly with an electro-shocker and dip-net at each sampling period for residue analysis and were killed upon sampling. Four to six uniformly sized fish (mean wt. 10 ± 5 g and mean length 8 ± 4 cm) in each species contributed to a composite sample size at each sampling period. Each composite sample, after being rinsed with water, was wrapped in aluminum foil, packed in a polyethylene bag and chilled immediately. It was then transported to the field laboratory where it was stored at -20°C until analysis.

In addition to wild brook trout, about 45 hatchery reared trout fingerlings of the same dimensions as the wild ones were placed in 3 cages (60 cm length, 60 cm width and 45 cm depth) with plywood top and bottom and surrounded on other sides by 13 mm aluminum screening. At each sampling period, two fish were removed from each cage and pooled to form a composite sample for chemical analysis to determine the intake and degradation of mexacarbate. Prior to analysis, each sample was processed as described above.

Tadpoles:

Green frog tadpoles *(Rana clamitans melanota)*, which were indigenous and abundant in the pond, were also sampled by

scooping them with an insect net (0.2 mm mesh) at each sampling period. Roots, debris, mud, stones, etc. were removed. Each composite sample consisted of about fifteen tadpoles. They were rinsed with clean water and processed and stored as described for fish.

Analytical procedures

Water:

The water sample (approximately 0.9 L) from each site was divided into 3 equal parts. Each part was extracted twice with 100 mL of dichloromethane. All the organic extracts corresponding to a specific sample were pooled and dried by passing through a 3-cm diam. x 5-cm length column of granular anhydrous sodium sulfate to remove all traces of moisture. The extract was then flash evaporated gently at 30°C to dryness and the residue was taken in ethyl acetate for gas-liquid chromatographic (GLC) analysis without any further cleanup.

Sediment:

The thawed sediment samples were filtered under suction to remove excess water. Ten gram aliquots of each sediment in triplicate were separately extracted first for 5 min with 50 mL of ethyl acetate using Sorvall Omni-Mixers set at the speed level 4 (RPM 2500). The supernatant extract was filtered through a sintered glass (Pyrex®) Buchner funnel (i.d. 60 mm, 10-15 µm pore size) containing a 3-cm layer of anhydrous Na_2SO_4. The extraction was repeated once more using the same volume of extractant and filtered through the same funnel. The filter cake in the funnel was rinsed with 20 mL of ethyl acetate. The extracts of each sample were pooled, flash evaporated gently to dryness and the residues were taken in 30 mL of acetonitrile. The polar acetonitrile was partitioned twice, each time with 10 mL of hexane. The hexane layers were discarded and the acetonitrile layer was flash evaporated gently at 30°C to dryness. The residue was taken in 10 mL of ethyl acetate for column cleanup so that 1 mL of extract was equivalent to 1 g of sample.

For column cleanup, Pasteur pipets (Fisher 13-678-8) (14.5 cm x 0.8 cm i.d.) were packed from bottom to top with a glass wool plug, 1 cm of Na_2SO_4, 5 cm of neutral Al_2O_3 (Merck-Activity Stage I; supplier Canlab, Toronto, Ont.) and 1 cm of NA_2SO_4. The packed columns were prewashed with 10 mL of ethyl acetate. Aliquots of crude extracts equivalent to 1 g of substrate were transferred quantitatively to the microcolumns and eluted with 10 mL quantities of ethyl acetate. The eluates were collected and concentrated in a stream of dry N_2 (Meyer N-evap) and their volumes were adjusted volumetrically for GLC analysis.

Aquatic plants (cattails, manna grass, moss, algae, water-cress and buttercup):

Prior to blending, the excess water present in the thawed plants was removed by pressing them in folds of absorbent paper. Each sample was cut into small pieces with a pair of scissors and mixed well. Ten gram aliquots of the mixed sample were homogenized thrice in a Polytron® PT-20 at speed setting of 3.5 with 50 mL of ethyl acetate each time. The pooled extract of each sample was processed and cleaned as described under sediment.

Aquatic animals (fish, tadpoles and mayflies):

Each composite fish and tadpole sample was chopped separately into small pieces using a sharp knife and mixed thoroughly, after being thawed and dryed with paper towels. Ten gram aliquots in triplicate of cut up samples were used for homogenization and processed further as described under aquatic plants. The mayfly samples collect-

ed at each sampling time were about 1 g. Therefore duplicate analysis was not possible for this substrate. The extractant volume was adjusted because of reduced sample size to 20 mL instead of 50 mL. Apart from this, the details of the extraction and cleanup procedures were the same as discussed for aquatic plants.

Glass plate rinses from collection units:

The ethyl acetate rinses were concentrated using a rotary vacuum evaporator at 30°C. The volumes of the concentrates were adjusted and analyzed directly by GLC.

Droplet Spectra from Kromekote cards:

The Kromekote cards were read under magnification using a Zeiss Opton stereoscopic microscope. Each card was first scanned and then read in 1 cm^2 grids to achieve accurate droplet stains ranging in diameter from 200 µm to 5 µm. The number and size of the droplet stains were recorded and grouped according to their stain size. Stain diameters were converted to droplet diameters using the spread factor value determined in the laboratory with the tank mix (Rayner and Haliburton 1955). The droplet size spectrum was then calculated from the droplet diameters. Droplet densities (droplets/cm^2), number median and volume median diameters (NMD and VMD) and maximum (D_{max}) and minimum (D_{min}) diameters were then calculated using the procedure described by Sundaram *et al.* (1985b).

Gas-liquid chromatographic analysis

The mexacarbate residues present in the final extracts were analyzed by the Hewlett Packard HP 5710-A gas chromatograph equipped with an N/P selective detector. A 1.83 m x 2 mm i.d. Pyrex glass column containing 1.5% OV-17 + 1.95% OV-210 on 80-100 mesh Chromosorb W, HP was used. Carrier gas (He) and plasma gas (H_2 and air) flow rates (mL/min) were: He, 30; H_2, 4 and air, 70. The operating temperatures (°C) were: oven, 185; detector, 250 and injection port, 200. The retention time (RT, min) for the insecticide under these conditions was 5.45.

Detector response was calibrated daily with an analytical standard prepared in ethyl acetate. The cleaned up extracts of each sample were injected thrice and the average peak height was calculated. Quantification of the samples was based on average peak heights of the external standard which was injected before and after the sample. The values recorded are the mean of three replicate measurements for each sample. The standard error (SE) in them was less than 10%.

Recovery levels and detection limits

For recovery, the prespray samples of water, sediment and cattails from the pond and bog moss, algae and brook trout from the stream were selected as examples to represent the entire spectrum of substrates studied. Aliquots of these samples, except water, were fortified separately in quadruplicate at 1.0, 0.1 and 0.01 ppm levels of mexacarbate. Water samples were fortified at ppb levels. All samples were extracted, processed and analysed according to the method described above. Each mean percentage with its standard deviation (Table 3) was derived from four replicates. The recoveries were quantitative (> 86%, range 103 to 86%) for the substrates at all the fortification levels indicating that the described method is effective and suitable for extracting mexacarbate from aquatic samples of forestry origin. These values were checked periodically during the study and were found to be consistent. Values reported in this paper have not been corrected for recoveries.

The GC detecton limit for the mexacarbate standard was 50 pg (10^{-12}g) and the

TABLE 3

Percent recovery of mexacarbate from various aquatic substrates after fortification

Substrate	Percent recovery ± SD (n = 4)		
	1.0 ppm	0.10 ppm	0.01 ppm
sediment (pond)	96 ± 5	94 ± 6	86 ± 9
cattails	102 ± 6	96 ± 5	94 ± 6
bog moss	98 ± 4	101 ± 7	92 ± 7
algae	96 ± 7	93 ± 8	90 ± 6
brook trout	101 ± 6	97 ± 5	93 ± 7
	1.0 ppb	0.10 ppb	0.01 ppb
Water (pond)	103 ± 5	97 ± 8	94 ± 9

limit for quantification (minimum detection limit, MDL) was fixed at 0.01 ppm for all the substrates except water. For water, the MDL was 0.01 ppb.

None of the prespray and control samples contained any mexacarbate and there was no evidence of co-extracted materials causing interference with the identification and quantification of the chemical.

Thin-layer chromatographic studies

The presence of mexacarbate and some of its common metabolites (Table 4) in the extracts was also studied by thin-layer chromatography (TLC) using the method described by Sundaram *et al.* (1980). In the TLC study, pre-coated high-performance (HP) silica gel plates containing a 250 nm fluorescent indicator (Baker HP-7011/4, 10 cm x 10 cm, 200 µm thickness) were used. The concentrated extracts were gently evaporated to dryness under vacuum and 20 µL aliquots of ethanolic solutions of the residues were spotted on the plate. The authentic pure samples (Table 4) acted as the reference standards. The R_f values and the actual TLC chromatogram obtained for the standards using the solvent system, ether:hexane:ethanol -77:20:3 (v/v%) are given respectively in Table 5 and Fig. 2.

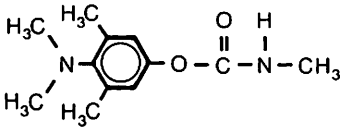
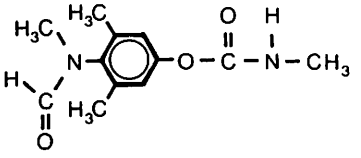
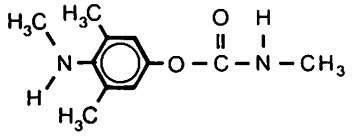
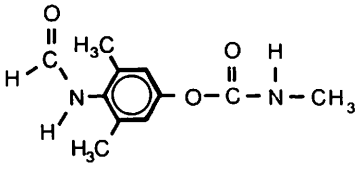
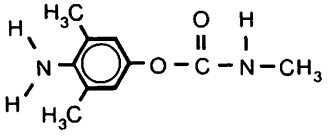
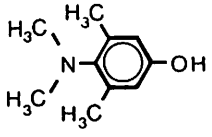
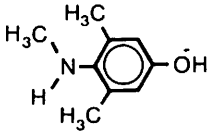
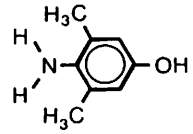
All solvents used in the study were pesticide grade. Anhydrous granular sodium sulfate was heated overnight at 260°C prior to use. Analytical standards of mexacarbate (> 99.5%) and some of its metabolites listed in Table 4 were supplied by Union Carbide Agricultural Products Company, Inc. Laboratory sources of contamination were monitored by conducting periodic reagent blank checks. Contamination of apparatus, glassware, etc. was found to be negligible during the period of study.

RESULTS AND DISCUSSION

Spray deposits and droplet size spectra

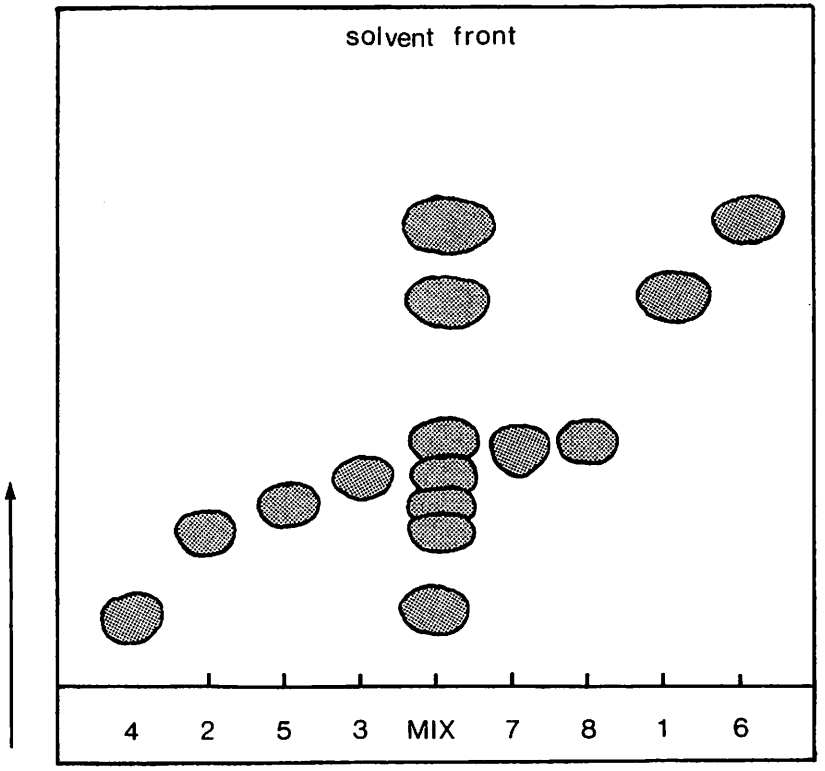
Table 6 gives the spray deposit and droplet size profiles observed for the two applications of mexacarbate formulation on 36 ground level Kromekote card-glass plate

Table 4 Mexacarbate and some of its common metabolites

No.	CHEMICAL STRUCTURE	NAME (IUPAC USAGE)	ABBR.
1		4-Dimethylamino-3,5-xylyl N-methylcarbamate	M
2		4-Methylformamido-3,5-xylyl N-methylcarbamate	MFM
3		4-Methylamino-3,5-xylyl N-methylcarbamate	MAM
4		4-Formamido-3,5-xylyl N-methylcarbamate	FAM
5		4-Amino-3,5-xylyl N-methylcarbamate	AM
6		4-Dimethylamino-3,5-xylenol	DMAX
7		4-Methylamino-3,5-xylenol	MAX
8		4-Amino-3,5-xylenol	AX

TLC OF MEXACARBATE AND ITS 7 METABOLITES

Figure 2



SOLVENT SYSTEM – DIETHYL ETHER:HEXANE:EtOH
77 : 20 : 3

Table 5

No.	ABBR.	R_f VALUE
6	DMAX	O.78
1	M	O.65
8	AX	O.40
7	MAX	O.39
3	MAM	O.36
5	AM	O.31
2	MFM	O.26
4	FAM	O.12

collection units. Average deposit levels and droplet densities between the two applications differed significantly. Generally the first application gave on average a rather sparse droplet density (1.7 drops/cm^2, range 1.1 to 2.3 drops/cm^2) compared to the second application (5.2 droplets/cm^2, range 0.22 to 8.1 droplets/cm^2). Except the single low value of 0.22 droplets/cm^2 found at SS3, the droplet density values observed in the second application were about 3 times higher than the first application. Similar trends were also observed in the ground deposition levels and the percent A.I. deposited. From the data in Table 6, it is apparent that the observed droplet density variances were directly relatable to the ground deposition levels.

The amount of deposit found on glass plates in the first application varied from 0.56 g A.I./ha to 0.91 g A.I./ha ($\bar{x}$ = 0.73 g A.I./ha) whereas in the second application, the corresponding values were 0.34 g A.I./ha to 2.9 g A.I./ha ($\bar{x}$ = 2.0 g A.I./ha). Similar variations were also found in the percent of A.I. deposited on the forest floor. Generally the % of A.I. deposited was rather low. In the 1^{st} application, the value obtained was 1% and for the second application it was 2.8%, nearly 3 times higher. As anticipated, a very low deposition level (0.34 g A.I./ha) was found at site SS3 in the second application, corresponding to its low droplet density (0.22), validating the direct relationship existing between the two parameters. The stream sampling site SS 3 (Fig. 1) was just outside the spray block and in all likelihood the spray pilot would have missed the swath during second application.

The deposit variance observed between spray applications in forestry spraying is not uncommon. In the 1984 spray application of mexacarbate emulsion, Sundaram and Nott (1985) found similar wide variations (0.31 g A.I./ha in the 1st application and 1.70 g A.I./ha in the 2nd application) between the 1st and 2nd applications. Wide variations were also observed in droplet densities (1.4 *vs* 5.3 droplets/cm^2). Such variations are usually attributable to micrometeorological conditions (temperature, atmospheric turbulence, wind, R.H. etc.) which existed during the time of spraying (Yates and Akesson 1973; Cramer and Boyle 1976). It would be impractical to fly the spray aircraft at an exact altitude, speed and angle of flight for each application because of differences in wind speed and direction and topographical changes (Hogan 1951). Although both spray applications were conducted under similar weather conditions (Table 2), it is likely that differences in wind speed (2.7 *vs* 4.8 km/h) and direction (W *vs* S-SW) and RH (90% *vs* 80%) may have caused differences in the deposition of mexacarbate on forest floor between the two applications.

Generally, deposit levels were very low in both applications ($\bar{x}$ = 0.73 g A.I./ha for the 1st and 2.0 g A.I./ha for the 2nd), which could be due to the high volatility of the aqueous formulation (Dennison and Wedding 1984). The formulation used in the present study generated spray droplets in the aerosol size category (< 50 µm) (the observed NMD in the present study is 19-20 µm), which are found to have low terminal velocities with poor impaction efficiency on the collectors (Matthews, 1979). The observed average values of droplet size range, NMD and VMD for the 1st and 2nd applications were respectively 5-84 µm and 5-76 µm, 20 µm and 19 µm and 39 µm and 33 µm. Since variations in droplet sizes between the applications are low, the droplet spectra for them would be nearly the same. According to Matthews (1979), the lifetime for extinction of a 100 µm aqueous droplet in still air from release point was 57 s and its fall distance was only 8.5 m.

TABLE 6

Spray deposit data from aerial application of an emulsion formulation of mexacarbate at 70 g A.I./ha over an aquatic forest environment in New Brunswick in 1985

Parameters	Application and sampling site											
	1st Application						2nd Application					
	Open forest floor*	SS 1	SS 2	SS 3	Pond	Average	Open forest floor*	SS 1	SS 3	SS 3	Pond	Average
Droplet density ($droplets/cm^2$)	1.8	2.3	1.8	1.1	1.5	1.7	6.8	4.7	8.1	0.22	6.2	5.2
Droplet range (µm)	5-90	5-80	5-90	5-105	5-55	5-84	5-90	5-70	5-60	5-50	5-110	5-76
NMD (µm)	16	21	22	21	19	20	18	17	19	22	20	19
VMD (µm)	32	34	41	60	29	39	36	32	31	31	33	33
Ground deposit** (g AI/ha)	0.85	0.91	0.70	0.56	0.64	0.73	2.4	2.2	2.9	0.34	2.1	2.0
Percent AI deposited	1.2	1.3	1.0	0.80	0.91	1.0	3.4	3.1	4.1	0.49	3.0	2.8

*Near pond area.

**Determined by GLC from glass plate eluates.

TABLE 7

Mexacarbate concentration (ppb) in stream and pond waters following its experimental aerial application at 70 g A.I./ha over a New Brunswick forest area in 1985

Time after spraying	Application and sampling site							
	1st Application				2nd Application			
	SS 1	SS 2	SS 3	Pond	SS 1	SS 2	SS 3	Pond
Prespray	N.D.*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 h	0.17	0.15	0.23	1.40	0.73	0.55	0.42	18.74
3 h	0.04	0.05	0.03	0.35	0.11	0.10	0.14	2.98
6 h	N.D.	N.D.	N.D.	0.18	0.03	T	0.03	0.75
12 h	N.D.	N.D.	N.D.	T**	N.D.	N.D.	N.D.	0.21
1 d	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.12
2 d	N.A.+	N.A.	N.A.	N.D.	N.A.	N.A.	N.A.	0.03
3 d	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	T
4 d	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

*N.D. - Not detectable, detection limit = 0.01 ppb
**T - Traces, 0.01 to 0.02 ppb
+N.A. - Not analyzed

TABLE 8

Concentrations of mexacarbate (ppb-wet weight) in some aquatic plants collected from stream and pond following its aerial application at 70 g A.I./ha over a forest area in New Brunswick in 1985

	1st Application						2nd Application					
	Cattails[a] (Pond)		Manna grass[b] (pond)		Bog-moss[c]		Cattails (pond)		Manna grass (pond)		Bog moss	
Time after spraying	Top	Bottom	Top	Bottom	Pond	Stream (SS 2)	Top	Bottom	Top	Bottom	Pond	Stream (SS 2)
Prespray	N.D.[d]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 h	543	N.D.	384	16	T[e]	N.D.	720	N.D.	482	29	81	N.D.
3 h	139	N.D.	316	N.D.	T	N.D.	489	N.D.	416	20	21	N.D.
6 h	92	N.D.	220	N.D.	N.D.	N.D.	326	N.D.	328	12	N.D.	N.D.
12 h	62	N.D.	111	N.D.	N.D.	N.D.	205	N.D.	198	T	N.D.	N.D.
1 d	34	N.D.	61	N.D.	N.D.	N.D.	94	N.D.	117	N.D.	N.D.	N.D.
2 d	20	N.D.	29	N.D.	N.D.	N.D.	46	N.A.	47	N.D.	N.D.	N.D.
3 d	N.D.	N.A.[f]	18	N.A.	N.A.	N.A.	25	N.A.	22	N.A.	N.A.	N.A.
4 d	N.D.	N.A.	N.D.	N.A.	N.A.	N.A.	N.D.	N.A.	T	N.A.	N.A.	N.A.

[a] Cattails *(Typha latifolia)*
[b] Manna grass *(Glyceria borealis)*
[c] Bog moss *(sphagnum* sp.)

[d] N.D. - Not detectable; detection limit = 5.0 ppb (wet wt.)
[e] T - Traces, 5.0 - 9.9 ppb (wet wt.)
[f] N.A. - Not analysed.

Thus the rapid evaporation of the spray droplet was responsible for the lower deposit levels found on the glass plates. The average droplet densities found on Kromekote cards and the mean deposit levels measured on glass plates showed good correlation ($r = 0.984$).

Mexacarbate concentration in stream and pond waters

The concentrations (ppb) of mexacarbate present in the top 1 cm of water collected at different intervals of time from the 3 stream sampling sites and from the pond following the double application of mexacarbate are given in Table 7. It is apparent from the data that the first application gave lower initial concentration levels of the chemical in water (stream sites: range 0.15-0.23 ppb; pond 1.4 ppb) than the second application (stream sites: range 0.42-0.73 ppb; pond 18.74 ppb). This is in agreement with the low droplet density and deposition levels found on the collection units from all the sampling sites during the first application.

The maximum concentration of 0.73 ppb was found at station SS 1 in the stream 1 h after spraying. Although SS 3 was not sprayed directly and had the lowest droplet density (0.22 droplets/cm^2), the 1 h residue level was rather high (0.42 ppb). This could be due to the mobility of the surface layer of mexacarbate downstream from sites SS 1 and SS 2 during the 1 h sampling interval, thus increasing the concentration. Because of the high discharge level observed around the site SS 3 (Table 1), good mixing of the chemical could have occurred during its flow from upstream.

The concentrations of mexacarbate found in stream waters after both spray applications were generally very low and dissipated quickly within 12 h from all the 3 sites. The estimated half-life was only about 1.8 h. The loss of the chemical could have been primarily through dispersion and dilution. Other processes such as photolysis (Crosby *et al.* 1965), volatilization, hydrolysis (Roberts *et al.* 1978) and sorption to particulate matter could have played minor roles. Although the solubility of mexacarbate in water is low, rapid dispersion of its emulsion to a water body is anticipated because of the presence of hydrophilic Triton X-114 emulsifier. We can also expect that appreciable water turbulence observed at SS 1 and SS 3 will enhance the attenuation and mixing processes. The water flow at SS 2 was rather slow but deep, consequently, because of rapid surface to subsurface mixing, there was no noticeable difference in residue levels among the three sites.

In pond waters, the peak 1 h postspray concentrations of mexacarbate found following the 1st and 2nd spray applications were respectively 1.40 ppb and 18.74 ppb. The average droplet densities found on Kromekote cards and the mean deposit levels measured on glass plates located near the pond, correlated with the residue data obtained. On both occasions, the concentrations fell rapidly. In the 1st application, the residue levels disappeared within 1 d whereas in the 2nd, detectable amounts remained up to 3 d because of a higher initial concentration (18.74 ppb). From the concentration-time profile, the approximate half-life of mexacarbate in pond water was found to be 2.0 h

Experiments at this laboratory and elsewhere (Hosler, Jr. 1974; Matthews and Faust 1977; Roberts *et al.* 1978) indicated that mexacarbate is degraded in water. Photodecomposition of the material (Crosby *et al.* 1965; Silk and Unger 1973) in the pond water was unlikely because of poor light transmission due to its murky nature. It is known that microbial organisms, *Pseudomonas* sp. and *Trichoderma viride* in

forest soils readily degrade mexacarbate (Benezet and Matsumura 1974). The chemical was also adsorbed onto suspended particles in water (Matthews and Faust 1981). In view of these findings, we venture to speculate that the dissipation of the chemical from pond waters was primarily due to microbial and chemical actions and sorption to particulate matter. Volatilization and dilution could have played minor roles.

Stream and pond sediments

Analysis of postspray samples of sediment collected from all the four sampling sites after both applications, did not show any residue of mexacarbate at the detection limit of 0.01 µg/g of wet sediment. The apparent absence of mexacarbate from the sediment samples is probably due to the extremely low initial surface concentrations found in stream and pond waters, which were respectively 0.0127 µg/cm^2 and 0.0137 µg/cm^2 (average of both applications). In stream water, the residue level was lost rapidly by dilution and by other physicochemical processes as it flowed downstream before reaching the sediment matrix. Similarly, to reach the sediment layer in the bottom of the pond, the chemical had to diffuse through a 0.5 m water column. During that interval, we can normally expect that the low levels of A.I. present would have been diluted and degraded completely.

Mexacarbate residues in aquatic plants

Among the plants sampled from stream and pond, only cattails *(Typha latifolia)*, manna grass *(Glyceria borealis)*, and bog moss *(Sphagnum* sp.) contained detectable levels (0.01 µg/g-wet weight) of mexacarbate (Table 8). Others, such as watercress *(Nasturtium officinalis)*, buttercup *(Ranunculus aquatilis)*, green alga *(Draparnaldia* sp.) and moss *(Fontinalis* sp.) did not act as sinks for the chemical probably because of the little interaction between the substrate and the chemical or the nonavailability of the latter.

Of the plants sampled from both stream and pond, the bog moss *(Sphagnum* sp.) was the only one common to both. Uptake of the chemical by the pond bog moss to a maximum initial concentration of 81 ppb occurred only in the second application, but the residue was lost within 6 h (Table 8). Stream samples did not accumulate the chemical.

The upper part of the cattail plants sampled during the spray program contained broad leaves only. No flowering spikes or pollen were present. Because of its posture, geometry and exposure, the top portion above the water surface acted as a good receptacle for the direct deposition of spray droplets. The initial 1 h peak concentration in the first and second applications were respectively 543 ppb and 720 ppb. The submerged part did not reveal any accumulated residues. In both instances, the concentration fell rapidly below the detection limit (0.01 ppm wet weight) within 3 d in the first application and within 4 d in the second application. The rapid loss may be the result of volatilization from the exposed leaf surface as reported previously from conifer tissue (Sundaram and Nott, 1985) or to biochemical and photolytic degradation. The average half-life of the chemical in cattails from the concentration-time profiles was about 3.9 h.

The other aquatic plant sampled from the pond as an indicator species for mexacarbate uptake was manna grass. The plants were in clusters with ribbonlike leaves and leafy stems standing just above the water surface forming dense meadows. From the data in Table 8, it is apparent that the floating leafy meadows acted as good receptors for spray droplets. The peak concentrations found in the sub-

strate on wet weight basis at both first and second applications were respectively 384 ppb and 482 ppb. The residue decreased gradually compared to cattail and was reduced to trace levels (<10 ppb) on the 4th day of sampling. The half-life found from the concentration vs time plot was 8.5 h, which is twice as long as in the cattail (3.9 h). Although the times are very short, these findings indicate that the chemical has a tendency to persist in manna grass more than in the other plants studied thus indicating that this aquatic plant could act as a microsink for the insecticide. The subsurface plant samples contained detectable levels at 1 h in the first application and measurable amounts up to 6 h in the second application with an estimated half-life of 3.4 h. The results suggest that mexacarbate has a tendency to partition from pond water to the plant substrate and accumulate in it. Such a phenomenon has been reported recently for fenitrothion by Eidt *et al.* (1984).

Mexacarbate residues in aquatic animals

The aquatic animals sampled from the stream were indigenous fish species such as Atlantic salmon *(Salmo salar)* (wild) and brook trout *(Salvelinus fontinalis)* (wild and caged) and mayfly nymphs *(Emphemerella* sp.). Caged and wild tadpoles *(Rana clamitans melanota)* were collected from the pond. On analysis, it was surprising to find that none of these samples contained any detectable levels (>10 ppb, fresh wt.) of mexacarbate. It may be due to the nature of the substrates wherein little absorption of the chemical took place or paucity of the chemical in the surrounding medium for partitioning sufficiently into the sample matrices.

Metabolic fate of mexacarbate in aquatic substrates

Rigorous TLC studies were carried out using the cleaned-up ethanolic concentrates of the following:

Pond water: 1 and 3 h samples of 2nd application.

Cattails (top portion): 1 and 3 h samples of both applications.

Manna grass (top portion): 1 and 3 h samples of both applications

Bog moss (pond): 1 h sample of second application

Other samples which did not contain the active material were also tested sporadically but no positive results were obtained. The identities of mexacarbate (M) its 4-methylamino (MAM) and 4-amino (AM) (its presence was inconsistent) analogues and the hydrolytic product 4-dimethylaminoxylenol (DMAX) were confirmed in the pond water, cattails, manna grass and bog moss samples. Possible degradation routes of mexacarbate in these substrates with the corresponding R_f values obtained for the parent material and its degradation products which agreed with the values of authentic compounds (Table 5) are represented in Fig. 3. Similar degradation products were also reported by others for a variety of other substrates (Abdel-Wahab and Casida 1967; Meikle 1973; Roberts *et al.* 1978; Sundaram *et al.* 1985a). From the data reported herein, the disappearance of mexacarbate in the aquatic substrates appears to involve N-demethylation of the 4-dimethylamino group as well as the hydrolysis of the carbamate ester bond. A similar sequence of degradations has been postulated by Meikle (1973), Roberts *et al.* (1978) and Sundaram *et al.* (1985a) for other substrates. The rapid disappearance of the

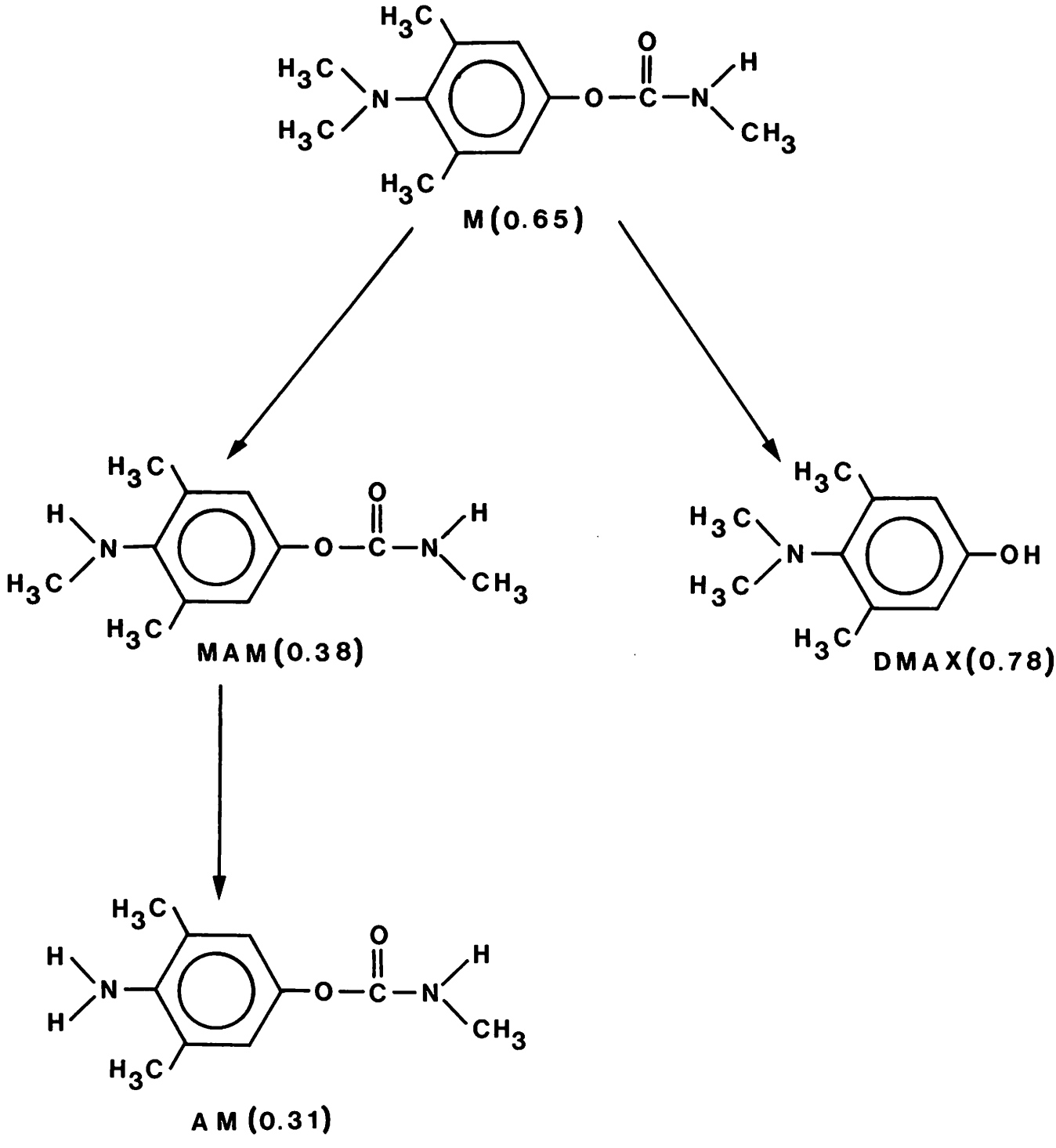


Figure 3.
Possible Degradation Routes Of Mexacarbate
In Some Aquatic Substrates

chemical in aquatic systems could thus be partly explained by the simultaneous degradation through hydrolytic and demethylation pathways as depicted in Fig. 3.

CONCLUSIONS

The research findings in the present spray trial showed that when a water-based mexacarbate formulation was applied twice by a fixed-wing aircraft, each at 70 g of A.I./ha over an aquatic ecosystem in a coniferous forest, only about 2% of the sprayed chemical reached the forest floor. The average droplet density, NMD and VMD respectively were 3.5 drops/cm^2, 20 µm and 36 µm. Maximum 1 h post spray concentrations of the chemical in stream and pond waters were 0.73 ppb and 18.74 ppb respectively. The residue level in stream waters disappeared very rapidly to below the detection limit (0.01 ppb) within 12 h but in pond waters it remained up to 3 d. The rapid loss was probably due to dilution and adsorption. Various physicochemical and microbial processes also could have played major roles. Only some aquatic plants such as cattails, manna grass and bog moss acted temporarily as sinks for mexacarbate. The maximum concentration found in one of them (cattails) was 720 ppb with a half-life of 3.9 h. Sediments and various aquatic animals including fish did not contain quantifiable levels (>10 ppb) of mexacarbate.

In the present era, unrestricted release of potent insecticides to control insect pests is viewed with extreme caution. From the present field study, it is apparent that mexacarbate with its high toxicity to target pests and low levels of persistence in the environment, could hardly pose any significant hazard to the forest ecosystem if safe and judicious use protocols have been followed.

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