

DISTRIBUTION, PERSISTENCE AND FATE OF
MATACIL® FORMULATIONS IN A STREAM
ECOSYSTEM

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INTRODUCTION

Aminocarb (Matacil®) insecticide [4-dimethylamine-m-tolyl N-methylcarbamate], as an oil soluble concentrate containing nonylphenol and a petroleum distillate Shell I.D. 585, has been used to control spruce budworm [*Choristoneura fumiferana* (Clem.)] since 1970. Recent concern over the effects of nonylphenol to aquatic organisms has caused explorative research to develop environmentally safe and ecologically acceptable Matacil® formulations without having any nonylphenol as an adjuvant and yet be as efficacious as the initial oil soluble concentrate.

Recently the Chemagro Chemical Company in Toronto (Ont.), marketers of Matacil® introduced a flowable (suspension concentrate) formulation of aminocarb (Matacil® 180F) without containing any nonylphenol adjuvant. Field studies were conducted during the summer of 1981 in a stream ecosystem to assess the distribution, persistence and fate of the new Matacil® 180F formulation (i) admixed with water and Atlox 3409F® surfactant as an emulsion (180 FE) and (ii) diluted with Shell I.D. (insecticide diluent - a petroleum distillate) 585 as an oil formulation (180 FO) and to compare these two formulations with the conventional oil soluble concentrate (180 D) containing nonylphenol and I.D. 585. The composition of the formulations is given in Table 1. The preliminary findings on the persistence, fate and dynamics of aminocarb present in these three formulations (180 FE, 180 FO and 180 D) following three separate stream injections are presented in this report.

MATERIALS AND METHODS

Experimental Site

The stream treatments were conducted in a small headwater trout stream (depth 10-50 cm, width 1-3 m) in the Goulais River watershed (Figs. 1 and 2) ca 50 km northeast of Sault Ste. Marie, Ontario.

Formulation 3 (180D) (Table 1) was first applied at site 1 of the downstream as marked in Fig. 2 on July 7, 1981 at 0740 h. After 1 week, during which sampling of different substrates (water, sediment and fish) at intervals were completed for residue analysis and monitoring, formulation 2 (180FO) was applied ca 250 m upstream at site marked 2 (Fig. 2). This procedure was repeated after a week for the formulation 180FE with a similar move upstream to the site 3 marked in Fig. 2. A far upstream section of the stream ca 300 m from site 3, served as the control for this study.

Spray Application

A "Micron ULVA Sprayer" was used to apply the aminocarb formulations. The applicator is capable of producing a narrow spectrum of droplet sizes with a VMD (volume-median diameter) of 70 μm . The sprayer was calibrated to emit ca 40 ml/min of water. In the field, the emission rate varied from 24 to 52 ml/min depending on the viscosity of the formulation. All the 3 applications were 5 minutes in duration. From the emission rate and estimated stream discharge, expected peak concentrations of aminocarb at the application sites were calculated and are recorded in Table 1.

Sampling of Substrates for Residue Analysis

Prior to each application, four sampling stations, 5, 50, 100 and 150 m from the spray location of each formulation were chosen for collecting surface (1 cm depth) water samples; sediment samples were collected from 5 and 50 m sites. Approximately 25 hatchery-reared rainbow-trout fingerlings (average length 13.3 ± 1.3 cm) were placed in cages (61 x 61 x 41 cm) a week earlier to the application at sampling stations 150 m (180FE) or 100 m (180FO and 180D) for the fish to get acclimatized to the new environment. Only one location served as the sampling station for water, sediment and fish in the control segment of the stream. Prespray and various post-spray samples of the three substrates were collected at intervals of time according to the established procedures.

Residue Analysis

Sampling, storage, transportation and final sample preparation of water, sediment and fish tissues were done according to the procedure developed in this laboratory. Extraction, cleanup and gas chromatographic (GC) analysis of the substrates were carried out according to the published methods developed by the author.

Results are presented in Tables 2 to 4. Samples from the control station did not show any positive response in the GC analysis.

Table 1
Compositions of Formulations and their application

No. of formulation	Designation of formulation and date of application	Composition of formulation (volume %)	Stream parameters Depth at the injection point (cm)	Water current (cm/sec)	Emission rate (ml/min)	Discharge (L/min)	Expected aminocarb concn.* (mg/L)
1	180 FE (0800 h EDT July 21, 81)	Matacil® 180F, 33.3 Atlox® 3409 F ¹ 1.25 Thodamine B ² dye 0.5 Water 64.95	4.6	9	32	600	3.20
2	180 FO (0755 h EDT July 14, 81)	Matacil 180F 33.3 I.D. 585 ³ 66.2 Automate B Red ⁴ dye 0.5	8.2	21	24	1,800	0.800
3	180 D (0740 h EDT July 7, 81)	Matacil 180D 33.3 Automate B Red dye 0.5 I.D. 585 66.2	13.2	34	30	6, 600	0.273

¹Atlox 3409F emulsifier supplied by Atlas Chemical Industries, Brantford, Ont., Canada.

²Rhodamine B (dye tracer) supplied by Allied Chemicals, Morristown, New Jersey, U.S.A.

³Shell insecticide diluent 585 supplied by Shell Canada Ltd.; Toronto, Ont., Canada.

⁴Automate B Red (dye tracer) supplied by Morton Williams Ltd., Ajax, Ont., Canada.

*[(Emission rate/stream discharge) x 180/3]

TABLE 2
Aminocarb Concentration (ppb) in Stream Water at Different Stations
After Spraying the Stream with Three of its Formulations

Time after spraying	Formulation 180 FE				Formulation 180 FO				Formulation 180 D			
	Sampling station from application (m)				Sampling station from application (m)				Sampling station from application (m)			
	5	50	100	150	5	50	100	150	5	50	100	150
Preaspray	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 min.	0.1	N.D.	N.D.	N.D.	301.9	N.D.	N.D.	N.D.	380.4	N.D.	N.D.	N.D.
3 min.	799.8	N.D.	N.D.	N.D.	3823.2	N.D.	N.D.	N.D.	1862.3	0.4	N.D.	N.D.
5 min.	1306.5	N.D.	N.D.	N.D.	15000.0	1.2	N.D.	N.D.	30.1	74.9	0.9	N.D.
10 min.	959.3	T	N.D.	N.D.	481.4	3.0	N.D.	N.D.	8.4	17.5	6.4	N.D.
15 min.	451.3	0.5	N.D.	N.D.	136.0	195.6	N.D.	N.D.	3.7	12.4	35.4	N.D.
20 min.	163.9	122.1	N.D.	N.D.	21.7	273.7	0.1	0.2	0.8	2.8	34.0	7.7
30 min.	28.5	363.0	N.D.	N.D.	3.3	13.8	127.2	0.2	0.1	0.3	2.4	25.0
1.0 h	2.2	15.9	256.1	0.3	0.6	3.9	29.1	109.5	N.D.	0.1	0.1	0.4
1.5 h	1.1	3.2	162.1	100.1	0.2	0.9	3.8	48.7	N.D.	N.D.	N.D.	0.1
2.0 h	0.5	1.0	33.5	109.7	0.2	0.3	1.5	15.9	N.D.	N.D.	N.D.	N.D.
3.0 h	0.3	0.4	3.6	38.6	T	0.2	0.1	0.4	N.D.	N.D.	N.D.	N.D.
4.0 h	0.2	0.2	1.3	4.7	N.D.	0.1	0.1	0.3	N.D.	N.D.	N.D.	N.D.
5.0 h	0.2	0.2	0.6	1.3	N.D.	N.D.	0.1	0.1	-	-	-	-
6.0 h	0.1	0.1	0.2	0.6	N.D.	N.D.	N.D.	0.1	-	-	-	-
9.0 h	N.D.	N.D.	0.1	0.1	N.D.	N.D.	N.D.	N.D.	-	-	-	-
25 h	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	-	-	-	-
50 h	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	-	-	-	-

T = Trace <0.1 ppb.

N.D. = Not detectable; detection limit 0.05 ppb.

TABLE 3

Aminocarb Concentration (ppb) in Stream Sediments

Time after spraying	Formulation 180 FE		Formulation 180 FO		Formulation 180 D	
	Sampling station from spray site		Sampling station from spray site		Sampling station from spray site	
	5 m	50 m	5 m	50 m	5 m	50 m
Prespray	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 min.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3 min.	3.5 (3.9)	N.D.	3.2 (4.0)	N.D.	T	N.D.
5 min.	20.2 (23.8)	N.D.	7.6 (8.6)	N.D.	T	N.D.
10 min.	9.4 (10.9)	N.D.	T	N.D.	N.D.	N.D.
15 min.	6.8 (7.9)	T	N.D.	N.D.	N.D.	N.D.
20 min.	3.5 (4.1)	T	N.D.	N.D.	N.D.	-
30 min.	T	T	N.D.	N.D.	N.D.	-
1.0 h	T	T	N.D.	-	-	-
1.5 h	N.D.	N.D.	N.D.	-	-	-
2.0 h	N.D.	N.D.	-	-	-	-
3.0 h	N.D.	N.D.	-	-	-	-

Residues in parenthesis were based on dry weight of sediment

T = Trace, <3 ppb based on wet weight of sediment

N.D. = Not detectable; detection limit 1.5 ppb based on wet weight of sediment

TABLE 4

Residues of Aminocarb (ppb)* in Rainbow Trout Fingerlings**
Kept in Cages on Stream-bed at Different Stations From
Site of Application of the Aminocarb Formulations

Time after spraying (hr)	Formulation and sampling station		
	180 FE (150 m)	180 FO (100 m)	180 D (100 m)
Prespray	N.D.	N.D.	N.D.
0.5	N.D.	T	17.1 ± 6.1
1.0	4.4 ± 3.2	4.6 ± 2.9	3.8 ± 2.8
1.5	85.1 ± 7.9	18.0 ± 4.9	T
2.0	106.6 ± 7.4	31.6 ± 6.7	N.D.
3.0	127.4 ± 8.8	T	N.D.
6.0	T	N.D.	N.D.

* Values are the mean of four determinations

** Average number of fish per cage (61 x 61 x 41 cm) = 25

Average mass of fish = 23.2 ± 6.4 g

Average length of fish = 13.3 ± 1.3 cm

T = Trace, <3.0 ppb based on wet weight of fish

N.D. = Not detectable; detection limit 1.5 ppb based
on wet weight of fish

DISCUSSION

The concentrations (ppb) of aminocarb present in the top 1 cm of water collected at different sampling stations and at different intervals of time following the stream injections are given in Table 2. Peak levels were found (1306.3 ppb and 15000.0 ppb) at 5 m downstream for the flowable (180F) after 5 min, whereas for the oil soluble concentrate (180D), a maximum (1862.3 ppb) was observed within 3 min. following the application. Evidently the maximum levels of the insecticide in surface layers are attributable for its poor mixing with the water column probably due to the presence of hydrophobic adjuvants in the formulation. Aminocarb itself has low solubility in water. When it is present as a solute in the petroleum distillate (180FO and 180D), then it will have a great tendency to concentrate near the surface as a slick than forming a solution or uniform suspension with the water column. Consequently the rate of movement of the surface layer downstream was rapid for the 180FO and 180D formulations primarily due to their hydrophobic nature coupled with high stream discharge (flow rate) (1,800 and 6,600 L/min respectively) noted at the injection site during the experiment. The comparatively slower downstream movement of aminocarb in 180FE is attributable to the hydrophilic nature of the Atlox® emulsifier in the formulation causing partial mixing of the insecticide in the water column and the slow flow rate (600 L/min) of the stream segment. These two factors also would explain the higher residue levels of aminocarb found at 150 m downstream 1.5 h after the application of the latter formulation. In all three cases, aminocarb

residues were not found after 9 h. In fact, the conventional oil soluble concentrate (180D) disappeared from the stream within 1 h followed by 180FO in 6 h. The causative factors for such a rapid loss of the chemical area largely due to dilution, followed by codistillation and to a lesser extent by dissolution and adsorption.

Aminocarb concentration in stream sediments (Table 3) were not high. The maximum concentration in sediment at the 5 m sampling station after 5 min following application, were 20.2 and 7.6 ppb (wet weight) for the new 180FE and 180FO formulations respectively which disappeared rapidly within a few minutes probably due to microbial activity, hydrolysis and desorption to aqueous phase. Aminocarb in the old oil based formulation (180D) was not adsorbed to sediment particles more than at 3 ppb (Trace) levels. Aminocarb concentrations in the sediment (Table 3) also reflect the influence of additives in the formulation and stream flow in deciding the overall accumulation and persistence of the insecticide in this substrate. Further studies in the laboratory under controlled conditions, are necessary to explain the role of additives in the uptake and degradation mechanisms of this chemical.

Residues of aminocarb found in caged rainbow trout fingerlings at intervals of time following the stream injections are recorded in Table 4. The maximum level of residue following a gradual build-up from non-detectable to 127.4 ppb was found in the tissues after 3 h with 180FE formulation. The residue was rapidly metabolized and after

6 h only trace amounts were found. Although concentrations were low, similar trends were also observed with the other two formulations again confirming the influence of additives on the uptake and accumulation of aminocarb in different substrates in the aquatic environment. This study shows that aminocarb appeared to be nonpersistent in the aquatic ecosystem and also non-toxic to fish at the applied dosage levels. No mortality or any noticeable unusual behaviour was observed in them during the study period. Hence the chemical in the three formulations (180FE, 180FO and 180D) studied exhibited low persistence, hence appears to be environmentally safe to be used as an insecticide.

SUMMARY AND CONCLUSIONS

1. Newly introduced aminocarb flowable (Matacil® 180F: a suspension concentrate) formulation was applied to different segments of a stream at intervals of time as (i) an aqueous emulsion (180FE) and (ii) as an oil formulation (180FO) along with (iii) the conventional oil soluble concentrate (180D) in I.D. 585.

2. Aminocarb residues disappeared very rapidly, within a few hours after injection, from the stream water primarily due to dilution and the rate of loss of the chemical was directly proportional to stream discharge.

3. Sediment samples contained extremely low but detectable levels of aminocarb for a short time.

4. The emulsion formulation (180FE) persisted in low amounts in water and sediments for a longer time compared to the two oil formulations (180FO and 180D) due to the presence of hydrophillic surfactant Atlox 3409 F®.

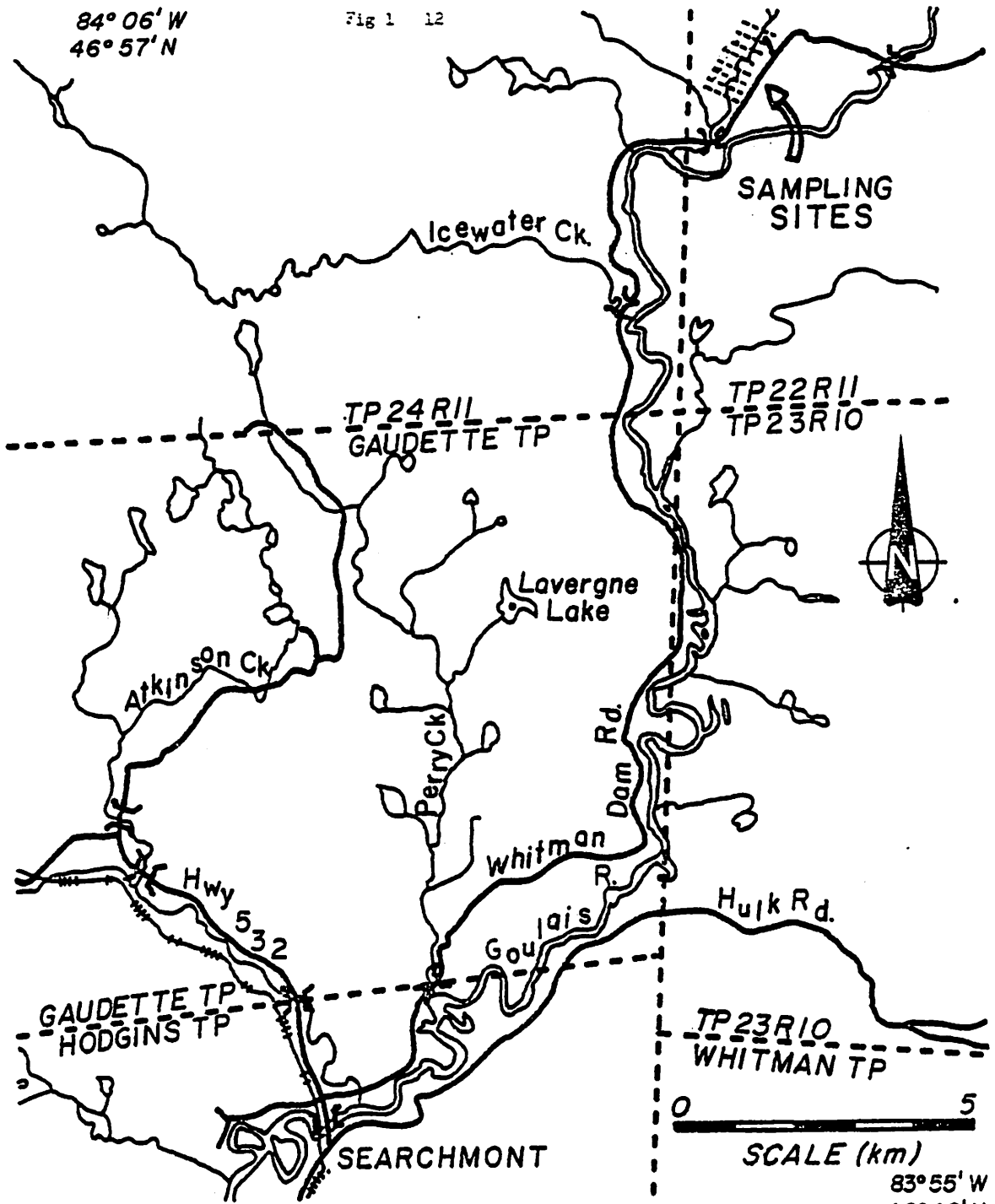
5. Caged fish samples contained low levels of aminocarb and the concentration varied according to the formulation injected. Usually the emulsion formulation resulted in noticeable accumulation of aminocarb in fish. No mortality or noticeable behavioural changes in fish were observed during the experimental period.

ACKNOWLEDGEMENTS

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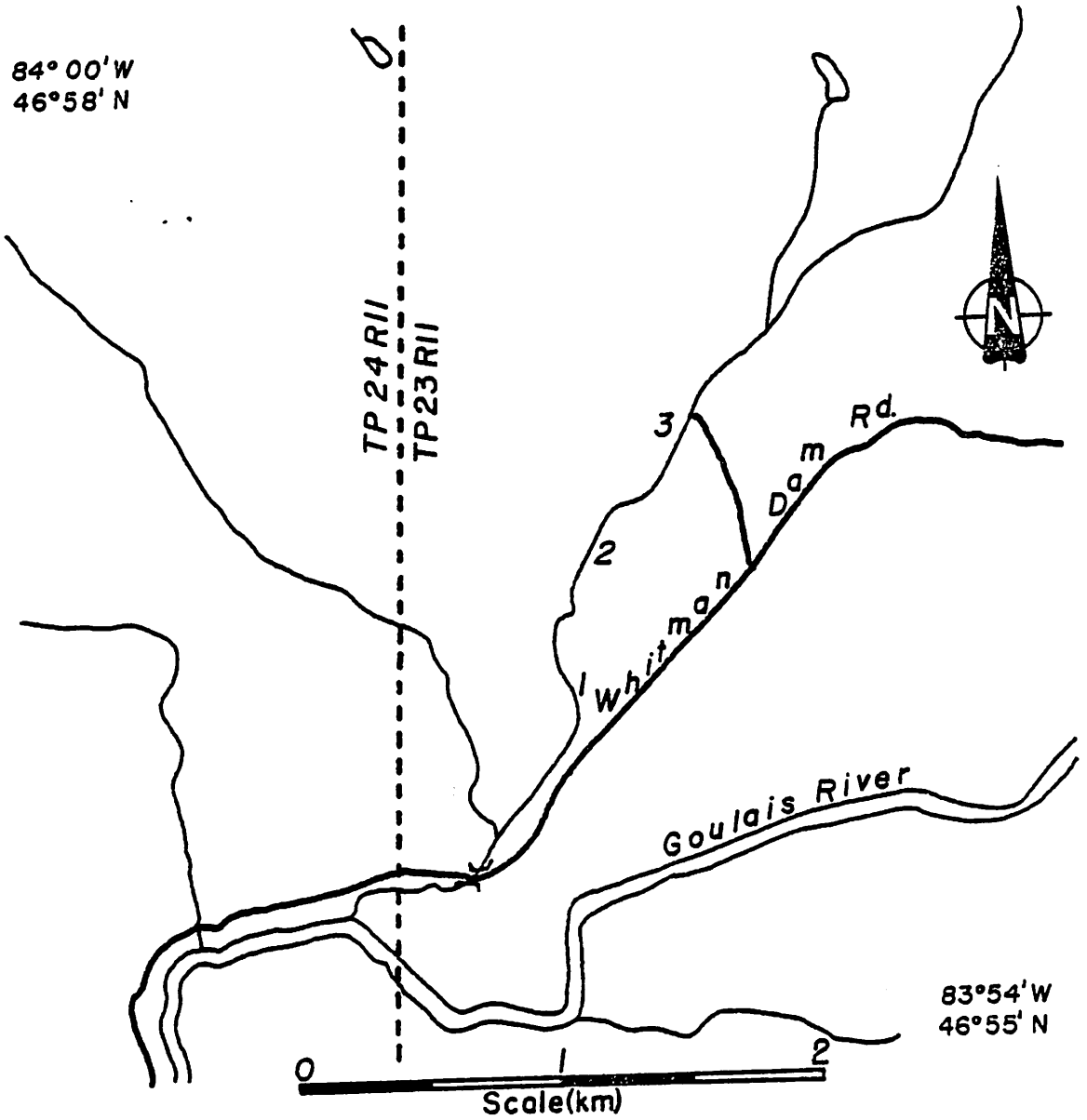
84° 06' W
46° 57' N

Fig 1 12



AMINOCARB EXPERIMENTAL RESEARCH
near SEARCHMONT ONTARIO.

83° 55' W
46° 46' N



**AMINOCARB STREAM INJECTION STUDIES
near SEARCHMONT ONTARIO**

APPENDIX I
Matacil® Concentration (ppb) in stream water
 Searchmont spray #0 - Aminocarb 180FE Containing Low
 Concentration of the active Ingredient

Time after application	Sampling position (meters)			
	5	50	100	150
1 min	31.30	N.D.	N.D.	N.D.
3 min	22.60	6.40	N.D.	N.D.
5 min	8.47	19.43	N.D.	N.D.
10 min	N.D.	10.13	29.20	T
15 min	N.D.	T	4.90	14.80
20 min	N.D.	N.D.	T	14.90
30 min.	N.D.	N.D.	N.D.	T
1 h	N.D.	N.D.	N.D.	N.D.
1.5 h	N.D.	N.D.	N.D.	N.D.
2 h	N.D.	N.D.	N.D.	N.D.
3 h	N.D.	N.D.	N.D.	N.D.
6 h	N.D.	N.D.	N.D.	N.D.
25 h	N.D.	N.D.	N.D.	N.D.

T = Trace < 0.1 ppb

N.D. = Not detectable; detection limit 0.05 ppb.

Stream water from control plot did not contain any aminocarb.

APPENDIX 2
SUMMARY OF THE ANALYSIS

1. <u>Samples analysed</u>		
water (regular 248 + control 28)		= 276
sediment (in triplicate)		
(regular 168 + control 6)		= 174
Fish (in quadruplicate)		
(regular 84 + control 12)		= 96
Total no. of samples analysed		= <u>446</u>
2. <u>Chemicals and other items used with</u> <u>estimated cost</u>		
Na ₂ Si ₄ (anhydrous, special grade)	40 kg	\$500
NH ₄ Cl (chemically pure)	0.5 kg	\$ 20
H ₃ PO ₄ (chemically pure)	0.5 kg	\$ 15
CH ₂ Cl ₂ (glass distilled)	45 L	\$200
Ethyl acetate (glass distilled)	100 L	\$600
Acetone	20 L	\$ 60
Gas for GLC		\$400
GLC accessories		\$200
Miscellaneous items (glass-wool, glassware, detergents, cleansing solvents, etc.)		<u>\$500</u>
Total cost		<u>\$2495</u>

(*No. overhead costs including, salary, operation and maintenance of GLCs and other instruemnts are included.)

3. PY spent in the study (Field and Laboratory) 265 days

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