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ENVIRONMENTAL INVESTIGATIONS OF THE 1980 SPRUCE BUDWORM SPRAY PROGRAM IN NEW BRUNSWICK

Major Contributors

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November, 1980

EPS-5-AR-81-3

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ACKNOWLEDGEMENTS

This report presents the results of research and monitoring activities conducted by the Environmental Protection Service, Atlantic Region, and Environment New Brunswick concerning the off-target effects of the 1980 New Brunswick spruce budworm spray program.

• K. Gordon (ENB), K. McLaggan (ENB), G. Julien (EPS) and W. Ernst (EPS) were responsible for the collection and analysis of field data. K. Doe (EPS) and R. Parker (EPS) conducted bioassay experiments and analyzed results. G. Pelly (EPS) and P. Silk (Research and. Productivity Council, N.B.) were responsible for chemical analysis of samples.

W. Ernst was responsible for interpreting data and compiling the manuscript.

Critical review was provided by H. Hall, G. Westlake, C. Duerden, K. Doe, R. Parker, G. Julien and K. Gordon.

J. Keating is gratefully acknowledged for patient and skillful typing of all manuscripts.

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ABSTRACT

This report describes environmental monitoring of the 1980 New Brunswick spruce budworm spray program by the Environmental Protection Service, Atlantic Region.

Field studies, conducted jointly with Environment New Brunswick, indicated that a 400 metre no spray "buffer zone" surrounding a small lake was sufficient to reduce the incidental deposit of formulation on the lake's surface by 92% and 80%, after first and second sequential sprays respectively, when compared with a similar lake which had no buffer zone. This observation was made after operational applications of fenitrothion at 210 g ai/ha in a water formulation using TBM aircraft equipped with TEE jet nozzles (11010 tips). A comparison of fenitrothion concentration in surface waters of the two lakes after the first application indicated a 56% reduction due to the buffer zone.

Laboratory toxicity studies were conducted on several species with some of the formulations, and their components which were used in 1980.

Nonylphenol toxicity was evaluated in lethal bioassays using rainbow trout (Salmo gairdneri) juveniles and embryos, and Daphnia pulex. The most sensitive organism to nonylphenol was Daphnia pulex followed by rainbow trout embryo and rainbow trout juveniles. While the LC50 values determined in these experiments were all greater than nonylphenol residues which are normally observed after forest sprays, they were also within the range of localized environmental concentrations which have been documented after seasonal maximum sprays.

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Bioassays were also conducted on rainbow trout and Daphnia in order to determine the toxicity of fenitrothion and Cyclosol 63, alone and in combination. Results indicated that the fenitrothion/Cyclosol 63 formulation is more toxic to rainbdw trout than a strictly additive treatment of the relative toxicity of its components would suggest. Concentrations of formulation as low as 32 ppb rapidly immobilized and ultimately proved lethal to Daphnia. The synergistic effect of fenitrothion and Cyclosol 63 in formulation may mean that safety margins to aquatic species in programs utilizing this formulation may not be as great as previously predicted.

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Résumé

Ce rapport decrit le contr8le environnemental du programme d'arrosage contre la tordeuse du bourgeon de l'epinette au Nouveau-Brunswick qui a ete fait par le Service de la Protection de l'Environnement de la region de 1'Atlantique.

Les etudes sur le terrain, faites de concert avec Environnement Nouveau-Brunswick ont constate qu'une zone tampon non arrosee de 400 metres autour d'un petit lac suffit, pour dimenuer la couche d'insecticide sur la surface du lac par 92 pourcent et 80 pourcent respectivement après les premier et deuxième arrosages, **et cela en comparaison avec un lac qui n'avait pas de zone tampon. Cette constatation a ete faite, apris des arrosages de fenitrothion a 210 gd, ingredients actifs par hectare dous une base d'eau et en se servant d'un avion TBM equipe d'ajutages de jet TEE (11010 pointes). Une comparaison de la concentration de fenitrothion dans les eaux de surface des deux lacs apres le premier arrosage a indique une difference importante due A is zone tampon.**

On a effectue des etudes de laboratoire sur la toxicite a certaines especes avec quelques-uns des insecticides et leurs composants qui etaient utilises en 1980.

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On a évalué la toxicité de nonylphénol dans des **essais mortels sur la truite arc-en-ciel (Salmo gairdneri) juvenile et embryon et sur Daphnia pulex. L'organisme le** plus susceptible à nonylphénol était Daphnia pulex et **deuxiimement la truite ars-en-ciel, embryon puis juvenile. Bien que les valeurs de LC5O determinees par ces experiences depassent tous les residus de nonylphenol qui sont normalement observes apres les arrosages de forit, elles etaient a portee des concentrations environnementales localisies qui ont ete constatees apres les arrosages maximums saisonniers.**

On a aussi effectue des tests biologiques sur la truite arc-en-ciel et Daphnia pulex pour determiner la toxicite de fenitrothion et Cyclosol 63, seul et en combinaison. Les resultats ont indique que l'insecticide fenitrothion/Cyslosol 63 est plus toxique pour la truite arc-en-ciel que ne laisserait croire un traitement purement additif de la toxicite relative de ses composants. Les concentrations d'insecticide aussi reduites que 32 pg./.1 ont vite immobilise et enfin tue les Daphnia. Les effets d'ordre synergique de fenitrothion et Cyslosol 63 en insecticide indiquent que la marge de sécurité pour les espèces aquatiques dans des programmes utilisant cet insecticide est peut-être **moindre que l'on ne croyait autrefois.**

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Investigations conducted by EPS, Atlantic Region, in 1980 with regard to the environmental behaviour and effects of forestry insecticide formulations consisted of two projects..

The first was a field project, conducted jointly with Environment New Brunswick, which was an attempt to determine the effectiveness of "no spray" or buffer zones in reducing the incidental deposit of spray formulations in non-target aquatic environments.

The second project was a laboratory toxicity χ^2 . **evaluation of several of the components of the spray formulations used in 1980, utilizing several species of aquatic.organisms. The chemicals tested were: fenitrothion, Cyclosol 63, and nonylphenol. The animals used .as test organisms were: Rainbow trout (Salmo gairdneri) juveniles and embryos, and water fleas (Daphnia pulex).**

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2 FIELD MONITORING

The protection of the aquatic environment from direct contamination by pesticides should be an important consideration during any aerial pesticide application, not only to reduce stress placed on aquatic organisms, but also to reduce the likelihood of spray chemicals entering domestic water supplies.

In New Brunswick, since 1978, regulatory agencies have required aerial spray operators to avoid spraying within 400 metres directly adjacent to, and surrounding, all bodies of water greater than 40 ha. These buffer zones, or no spray zones, have also been applied to all major rivers.

The rationale for applying the above stipulation to water bodies greater than 40 ha is that this is probably the minimum size that may be sighted from the air while allowing reaction time on the part of the spray pilots (K. Browne, (ENS), pers. comm.). The effectiveness of such buffer zones depends upon such variables as aircraft type, meteorological conditions, use of drift control agents, spray droplet size, spray formulation, and operator skill.

Studies conducted by EPS (Wilson and Wan, 1975) on aerial herbicide applications employing helicopter mounted spray equipment have determined that buffer zones of 50 metres were sufficient to reduce aquatic contamination. That study generally concluded, however, that fixed wing delivery, with higher air speeds and greater wing vortexing, requires greater buffer zone widths.

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During the past two years EPS, Atlantic Region, has attempted to evaluate the effectiveness of buffer zones employed in the New Brunswick spruce budworm spray program.

In 1979, two lakes, one greater than 40 ha (thus subject to buffer zones) and one smaller than 40 ha (which likely received spray to the margin), were sampled after an aerial spray program employing 85 grams of aminocarb per hectare. Analysis of water for aminocarb and nonyl phenol residues indicated a reduction in deposit of formulated materials as a result of buffer zone protection, however, reliable quantitative interpretations could not be made (EPS Unpublished Report).

The study, slightly elaborated, was repeated in 1980, in an effort to derive reliable quantitative data. The study in 1980, as in 1979, was a cooperative program between Environment New Brunswick and EPS.

2.1 Materials and Methods

Two lakes in fenitrothion spray blocks which were to be sprayed by TBM Avenger aircraft, and two lakes in Matacil spray blocks which were to be sprayed by DC 6 aircraft were selected as study sites. TBM aircraft were equipped with TEE jet nozzles which had 11010 tips and were calibrated to deliver a formulation of 11% technical fenitrothion, 1.5% Dowanol TPM, 1.5% Atlox 3409F, and 86% water at a rate of 210 g ai/ha. DC 6 aircraft had the same nozzles and tips and were calibrated to deliver a formulation of 26.7% Matacil 1.8 D and 73.3% 585 Diluent oil at a rate of 70 g ai/ha.

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Lakes selected according to the following criteria: one lake was excluded from a buffer zone requirement and the other was subject to a buffer zone requirement, similar morphology and water quality characteristics; similar topography and covering vegetation•of surrounding watershed; and occurrence of both lakes within the same spray block.

The two lakes which were selected for the TBM delivery comparison were situated in fenitrothion spray block 88 and were located in an isolated area approximately 20 miles west of Saint John. The smaller lake (Munsen) had a total area of 58 ha and a maximum depth of 8 m. The larger lake (Mosquito) had a total area of 98 ha and a maximum depth of 6.7 m. Forest Protection Ltd. agreed to spray the smaller lake to the margins and observe the set back on the larger.

Spray deposit samplers, which consisted of 15 mm x 150 mm glass petri plates mounted on wooden dowels• attached to styrofoam floats, were anchored on the lake surface according to the pattern indicated in Figures 1 and 2. Deposit samplers were deployed in strings approximately equidistant across the lakes with the closest shore stations 5 metres from the shore. Deposit plates were washed every evening and morning with pesticide grade hexanes in anticipation of spray. One hour after spray occurred, composite samples of deposit were made by rinsing 5 deposit plates (e.g. all of T1) with pesticide grade hexanes (approximately 5 ml) into 1 litre brown glass bottles which had previously been hexane rinsed and were sealed with caps lined with hexane washed aluminum foil. Composite samples, therefore, contained samples from several transects which paralleled **the shore (within 5 m) and several transects which ran the center of the lake. Collection of residue from deposit plates on Mosquito Lake after the first spray event deviated from this design in that all of those plates in transects perpendicular to the shoreline (i.e., transect ABCD) were pooled to make a composite sample. Samples were placed in ice and transported to the Halifax lab. Samples were evaporated down to 1 ml and analyzed for parent fenitrothion using a Hewlett Packard 7000 gas chromatograph equipped with alkali flame detector, an oven temperature of 190', and an 8 ft. 1/4" column of 3.6% 0.V. 101, 5.5% 0.V. 210.**

Water and sediment were sampled at 3 stations on each lake (Figures 1 and 2) which corresponded with the leeward, middle and windward portions of each lake, at several times post spray as well as prior to spraying. Water was sampled at the surface by immersing 1 litre • brown bottles, which had been soap and water washed and rinsed with distilled water and pesticide grade hexanes. The mouth of each bottle was held close to the surface in order to collect as much of the surface film as possible. Bottles were sealed using caps lined with hexane rinsed aluminum foil, placed on ice, and transported on ice in the dark to the Environment New Brunswick lab in Fredericton where they were extracted within 24 hours. Extracts were then shipped to the EPS lab in Halifax for analysis. Sediment samples were taken by hand in depths less than 2 m using washed (soap solution, distilled water and pesticide grade hexanes) wide mouth mason jars. An attempt was made to sample only the top 1 cm of sediment. Sample jars were capped with lids lined with hexane washed aluminum foil, placed in dry ice in the dark, and shipped to the EPS lab in Halifax where they were extracted and analysed.

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FIGURE 1 MUNSEN LAKE SAMPLE STATIONS

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FIGURE 2 MOSQUITO LAKE SAMPLE STATIONS

Surface water was sampled for dissolved oxygen, pH, and temperature at the above three stations. Precipitation events and windspeed were measured prior to and immediately after spray.

The sampling procedure was repeated for the second spray application.

The two lakes which were selected for the DC 6 delivery comparison were situated in the Matacil spray block 2 approximately 42 km northeast of Plaster Rock in the central portion of the province. The smaller lake, Blind Lake (Figure 3), had a total area of 15.4 ha and a maximum depth of 14.6 m. The larger lake, Britt Brook Lake (Figure 4), had a total area of 99 ha and a maximum depth of 5 m. By prior agreement, FPL ensured that the smaller lake received spray to its margins while the larger lake was protected by the 400 m buffer.

Sampling procedures duplicated those described above for the fenitrothion block with the exception that additional water samples were collected at 1, 10 and 66 hours post spray for nonylphenol analysis. These additional samples were preserved immediately with 25 ml dichloromethane and shipped to the IWD Water Quality Lab in Moncton for analysis.

2.2 Results

2.2.1 TBM Blocks

The first application in block 88, of fenitrothion at 210 g ai/ha, occurred on May 28. No precipitation occurred from the period 72 hours

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FIGURE 4 BRITT BROOK LAKE SAMPLE STATIONS

pre-spray to the time when the last sample was taken. Wind was from the north and averaged 3-5 km/hr.

The spray deposit measurement from plate washings taken 1 hr. after the first spray event are presented in Table 1.

TABLE 1 FENITROTHION RESIDUE DEPOSIT MEASURED FROM COMPOSITE PLATE WASHINGS AT 1 HR. AFTER FIRST SPRAY EVENT (MAY 28, 1980)

The second application in block 88, of fenitrothion at 210 g ai/ha, occurred on June 4th. Conditions at that time were wind from north at 5-8 km/hr with light precipitation. Approximately 1.25 cm of precipitation had occurred in the previous 48 hours. Precipitation amounted to .05 cm in 24 hours after spray.

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The spray deposit measurements from plate washings at 1 hour after the second spray event are presented in Table 2.

TABLE 2 FENITROTHION RESIDUE DEPOSIT MEASURED FROM COMPOSITE PLATE WASHINGS AT 1 HR. AFTER SECOND SPRAY1EVENt (JUNE 4,'1980)

LAKE	TRANSECT	TOTAL	% EMITTED
		DEPOSIT (g/ha)	DOSE
Munsen.		12.3	5.9
(smaller;	$\mathbf{2}$	11.3	5.4
unprotected)	3	6.9	3.3
	4	14.2	6.8
Mosquito		3.9	1.9
(larger;	$\overline{2}$	1.5	0.7
protected)		2.7	1.3
	4	1.5	0.7
	5	2.0	1.0

After both spray events, all deposit on plates from the unprotected lake were greater than on the plates from the lake protected by buffer zones.

A, **two tailed t test indicated a significant difference in the total deposit at 98% and 95% confidence limits between the two lakes for the first and second spray events respectively (Table 3). There was a 92.4% reduction and an 80.5% reduction in the total amount of deposit as a result of the buffer zone on the first and second applications respectively.**

SPRAY PERIOD	LAKE	MEAN DEPOSIT (g/ha)	STANDARD DEVIATION		t VALUE* CONFIDENCE PERCENT LEVEL	DIFFERENCE DUE TO
						BUFFER
1st	Munsen	15.8	3.1			0
	Mosquito	1.2	0.9	4.52	95%	92.4
2nd	Munsen	11.8	3.1			$\boldsymbol{0}$
	Mosquito	2.3	2.0	3.06	95%	80.5

TABLE 3 DIFFERENCE IN RESIDUE DEPOSIT DUE TO BUFFER ZONES IN FENITROTHION BLOCKS

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 t = $\overline{x}_1 - \overline{x}_2$, 0D = $\sqrt{\sigma \theta_1^2 + \sigma \theta_2}$,

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1 an where 601, is the standard error of sample 042 is standard error of sample 2.

Analysis of surface water 'samples (Table 4) indicated that the greatest concentration of fenitrothion occurred in the smaller unprotected lake. Maximum concentrations occurred between one and ten hours post-spray. Residue from the first spray was found at trace levels in the unbuffered lake at 148 hours after the first spray event.

TABLE 4 FENITROTHION RESIDUES IN SURFACE WATER

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TABLE 5 DIFFERENCE IN SURFACE WATER FENITROTHION RESIDUES AS A RESULT OF BUFFER ZONE UP TO 24 HRS. AFTER INITIAL SPRAY

The difference in the mean fenitrothion concentration in water between the two lakes up to 24 hours post spray was significant at the 80% confidence level (Table 5). The difference expressed as percent reduction in water concentration due to the buffer zone was 56%.

Fenitrothion residues were undetected in all sediment samples with the exception of two samples (Table 6). Both of these samples were collected from the windward end of the unbuffered lake at 10 hours after the second application. The higher of these concentrations was from a sample collected at the margin of the lake. A light foam was seen at the edge of the lake at this time.

TABLE 6 FENITROTHION RESIDUES IN SEDIMENT

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2.2.2 DC 6 BLOCKS

The application of aminocarb in Matacil block 2, at the rate of 70 g ai/ha, occurred on June 4. There was no precipitation in the period from 72 hours prior to spray to the final sampling. Wind was from the north and averaged 2 - 3 km/hr. Unfortunately, the spray aircraft made only one pass along the eastern edge of the unbuffered lake (Blind) and did not return. This meant that the lake would receive only one-half of the maximum spray deposit complement.

Spray deposit measurement from plate washings at one hour after the spray event are presented in Table 7.

TABLE 7 AMINOCARB RESIDUE DEPOSIT MEASURED FROM COMPOSITE PLATE SAMPLES AT 1 HOUR AFTER SPRAY

LAKE	TRANSECT	TOTAL RESIDUE g/ha	% EMITTED VOLUME 1.5 2.5 1.2	
Blind Lake . $(s$ maller; unprotected)		1.04 1.77 ₁ .28 .87		
Britt Brook (larger; protected)	5	trace .19 .54 1.51 .33	N.A. $\boldsymbol{\cdot}$ 3 \cdot 8 2.2 \cdot 5	

This table indicates generally higher residue deposit in the smaller, unprotected lake, however, a t test indicated that the difference in the means was not significant at the 80% level.

Analysis of surface water samples (Table 8) indicates that the highest concentration of aminocarb residue occurred in the lake with the buffer zone. Maximum concentrations occurred at 1 hr. post-spray. There was no significant difference between lakes in the mean aminocarb concentration.

Nonylphenol residue concentrations in surface water of Britt Brook Lake were maximal (12.0 µg/l) at one hour **post-spray (Table 8). They were undetectable (<1.0 ug/1) at 66 hours post-spray.**

Aminocarb residue concentrations in sediment were all below the 100 ppb detection level.

TABLE 8 AMINOCARB RESIDUES IN SURFACE WATER

TABLE 9 NONYLPHENOL RESIDUES IN SURFACE WATER ON BRITT LAKE (BUFFERED)

2.3 Discussion

While limited data are available which document the effectiveness of various buffer zone widths in reducing the incidental deposit of forestry insecticides on non-target environments, there have been several recent publications which deal with the problem of pesticide drift (Crabbe, et. al., 1980; Crabbe, 1979; Picot, et. al., 1980; and Wood in EMOFICO, 1980). Picot (1980) indicates that under conditions of moderate atmospheric stability, the drift of spray droplets beyond 300 m downwind of spray lines is of the order of 1% of the emitted mass of material. Crabbe (1979) and Crabbe, et. al. (1980) indicate, however, that because of evaporation of the carrier and diluent chemicals, most of the more distant drift is active ingredient rather than formulated material and suggest that 16% of the emitted active ingredient mass is still airborne at approximately 7.5 km under the same conditions.

The deposit data presented in Tables 1 and 2, suggest that drift of active ingredient was not as great as that described by Crabbe, et. al. (1980). This difference may be attributable to the phenomenon described in the model of Picot, et. al. (1980) which indicated that drift of aerosol clouds is greater under stable condtions than under conditions of slight turbulence (such as existed in this study).

Rather surprising is the fact that there was little difference in the composite samples from the same lake, which suggests that the spray cloud is dispersing evenly over the surface of the lake. This can probably be related to the limited number of samples.

The most significant result was the reduction in total deposit as a result of the buffer zone in the TBM block. The reduction of 92.4% and 80.5% in spray deposit when the buffered lake was compared to the unbuffered lake is probably the maximum protection that can be expected with a buffer zone of 400 m, due to the fact that meteorological conditions experienced during spray events (i.e. low wind) were conducive to minimal drift. The results demonstrate, however, that the 400 m buffer zone is adequate in reducing the incidental deposit of insecticide on non-target environments - at least for the use of a water based formulation applied with the described technology.

Little useful data were obtained from deposit measurements in the DC 6 block, due to the previously described problem of insufficient coverage to the unprotected lake. A comparison between the TBM/water formulation and DC 6/oil formulation cannot be made.

The reduction in deposit on plates as a result of the buffer in the TBM block was not directly reflected in the reduction of surface water residue concentrations. A reduction of 92.4% in deposit on plates after the first spray•event was accompanied by a reduction of only 55.5% in surface water residue concentration. Part of the reason that water concentration reduction does not mirror plate deposit reduction may be that peak water concentrations did not occur until 10 to 24 hours after spray. Since deposit plates were collected at 1 hour post-spray, it is probable that they were collected before total deposit had occurred. Since the smaller droplets would remain suspended the longest (Armstrong, 1979), they would be more subject to drift and their

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ultimate deposit on the water surface would tend to decrease the difference in deposit resulting from the buffer zone. Different rates of disappearance of the parent fenitrothion in the two lakes, due to microbial or chemical decomposition, may also explain the discrepancy between deposit sample comparisons and water concentration comparisons. For example, since it is known that fenitrothion decomposition occurs more slowly under conditions of low pH (NRCC, 1975) and since the pH of the larger, buffer zone protected lake, had a lower pH (5.7) than the smaller, unprotected lake (6.9), the fenitrothion residue may be disappearing at a more rapid rate in the smaller lake.

With two exceptions, fenitrothion residues were undetected in sediment samples. This is not surprising in light of the fact that monitoring efforts have consistently been unable to demonstrate significant concentrations of parent fenitrothion in sediments after operational sprays (Kingsbury, 1978a; Anon, 1977; Wells, et. al., 1979). It has been speculated (MaGuire and Hale - EMOFICO, 1980), that the absence of detectable concentrations of parent compound in sediments may be due to rapid microbial reduction to aminofenitrothion, which is tightly bound to organic compounds of the sediment.

The two sediment samples which registered detectable levels of fenitrothion were taken from the windward shore station at 10 hours post-spray during which time the wind had been between 5 to 18 km/hr. These exceptionally high values are thought to be due to the collection of a wind driven slick of formulation as

a light milky foam was seen along the edge of the lake at this time. This finding is evidence of the fact that natural forces may act to locally concentrate pesticide formulations and effects such as this must be expected to accompany even the most carefully conducted spray program.

While a comparative evaluation of the effect of the buffer zone on water aminocarb concentrations cannot be made at this time due to the above-described problem of incomplete spray coverage, comparisons may be made with the results of other investigators. The maximum aminocarb residue of 4.5 ppb found in Britt Brook Lake at 1 hour post-spray is greater than the maximum residues found by Sundaram, et. al. (1976) (2.1 ppb) and Holmes (1979) (3.3 ppb) after similar operational sprays. Other investigators (Coady, 1978; Holmes and Kingsbury, 1980) have found aquatic concentrations of aminocarb somewhat higher (24 ppb and 24.2 ppb) than those documented in this study, after operational doses of 90 g/ha and 175 g/ha respectively.

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The maximum nonylphenol concentrations observed in the surface waters of the buffered lake (12.0 µg/l) **were greater than those which Holmes and Kingsbury (1980) state would normally be found in water when nonylphenol is applied at twice the dose that occurred in this case.** They were much less than the 1,100 _ug/l maximum concen**tration which they observed in a local concentration, however. The disappearance of nonylphenol was rapid and is compatible with results presented in a later section of this paper.**

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3 BIOASSAYS

3.1 Nonylphenol

The aquatic toxicity and environmental behaviour of nonylphenol, an adjuvant comprising approximately 20% of the Matacil 1.8 D formulation, has been the subject of recent intensive investigation (Holmes and Kingsbury, 1980, McLeese, et. al., 1980). Enough concern was generated by the preliminary results of a number of investigators that a meeting was called by Agriculture Canada in November of 1979 with the purpose of determining whether sufficient data were available which would necessitate a change in the regulatory status of the Matacil formulation. It was concluded from this meeting that present data indicated that concentrations 'of nonylphenol which would be toxic to aquatic fauna would be unlikely under operational conditions. Further research into the aquatic toxicity and behaviour of the compound were strongly recommended.

The Environmental Protection Service, Atlantic Region, undertook several laborabory toxicity studies which were designed to further elucidate the contamination potential of nonylphenol.

3.1.1 Materials and Methods 3.1.1.1 Nonylphenol Juvenile Rainbow Trout Bioassay

Fingerling rainbow trout (Salmo gairdneri) from Goossens Trout Farm, Ontario were used in 4-day static bioassays. Water used in the bioassays was limed, fluoridated and chlorinated Dartmouth City water which was passed through activated charcoal filters and

ultra-violet sterilizers for dechlorination. In summary, this water was soft, slightly alkaline and has a low buffering capacity. Further characteristics of this water are presented in Appendix #3. Ten fish (average weight 1.4 gm+.4 cm, average length 5.2 cm+0.4 cm) were placed in 40 1 cylindrical tanks lined with rinsed polyethelene bags and observations made at exponentially decreasingly frequent intervals. All solutions were aerated at a rate of 100-200 ml/min. and a total of 6 toxicant concentrations were used. Stock toxicant solutions were mixed by combining 10 gm of practical grade p-nonylphenol (Eastman Kodak Co. Lot # A8D, Cat # P-7956) with 100 ml of ethanol and further diluting 10 ml of this solution into 90 ml of ethanol. Exposure concentrations were mixed by diluting the above stock toxicant into dechlorinated water. Controls included a diluent water control as well as a control which received as much ethanol as occurred in the highest toxicant concentration.

Actual nonylphenol concentrations were measured by G. Brun, Inland Waters Directorate (IWD), Moncton. Approximately 800 ml samples were withdrawn from treatment tanks into pre-hexane rinsedl litre amber bottles. Fifty ml pesticide grade hexanes were added, and the bottles capped with, hexane rinsed, aluminum foil lined screw caps. The samples were shipped immediately to the IWD lab (transit time less than 48 hours) where they were analyzed using HPLC according to the method of Brun and MacDonald (1975). Detection limits for this analysis are approximately 1 ppb for aqueous samples. Water for nonylphenol determinations was sampled at the beginning and end of the bioassays as well as at an intermediate time in some cases.

This assay was repeated using 5 fish (average weight 1.7+0.43 gm, average length 5.2+0.45 cm) per test concentration.

For the two tests, temperature, dissolved oxygen and pH were measured daily, and ranged from 15-16°C, 4.6-10.6 mg/1 and 6.2-8.3 respectively.

LC50 estimations were made from mortality data using a modified BMD 03S program (according to Dixon, 1970) where two or more partial mortalities were available, and graphically according to the method of Litchfield and Wilcoxon (1949) where fewer than 2 partial responses were available. Nominal concentrations were used for all determinations.

3.1.1.2 Nonylphenol Rainbow Trout Embryo Bioassay

Approximately 2000 Rainbow Trout (Salmo gairdneri) embryos at late development were obtained from Goossens Trout Farm, Ontario. Eggs were held for 3 days in a flow-through chamber which had a flow rate of 2 1/min, chlorine concentrations of 30-50 ppb, a temperature of 7° to 10.5°C, a dissolved oxygen content of 11.6 to 12.3 ppm, and a pH which ranged from 8.0 to 9.1. Three days after receipt of eggs, they were divided into 14 lots of 100 eggs each and placed in 1.0 litre uncovered open glass trays inside glass petrie dishes. Five separate concentrations of nonylphenol ranging from 90 ppb to 10,300 ppb (measured) as well as a diluent water and ethanol control were used; with 200 eggs per treatment. Toxicant concentrations were made up in the same manner as that described for fish. Water samples (800 ml) were taken in the same manner as previously

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described and shipped to IWD in Moncton for non-phenol analysis. All baths were continually circulated using magnetic stirrers. Static exposures of eggs to toxicant were 24 hours in duration, after which the eggs were removed and placed in a flow-through trough which was divided into chambers by plexiglass partitions. These chambers received water at a rate of 3 1/min, had a chlorine concentration of 15-50 ppb, a dissolved oxygen concentration of 11.6 - 11.9 mg/1, and a pH range of. 7.3 - 8.7. Temperature during the exposure ranged from 9.5- 11°C, however, a cooling system failure caused temperatures to rise to 20.0-28.5°C for approximately 12-24 hours during the experiment. Mortality observations were made daily and dead eggs removed. Criteria for death was opacity of yolk sac. Eggs were observed until total mortality or 90% hatch. An LC50 was calculated from the mortality data using a BMD 03S program and initial measured nonylphenol concentrations.

3.1.1.3 Daphnia pulex Bioassay

Individual water fleas (Daphnia pulex) were placed in uncovered 150 ml glass cylinders (31 mm x 95 mm) which contained 50 ml of toxicant solution. Solutions were mixed using water from Daphnia holding tanks which had been filtered and were non-aerated for the duration of exposure. All animals were at least 48 hours old at the commencement of exposure runs and were starved during the exposure period. Initial and final exposure solutions were analyzed for nonylphenol content by. IWD, Moncton.

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Tests took place in a temperature controlled incubator (temperature 23°C - 27°C with a photoperiod of 16 light, 8 dark). Six toxicant concentrations ranging from 13 ppb to 470 ppb (measured concentrations) were used to establish a 48 hour LC50. Ten animals were individually exposed to the toxicant at each concentration. Criteria for death was cessation of heartbeat and antennal movement.

3.1.2 Results

3.1.2.1 Nonyiphenol Loss

The demonstrated loss of nonylphenol from exposure tanks is presented in Table 10.

The loss of nonylphenol from exposure tanks was rapid and occurs most rapidly during the first 24 hours of exposure.

TABLE 11 TEST CONDITIONS

The above table indicates that while sufficient variability existed in test conditions to preclude definite conclusions, surface area to volume ratios of test containers may affect dissappearance of nonylphenol to the greatest extent. Water movement (aeration or stirring) may also have an effect on nonylphenol loss. It is possible to speculate that volatilization may be the primary route for nonylphenol disappearance.

3.1.2.2 Trout Embryo, Trout Juvenile and Daphnia Mortality Due to Nonylphenol Exposure

The trout embryo and larval mortality up to 72 hours after introduction to the toxicant is presented in Appendix 2. Many of the eggs began to hatch the day that they were introduced to toxicant. An LC50 was, therefore, calculated by means of a BMD 03S program using the total embryo and larvae mortality. An LC50, based on initial measured nonylphenol concentrations, and mortality occurring during 24 hours exposure to toxicant and up to 48 hours after being transferred to clean water was 484 ppb (95% fiducial limits 364 ppb - 604 ppb).

Table 12 compares the LC50 values established for trout embryos, trout juveniles and Daphnia pulex, based on nominal concentrations in the case of trout juveniles and Daphnia pulex and measured concentrations in the case of trout empryos.

TABLE 12 NONYLPHENOL LC50 VALUES FOR TROUT EMBRYOS TROUT JUVENILES AND Daphnia pulex

*** Confidence limits are 95% fiducial limits for probit analysis.** Indicates range (0%-100% Mortality).

The order of susceptibility to nonylphenol of the aquatic animals tested appears to be Daphnia pulex.> Rainbow Trout Embryos > Rainbow Trout Juveniles.

3.1.3 Discussion

The disappearance of nonylphenol from aqueous solution is rapid with up to 90% loss occurring in 48 hours. This is a less rapid disappearance for nonylphenol than that determined by Holmes and Kingsbury (1980) for residues in natural waters, however, it is much more rapid than the previously noted half-life of 2.5 days (open system) and 16.5 days (closed system) in spiked laboratory water samples (Szeto, 1979).

The possible routes of nonylphenol loss in aqueous systems may be due to volatilization, chemical or microbial breakdown and photodecomposition. While results presented here are not conclusive, nonylphenol disappearance would seem to be related most to surface area/volume ratios of the test containers and aeration, which leads to the speculation that volatilization is the primary route of disappearance. Further investigation into the primary route of nonylphenol loss is warranted. •

Ethanol, which was the chosen dispersant agent for the only slightly soluble nonylphenol has a 96 hour LC50 of approximately 8100 mg/1 to juvenile rainbow trout (EPS Atlantic Region unpublished data). Since the greatest ethanol concentration resulting from its use as a carrier in these experiments was 140 mg/1 it is felt that the contribution of ethanol to the overall toxicity is negligible. By comparison, 43.6 mg/1 and 386.6 mg/1

were the highest amounts used as a carrier in the Daphnia pulex and rainbow trout embryo exposures respectively.

The 96 hr. LC50 values obtained for rainbow trout juveniles (560-920 ppb) are comparable to those determined by McLeese, et. al. (1980) for Atlantic salmon (900 ppb) and those obtained by Holmes and Kingsbury (1980) for rainbow trout (230 ppb) and brook trout (145 ppb under field conditions). While our field observations in 1980 indicated that the concentration of nonylphenol in lake water after operational sprays of 70 gm ai/ha is approximately 1/60 of the acutely lethal dose to rainbow trout, other investigators (Holmes and Kingsbury, 1980) have determined that under certain conditions after application of the maximum registered dose of nonylphenol, concentrations that exceed the above LC50's are occasionally present in aquatic systems. Therefore, the potential exists for salmonid mortalities after operational sprays using the Matacil 1.8 formulation, given the limitations of present delivery technology which may result in higher than calculated spray deposit.

It was anticipated that the toxicity of nonylphenol to trout embryos would be much greater than the toxicity to juvenile fish due to the lipophilic properties of phenolic compounds (Anon, 1976) which would facilitate penetration of the zona radiata. The finding that nonylphenol was only slightly more toxic to embryos than juveniles is, therefore, somewhat surprising. These results may be partially explained by the shorter duration of the embryo exposure but may also be due to decreased membrane permeability as a result of alkyl side chains.

Rainbow trout (S. gairdneri) are not present in Atlantic Canada freshwater systems to any great extent. Where present, they are spring spawners (March to August) and hatch in 4 to 7 weeks, depending on water temperature (Scott and Crossman, 1973). The possibility exists, therefore, that they would be exposed to forest sprays as late stage embryos under conditions of early spawning and late spray. As well, embryos of fall spawning salmonids such as Atlantic. salmon (Salmo salar) and brook trout (Salvelinus fontinalis) could be exposed to forest sprays if spraying occurred early and water temperatures had been cold during development.

Given the above, the potential for embryo and early life stage mortality as a result of forest spraying with the present Matacil formulation does exist and this potential appears to be greater with embryos than with more developed fish.

Daphnia pulex were found to be more sensitive to nonylphenol than rainbow trout and toxic concentrations were within the range of aquatic residues detected by Holmes and Kingsbury (1980) after simulated maximum allowable seasonal dosages of nonylphenol.

Daphnia, and cladoceran species in general, are important constituents of lacustrine systems. The above results indicate that there may be mortality to these animals as a result of forest spraying with Matacil formulations. The effects that such mortality would have on higher trophic levels remains to be determined and is worthy of further investigation.

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3.2 Fenitrothion Cyclosol Formulations

Cyclosol 63 is a registered insecticide solvent oil which was used in New Brunswick for the first time in 1980. It is a heavy aromatic oil (specific gravity = .881 - .898 at 15.6° C), has a moderately high boiling point (179° C - 207° C), reasonably low vapour pressure (3.0 at 38° C), and is negligibly soluble in water.

Forest Patrol Ltd. used a formulation containing 23.6% technical fenitrothion and 76.4% Cyclosol 63 on approximately 450,000 acres of the J.D. Irving Co. freehold property in 1980.

Since the above use is new to New Brunswick, involves areas of significant size, and may portend future shifts to this formulation by all forest sprayers, the Environmental Protection Service, Atlantic Region, conducted tests in the past year to determine the toxicity to aquatic fauna of Cyclosol 63 and the fenitrothion/Cyclosol 63 formulation.

3.2.1 Material and Methods

The spray formulation mixing tanks at the Clearwater airstrips on the J.D. Irving freehold property were grab-sampled on June 8, 1980 and a total of four gallons of mixed spray formulation (23.6% technical fenitrothion and 76.4% Cyclosol 63) were placed in hexane washed glass bottles and shipped immediately to the EPS Halifax lab where they were stored at 4° C in the dark until bioassays were run.

Technical grade Cyclosol 63 was donated by Shell Canada Ltd. It was also stored at 4° C in the dark until bioassays were run.

Technical grade fenitrothion was donated by Forest Protection Limited and was stored under the above described conditions prior to its use in bioassays.

Bioassays were conducted on rainbow trout fingerlings and Daphnia pulex using fenitrothion, Cyclosol 63, and the formulated fenitrothion/Cyclosol 63 mixture as stock toxicants. Conditions duplicated those described for the nonylphenol bioassays. In the juvenile trout bioassays, fish weights ranged from 6.62 g to 10.52 g and fish lengths ranged from 8.0 cm to 9.9 cm. Temperature in these bioassays ranged from 13.-26°C, pH ranged from 6.5 to 9.3 and dissolved oxygen ranged from 8.8 to 10.7 mg/l. In the Daphnia pulex bioassays, temperature ranged from 21.5 - 26.5°C, pH ranged from 6.7 - 7.4, and dissolved oxygen ranged from 6.9 - 9.1 mg/1. Initial and final measurements of fenitrothion concentrations were made at the Halifax EPS laboratories using a HP7000 gas chromatograph. No technique presently exists for the analysis of Cyclosol 63 at low concentrations and, therefore, LC50 values for Cyclosol 63 alone are based on nominal concentrations. LC50 calculations for Cyclosol 63/fenitrothion were based on fenitrothion concentration measurements and a presumed fenitrothion/Cyclosol 63 content of 23.6% and 76.4% respectively in the sampled formulation.

3.2.2 Results

A comparison of the toxicity of fenitrothion, Cyclosol 63, and the formulation consisting of a mixture of the two is contained in Table 13.

TABLE 13 TOXICITY OF FENITROTHION, CYCLOSOL 63 AND FORMULATIONS TO AQUATIC FAUNA

* Indicates concentration at which Daphnia pulex were immobilized.

In the case of rainbow trout juveniles, the technical fenitrothion was most toxic, the fenitrothion/ Cyclosol 63 formulation about half as toxic as technical fenitrothion and Cyclosol 63 alone was least toxic.

The fenitrothion/Cyclosol 63 formulation was more toxic to Daphnia pulex than either fenitrothion or Cyclosol 63 alone. The fenitrothion/Cyclosol 63 formulation was at least two orders of magnitude more toxic than the Cyclosol 63 alone. It was also observed that the fenitrothion/Cyclosol 63 formulation was very effective at mobilizing Daphnia. At 0.032 ppm, the lowest concentration tested, all of the test animals had ceased actively swimming and had sunk to the bottom of the test container, within 4.5 hours of being introduced to the toxicant solution. Similar results were obtained with the technical fenitrothion. At 0.1 ppm, the lowest concentration tested, all test animals had ceased actively swimming within 2 hours of being introducted to the toxicant solution.

3.2.3 Discussion

The Cyclosol 63 solvent oil is much more toxic to aquatic fauna than previously used solvents. For example, fuel oil #2 and #4 has a 96-hour LC50 to rainbow trout of 1000 mg/1 (Lord et. al., 1978), which is almost two orders of magnitude greater than the Cyclosol 63 toxicity determined in these tests.

The four day LC50's for technical fenitrothion determined in these tests agrees with the finding of other investigators (Lord, 1978, Anon, 1974).

By calculating component toxicities, (Sprague, 1970) it can be determined that the fenitrothion/Cyclosol 63 formulation is more toxic (5.0 ppm) to rainbow trout than a strictly additive treatment of the relative toxicity of its components would suggest (i.e. 23.6% x 1.9 + 76.4 x $18.5 = 14.6$.

The LC50 values obtained for the technical grade fenitrothion in the Daphnia tests are difficult to compare with those documented by Symons (1977) for Daphnia pulex but appear to be in the same range. Tests with the formulation indicate that very low levels (<0.032 ppm) will cause rapid immobilization and subsequent mortality. It remains to be determined, however, whether the immobilization is reversible and tests are planned to further investigate this effect.

The fact that the fenitrothion and Cyclosol 63 have a synergistic effect with regard to toxicity on the freshwater fauna tested is of some concern. What this means is that the active ingredient is not the sole source of toxicity in these formulations. In the past, environmental monitoring has been concerned with documenting the residues of active ingredient in the environment after forest sprays. Such monitoring has indicated that maximum concentrations of parent active ingredient are at least two orders of magnitude less than the 96 hr. LC50's for aquatic vertebrates (Lord, et. al., **1978) and are close to the lethal levels for several species of aquatic invertebrates (Symons, 1979). The results in this report indicate that the margins of safety to aquatic fauna may be less than that which has been based on measurement of active ingredient alone. This conclusion when considered in relation to the limitations**

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of control over operational programs, and such possibilities as swath-overlap which lead to deposit greater than intended, may mean that presently conducted spray programs can produce environmental concentrations of total formulation which are closer to lethal thresholds for certain fish species than previously predicted.

- **Anonymous, 1974. Trade Memoranda of Canada, Department of Agriculture, Ottawa, October, 1974.**
- **Anonymous, 1976. The Merck Index: An Encyclopedia of Chemicals and Drugs, Ninth Edition. ed. M. Windholz, S. Budavari, L.Y. Stroumtsos, M.N. Fertig. Publ. Merk & Co. Inc., Rahway, N.J. U.S.A.**
- **Anonymous, 1977. A Preliminary Report on EPS Monitoring of the 1977 Spruce Budworm Spray Program in New Brunswick. Unpubl. EPS Report.**
- **Armstrong, J.A., 1979. Effect of Meteorological Conditions on the Deposit. Pattern of Insecticides. Mosquito News 39: 10-13.**
- **Brun, G.L. and R.M. MacDonald, 1979. Analysis of Nonylphenol in Water and Sediment by High Performance Liquid Chromatography. Environment Canada, Unpublished Report, Environment Canada, Moncton, N. B.**
- **Buikema, A.C., Jr., M.J. McGinniss and J. Cairns, Jr., 1979. Phenolics and Aquatic Ecosystems: A Selective Review of Recent Literature. Marine Environ. Rpt. 2: 87-181.**
- **Coady, L.W., 1978. Immediate Chemical and Toxicological Influences of Aerially Applied Fenitrothion and Aminocarb in Selected Newfoundland Streams: Summary Report on 1977 Field Monitoring. EPS Surveillance Report, Atlantic Region, EPS-5-AR-78-1.**
- **Crabbe, R.S., 1979. A Gradient-transfer Model for the Long Range Drift and Deposition of an Aerosol Cloud. NRCC National Aeronautical Establishment Laboratory. Report LTR-UA-47.**
- **Crabbe, R., L. Elias, M. Krzymien and S. Davie, 1980. New Brunswick Forestry Spray Operations: Field Study of the Effect of Atmospheric Stability on Long-range Pesticide Drift. NRCC National Aeronautical Establishment Laboratory Report LTR-UA-52.**
- **Dixon, W.J. (ed.), 1970. Biomedical Computer Programs, University of California Press, Berkeley, Calif. 600 p.**
- **EMOFICO, 1980. Environmental Surveillance in New Brunswick, 1978-79. Effects of Spray Operations for Forest Protection Against Spruce Budworm. Compiled by: I.W. Varty, Chairman, Publ. University of New Brunswick.**
- **Holmes, S.B., 1979. Aquatic Impact Studies of a Spruce Budworm (Christoneura fumifera Clemens) Control Program in the Lower St. Lawrence Region of Quebec in 1978. Forest Pest Management Institute Report FPM-X-26.**
- **Holmes, S.B. and P.D. Kingsbury, 1980. The Environmental Impact of Nonylphenol and the** Matacil **Formulation, Part 1: Aquatic Ecosystems. Forest Pest Management Institute Report FPM-X-35.**
- **Kingsbury, P.D., 1978a. A Study of the Distribution Persistence and Biological**. **Effects of Fenitrothion Applied to a Small Lake in an Oil Formulation. Forest Pest Management Institute Report FPM-X-13.**
- **Kingsbury, P.D., 1978b. Aquatic Impact Studies by FPMI in Quebec Spruce Budworm Spray Blocks, 305, 1979. Forest Pest Management Institute Report FPM-X-12.**
- **Litchfield, J.T. and F. Wilcoxon, 1949. A Simplified Method of Evaluating Dose-Effect Experiments.**. **J. Pharmacol. Exp. Ther. 96: 99-113.**
- **Lord, D.A., R.A.F. Matheson, L. Stuart, J.J. Swiss, P.G. Wells, 1978. Environmental Monitoring of the 1976 Spruce Budworm Spray Program in New Brunswick, Canada. Environmental Protection • Service, Atlantic Region, Surveillance Report. • EPS-5-kAR-78-3.**
- **McLeese, D.W., V. Zitko, C.D. Metcalfe and D.B. Sergeant, 1980. Lethality of Aminocarb and Components of the Aminocarb Formulation to Juvenile Atlantic Salmon, Marine Invertebrates and a Freshwater Clam. Chemosphere: 9: 79-82.**
- **National Research Council of Canada Associate Committee on Scientific Criteria for Environmental Quality, 1975. Fenitrothion: The Effects of its Use on Environmental Quality and its Chemistry. Publ. No, NRCC 14104 of the Environmental Secretariat.**
- **Picot, J.J.C., D.D. Kristmanson, B. Chitrangad, G. Henderson, 1980. Near Field Drift in Aerial Spraying. Dept. of Chemical Engineering, University of New Brunswick, Fredericton, N.B. Technical Report.**
- **Scott, W.B. and E.J. Crossman, 1973. Freshwater Fishes of Canada. Fisheries Research Board of Canada. Bull 184, Information Canada, Ottawa.**
- **Sprague, J.B., 1970. Measurement of Pollutant Toxicity to Fish II Utilizing and Applying Bioassay Results. Water Research 4: 3-32.**
- **Sundaram, K.M.S., Y. Volpe, G.G. Smith and J.R. Duffy, 1976. A Preliminary Study on thg Persistence and Distribution of Matacil in a Forest Environment. Chemical Control Research Institute Report CC-X-116.**
- **Symons, P.E.K., 1977. Dispersal and Toxicology of the Insecticide Fenitrothion; Predicting Hazards of Forest Spraying Residue Reviews: 38: 1-36.**
- **Szeto, S., 1979. Minutes: Nonylphenol/Matacil Meeting, November 14, 1979. Plant Products and Quarantine Division, Ottawa, Ontario.**
- **Wells, P.C., R.A. Matheson, D.A. Lord and K.G. Doe, 1979. Environmental Monitoring of the 1978 Spruce Budworm Spray Program in New Brunswick, Canada - Field Sampling and Aquatic Toxicity Studies with Fish. Environmental Protection Service, Environment Canada, Halifax. EPS-5-AR-79-1.**
- **Wilson, D.M. and M.T.K. Wan, 1975. Effectiveness of Stream Buffer Zones During Aerial Applications of Chlorophenoxy and Picloram Herbicides. Pollution Abatement Branch, Environmental Protection Service, Pacific Region, EPS-5-PR-75-3.**

APPENDIX 1

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 $\begin{aligned} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} & = \frac{1}{2}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \end{aligned}$

MEAN SURFACE WATER QUALITY VALUES FROM N.B. LAKES MONITORED BY EPS IN 1980 BUDWORM PROGRAM

APPENDIX 2

CUMULATIVE EGG AND LARVAE MORTALITY (PERCENT) EXPOSED TO NONYLPHENOL

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APPENDIX 3

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SUMMARY OF WATER QUALITY PARAMETERS. DECHLORINATED DARTMOUTH CITY WATER. EPS FISH LABS, BEDFORD INSTITUTE OF OCEANOGRAPHY. MARCH - JULY, 1980.* TEMPERATURE AND pH ARE FOR INCOMING WATER AND DO NOT REPRESENT ACTUAL TEST CONDITIONS

*** Most of the bioassay tests.included in this report were conducted during this period. Tests on technical grade fenitrothion were conducted later, but this water quality data was not available at the time of writing.**

**** On one day, the value reached 70 ppb. Usually.<30 ppb and most often non-detectable (ND).**

Environment Canada - Environmement Canada Environmental investigations of the 1980 spru
ce budworm spray program in New Brunswick ERNST, B 7014072D TD 172 C3352 NO. 81-3 C.1 **NSDE**