

ROLE OF THE TOXIC CHEMICALS SECTION IN  
THE FIELD AND LABORATORY STUDIES  
CONDUCTED DURING 1981

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## Introduction

Among the various control methods available for the forest pests in Canada, aerial application of the insecticides is still by far the most effective and economical method for large scale spray operations. Currently large quantities of environmentally acceptable and ecologically safe organophosphate and carbamate insecticides are sprayed every year over large areas of forest for spruce budworm control. The primary objective of the Toxic Chemicals Section at Forest Pest Management Institute is, in addition to methods development for the toxic components and their adjuvants, to study the environmental fate, persistence, toxicity and dynamic cycling of the released materials in different components of the ecosystem and to generate data on their usefulness, compatibility, biological consequences and overall environmental safety. This report outlines some of the major advances made in laboratory and field studies conducted during the year 1981.

*Distribution, persistence and fate of three aminocarb [flowable oil (180 FO) and emulsion (180 FE) and an oil (180 D)] formulations in a forest environment*

Recent controversy over the environmental affects of nonylphenol, an adjuvant of commercial aminocarb oil formulation, has led to research on new aminocarb formulations. Using the new aminocarb flowable formulation admixed with water (180 FE) and mixed with I.D. 585 oil (180 FO) and the conventional oil formulation containing

nonylphenol mixed in Sunspray 7N oil (180 D), the dynamics and deposition patterns of aminocarb as well as its persistence and fate was studied in a forest near Bathurst, N.B., and in a headwater trout stream near Searchmont, Ont. Following the spray application, twice at 70 g AI/ha, deposition on glass plates, aminocarb concentration in fir foliage, soil and litter, samples were measured by GLC at intervals of time. Droplets deposited on Kromekote cards were also counted and sized. Similar measurements were conducted on water, sediment and fish samples collected at intervals after injecting the stream with the three formulations using a "Micron ULVA" sprayer.

Deposit concentrations in foliage, soil and litter were small but varied according to the additives present in the formulations. The oil formulations 180 D and 180 FO, gave in foliage (fresh weight) initial concentrations of 2.76 and 2.27 ppm, compared to the emulsion (water based) formulation 180 FE, of 2.41 ppm. The active material dissipated rapidly from all the three substrates; again the rate of dissipation was found to be influenced by the additives present and followed the order: 180 FE > 180 FO > 180 D. After 21 days following the second application, the concentrations in foliage (as sampled) were 0.34 ppm for 180 FE, 0.78 ppm for 180 FO and 1.64 ppm for 180 D. Although the concentrations were low the insecticide persisted longer in forest litter compared to the soil.

There was a wide variation in deposits on the glass-plate-Kromekote card collection units. Deposits under the tree and in the openings were not significantly different due to channelling effects and turbulence under the canopy. Assessment of deposits on ground, in random locations over the entire plot, indicated that only a small fraction of the insecticide in the emulsion formulation (180 FE) reached the forest floor compared to 180 D. This was also evident from the droplet density measurements using Kromekote cards. No correlations could be established between droplet densities and foliar concentrations.

In the stream ecosystem studies following the injection of the three formulations, the patterns were entirely different. The emulsion formulation (180 FE) persisted in low amounts in water and sediment for a longer time compared to the two oil formulations (180 FO and 180 D). This is anticipated because of the influence of hydrophilic surfactant, Atlox 3409®. Caged fish samples collected from the stream treated with 180 FE, contained low levels of aminocarb and its common metabolite MA. In general, the disappearance of the chemicals (AI and MA) from the stream ecosystem were rapid primarily due to dilution effect whereas in the forest ecosystem, physical factors could have played a major role in the dissipation of AI.

*The dissipation of nonylphenol in an aquatic model ecosystem*

Nonylphenol, a major component in the commercial formulation of Matacil® has been incriminated for the mortality of various aquatic organisms such as juvenile Atlantic salmon and certain species of marine and fresh water invertebrates. This study was undertaken to investigate the stability and dynamics of nonylphenol in a static aquatic environment and examine whether the adjuvant under operational doses could really pose a threat to the aquatic organisms.

The dissipation of 1.0 ppm of nonylphenol in stream and pond water, incubated in flasks at 16°C under simulated field conditions up to 44 days indicated that the half-life ( $T_{1/2}$ ) was 2.5 days if the flasks were open, 16 days if they were closed showing that even at this very high concentration (20-50 fold high) of the adjuvant compared to spray conditions, it dissipated rapidly. A transformed polar product (could be a hydroxylated metabolite) was detected in the closed flasks.

Translocation of nonylphenol in water occurred when treated water samples were incubated in the presence of sediment. After 10 days, nonylphenol was detected only in the sediment, but not in water. About 80% of the nonylphenol was degraded in 71 days, but no degradation occurred if the water and sediment were autoclaved prior to incubation indicating the role of microbes in the dissipation process of the adjuvant.

*Studies on the influence of adjuvants present in the spray formulations of fenitrothion and aminocarb on foliar deposition and persistence*

The role of additives and volume expanders in the tank-mixes often influence the distribution deposition and persistence of pesticides. This important area has been either ignored or received only partial treatment in the past. An indepth study has been undertaken and some of the current findings are summarized below.

Foliar deposition and persistence of fenitrothion and aminocarb was studied following simulated aerial application on to white spruce trees. Foliar concentrations were measured by gas-chromatography.

The additives in the formulation played a significant role in the degree of foliar deposition and persistence, thereby influencing the biological activity of the spray mixture. A volatile and low-viscous solvent gave rise to low foliar deposition and persistence of the active ingredient. In this respect fuel oil appeared to be a better diluent than Arotex® with both insecticides. With aminocarb, however, nonylphenol showed definite advantages over other additives, as it gave rise to the highest foliar deposits and persistence.

*The persistence and fate of chlorpyrifos-methyl (Reldan®) in a forest environment and in two aquatic model systems*

Reldan® was applied twice at 70 g AI/ha by aircraft to a mixed coniferous forest in New Brunswick. Residue in balsam fir foliage was 1 ppm wet weight 1 hr

after spraying and rapidly declined, but persisted at ca. 0.03 ppm for 125 days. Reldan® persisted longer in forest litter than in soil. In stream water the residue dissipated to less than 10% of the initial concentration within 3 hours and was not detected after 4 days. Sediment samples contained less than 0.1 ppm wet weight up to 10 days. Brook trout and slimy sculpin captured in the stream within 3 days of the second application contained ca. 0.05 ppm (fresh weight) of residues but they disappeared rapidly.

Two aquatic models were set up separately in an environmental chamber at 15°C to investigate the movement, metabolism and persistence of 400 ppb chlorpyrifos-methyl in flooded soil and the behavior and degradation of 200 ppb of this chemical in natural water. Model I consisted of a 4.5 cm bottom layer of uncontaminated sandy loam, a 1.5 cm second layer containing 400 ppb of chlorpyrifos-methyl, and 80 l of lake water in a 100 l glass aquarium. Model II was similar, except all soils were uncontaminated and the water contained 200 ppb of chlorpyrifos-methyl. Both models and a control were held in an environmental chamber at 15°C for 90 days.

Chlorpyrifos-methyl was strongly adsorbed on the soil particles even when flooded; very little had desorbed and then dissolved in water. The maximum concentration in the water of Model I was 1 ppb, detected 0.7 days after incubation. Chlorpyrifos-methyl

metabolized rapidly in the flooded soil; the major breakdown product was 3,5,6-trichloro-2-pyridinol. While the concentration of the parent compound in the flooded soil declined that of the pyridinol increased gradually and reached a maximum in about 27 days, then declined thereafter. The pyridinol was never detected in water. Both compounds were almost completely dissipated in 90 days.

In Model II chlorpyrifos-methyl moved rapidly from the water to the flooded soil. After incubation for 13 days, its concentration increased from non-detectable to a maximum of 560 ppb in the flooded soil, but decreased from 200 ppb to 40 ppb in the water. Both chlorpyrifos-methyl and its breakdown product, 3,5,6-trichloro-2-pyridinol, were readily degraded in soil and water; only 0.1 ppb and 10 ppb remained in the water and in the flooded soil respectively after incubation for 83 days.

*Toxicity of aminocarb flowable formulation 180 F to fish and its in vivo metabolism*

Fingerling rainbow trout (*Salmo gairdneri* Richardson) were used to determine the lethal toxicity of Matacil® 180 F and Matacil® 180 D ready-to-use formulations. The 96 h LC<sub>50</sub>s were 21.3 mg/l for water-based Matacil® 180 F; 29.1 mg/l for oil-based Matacil® 180 FO and 0.36 mg/l for Matacil® 180 FE.

Aminocarb (4-dimethylamino-m-tolyl N-methylcarbamate) and MA (4-methylamino-m-tolyl N-methylcarbamate) were detected in fish tissue 96 h after exposure. More than 50% of the total residue (Aminocarb + MA) were the parent compound. The bioaccumulation ratio ranged from 1.70 to 3.32 at different concentrations of aminocarb. Both aminocarb and MA were rapidly eliminated after the fish had been transferred to clean water; the total residue declined by more than 90% in 72 h and became nondetectable in 96 h.