Spray Deposition Pattern of Aminocarb Formulations of Variable Physicochemical Properties

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- improper title page format

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Note: I think my major editorial comment here is that you should stick to the established terminology for deposit sampling and analysis. Failure to do so makes this report very confusing, ambiguous and, as a result, difficult to read. For example the following comparative table:

Established Term	Your Equivalent Term
sample unit	collection unit
Kromekote® card	K-card
diameter class	size range classification
droplet diameter spectrum	drop size spectrum (this term actually implies viscosity)
deposit density (droplets/cm²)	droplet density
? ? ?	droplet frequency

Also, you tend to repeat things many times in different ways to be sure the reader understands. This is sometimes acceptable in a lecture, but is tedious and confusing in the written word.

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INTRODUCTION

Pesticide spray efficiency is a highly complex, multidisciplinary problem, and there is a need to understand the processes causing the observed variability in spray deposition on biological targets. Neither the emission rate nor the deposition rate is a reliable measure of pesticide efficacy (Himel and Uk 1975). Only a fraction of the applied amount secures the desired biological effect in many pesticide spray operations (Holly and Turner 1978). The pathway from the spray tank to the site of action is complex. The spray drops may be lost by evaporation and/or drift, or the drop size may be such that they may have a low impaction efficiency on target objects (Himel 1969; Seymour 1969). For forest tree protection, it is necessary for the initial deposit to reach a prescribed level in the target zone, and therefore, it is very important to obtain information on foliar deposit concentrations to monitor the efficiency of every aerial spray operation. However, it is also important to monitor the ground deposition, since it is a measure of ground contamination and wastage of pesticide materials.

The presence of certain volatile components in a spray formulation leads to droplet evaporation in flight and reduces their size before impaction on target objects (Seymour 1969). This is likely to increase the percentage of smaller droplets in a spray cloud, resulting in low deposition efficiency on targets and in high environmental drift (Yates and Akesson 1973). The present study was designed to investigate the role of formulation properties on spray droplet evaporation, drop size spectrum and on foliar and ground deposition. Aminocarb was formulated in three media as: an emulsion (180 FE), an oil-based medium (180 FO) of low viscosity with appreciable droplet evaporation, and an oil-based medium (180 D) of high viscosity without droplet evaporation. These were aerially sprayed over conifer forest to investigate the foliar and ground deposition by gas-liquid chromatography (GLC), colorimetry and analysis of droplet spectra.

MATERIALS AND METHODS

Plot selection

Four 50 ha (1000 m x 500 m) spray plots (PI, PIII, PV and C), located approximately 2 km from one another to avoid contamination by the insecticidal drift, were selected in a mixed, mature coniferous forest about 40 km southwest of Bathurst, N.B. (Fig. 1) for the Matacil® (aminocarb) treatment. Plots PI, PIII and PV served as treatment plots and Plot C served as the control. The conifer and hardwood components of the plots are given in Table 1. Most of the trees in the plots showed evidence of moderate-to-severe defoliation due to spruce budworm outbreaks in past years and the crowns were not well developed. Twelve balsam fir, *Abies balsamea* (L.) (Mill) trees of nearly uniform size and shape ca. 14 m in height and DBH 16.5 cm with adequate foliage content were selected randomly in each plot transecting it partly across the centre. Each trees was tagged with plastic ribbon and numbered as 1 to 12 prefixed with the block number to identify the trees selected in each block. Layouts of trees in the three spray plots are given in Figs. 2 to 4. Ground vegetation and neighbouring trees surrounding each sampling tree were cleared up to a radius of 5 m to enhance exposure to spray cloud.

Spray formulation and spray application

Air-milled particles of aminocarb (2-3 μm diameter) suspended in a heavy oil (Sunspray® 6N) was provided by Chemagro Chemical Company (Mississauga, Ontario), as a flowable concentrate (Matacil® 1.8F). This was diluted at the spray site either as a water-based emulsion (180 FE), an oil-based medium in the insecticide diluent 585 (180 FO) or an oil-based medium in Sunspray® 6N (180 D); these were applied to each spray plot (PI, PIII and PV, respectively) at 70 g (AI)/ha per application. The composition of each tank mix (volume %), dosage of g AI/ha, volume application rate and the plots sprayed with are given in Table 2. Aircraft/spray data, spray parameters and meteorological conditions existed during the spraying are given in Tables 3 and 4, respectively.

Formulation properties

Viscosity and droplet evaporation rates are known to be the most important properties of a spray formulation that affect the spray deposition efficiency (Hartley 1969; Seymour 1969). Therefore these two parameters were measured for each spray mix. Viscosity was measured at 20°C using Ostwald's viscometer (Table 5). For measuring the rates of evaporation of droplets of variable size range 40 to 200 μm diameter, uniform sized droplets were produced using the rotary device designed by Rayner and Haliburton (1955), and were captured on glass fibre of known thickness 't'. The short and long diameters 'a' and 'b' of the ellipsoid formed on fibre were measured at various time intervals at 20°C in still air. From the volume V of the ellipsoid, the spherical diameter 'd' was calculated using the equation:

$$V = (\pi/6)d^3 = (\pi/6)a^2b - (\pi/4)t^2b$$

The rate of evaporation was expressed in percentage of droplet volume remaining after the elapse of 10 min. (Table 5).

Foliar sampling and analysis by GLC

Field sampling, storage, transportation and final sample preparation for GLC analysis were carried out according to the procedure developed by Szeto and Sundaram (1982). The only difference was in field sampling of foliage; the buds of the current year were also included in the collection of mature foliage of the previous season's growth for residue analysis. This change in sampling was necessitated due to the severe defoliation of the trees; consequently foliage samples from the previous year's growth alone were not adequate for the residue analysis.

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The extraction, column cleanup and GLC analysis of aminocarb residues were carried out according to the (established) method developed by Szeto and Sundaram (1980). Results are given in Table 6.

Ground deposit assessment

Two glass slides (each 7.5 cm x 5.0 cm) along with a Kromekote® card (10 cm x 10 cm) mounted on a folding aluminum plate (Randall 1980) were used as the collection units for droplet and deposit assessment. Thirty-six collection units per plot were placed on aluminum stands ca. 15 cm above the ground level ca. 0.5 hr prior to application and were positioned as follows: 3 collection units per tree for a total of 12 trees per plot; one in the upwind direction under the tree, one in the downward direction under the tree, and one in the adjacent clearing in the upwind direction. Care was taken to ensure that ground vegetation did not obscure the surface of the collection units in any way.

The collection units were harvested at 1 hr after spray application, transported in coolers at once to the field laboratory where the deposits on the glass plates were removed by washing with 3 x 5 ml of pesticide-grade ethyl acetate and the eluates were stored in tightly-sealed amber-coloured bottles away from heat and sunlight.

In the laboratory, the eluates were first analysed for the AI by GLC and later were flash evaporated gently to dryness, and the residues were taken either in toluene (Automate B Red) or methanol (Rhodamine B) for colorimetric analysis of the dye tracer. The deposits were expressed in g AI/ha and are presented in Tables 7 (GLC data) and 8 (colorimetric data).

The Kromekote® cards were examined under a magnification of 40 or 100X using dissecting microscopes and the spray droplet stains were counted and sized. The resulting data were grouped according to suitable size ranges (Table 10) and the droplet number and volume distribution precentages (Tables 10 and 11) were calculated using a correction factor (spread factor, SF) for converting stain sizes into drop sizes. SF values were measured by producing uniform droplets of variable size range from 30 to 120 μm using the droplet generator as mentioned above, and by allowing them to impact on the Kromekote® card and on glass fibres. At two hours after impaction, the stain diameter 'D' was read under magnifications of 40 and 100X. The corresponding drop diameter 'd' was calculated from the volume of the ellipsoid formed on glass fibre. SF values were calculated using the relation SF = D/d and are presented in Table 9. Drops/cm^2 for individual sampling stations are given in Table 12.

A sample of the three tank mixes were analysed by GLC prior to spray application for the actual aminocarb content; results are presented in Table 13 along with the summary of foliar and ground deposit data.

RESULTS AND DISCUSSION

Formulation properties

From the viscosity data in Table 5, it is apparent that the two formulations 180FE and 180FO are of low viscosity (for describing liquids of low and high viscosity the terms 'light' and 'heavy' are used throughout this paper), whereas formulation 180D is of high viscosity. The evaporation rates of droplets indicate that 180FE evaporates to a lesser degree (26% at 10 min) than 180FO (57% at 10 min). This is rather unexpected; usually droplets of water-based formulations are known to evaporate more than the oil-based ones (Seymour 1969). The observation with 180FE appears to be a special case: it is suggested that as the droplet evaporates, the water composition decreases gradually and at a particular ratio of water to oil, the non-volatile Sunspray® 6N oil engulfs the water portion of the droplet forming a protective film around it. This phenomenon would explain the present observation of low evaporation rate. Such engulfing processes (either partial or complete engulfing) are known to occur with oil-in-water droplets if the interfacial tension values are optimum (Torza and Mason 1969).

It is worth mentioning that the evaporation rates of both formulations 180FE and 180FO are much lower than those of some tank mixes used at present in forestry spray operations (unpublished data of the senior author).

The non-volatile formulation 180D had a high viscosity, suggesting a possible inverse relationship between viscosity and volatility.

Droplet analysis on Kromekote® cards (K-card) at ground level

i) Droplet density (drops/cm²)

Droplet analysis data indicated a low value for drops/cm² (Table 12) for the emulsion formulation but higher values for 180FO and 180D. This could mean one or both of the two things: for 180FE, the droplet concentration in the air mass at ground level could be actually low, or the droplet sizes could be so small (perhaps due to droplet evaporation) that inefficient deposition had occurred on K-cards. For the oil-based formulations however, both droplet concentrations and size ranges could be large enough to cause appreciable drops/cm² on the card. In the absence of data on a size spectra of the spray clouds produced for the three tank mixes at the spray emission point, and in in-flight evaporation rates of the descending spray droplets, the relative contribution of these two factors to the low drops/cm² observed for 180FE cannot be well understood.

ii) Droplet spectra on K-card

Tables 10 and 11 present data on the size range classification, droplet frequency and volume distribution patterns, and cumulative frequency and volume percentages. From these, parameters describing the droplet spectra (the number and volume median diameters, NMD and VMD, respectively; the maximum and minimum droplet diameters

You don't need all this — it makes the sentence very awkward and hard to follow; and anyway, as you point out in the sentence, it's all in Table 13.

~~observed on card, $D_{max.}$ and $D_{min.}$ respectively; and the number mode~~) were calculated ~~and~~ as presented in Table 13. Results clearly demonstrate the influence of viscosity of spray mixes on NMD, VMD and related ~~parameters~~ characteristics. The least viscous formulation, 180FE, produced the smallest values for all droplet parameters examined. ~~The formulation with~~ The medium-viscosity formulation, 180FO, produced intermediate values, whereas the heavy, oil-based 180D produced the highest values among the three spray mixes. ~~With 180D,~~ Droplet evaporation was negligible with 180D, producing ~~minimal (almost nil) and hence higher~~ drops/cm² and ~~large~~ higher values for NMD, VMD and other parameters ~~were~~ observed at ~~the~~ ground level.

"Parameters" are limits within which you work or within which something happens. I don't think VMD and NMD are parameters (see Webster!). They are characteristics of a spray and which permit determination of other characteristics such as, perhaps, droplet spectrum.

~~The width of the droplet spectra can also be related to formulation properties.~~ The lighter formulations, 180FE and 180FO, each ~~showed~~ produced a narrow droplet spectrum (7–73 µm and 16–85 µm, respectively), whereas ~~the~~ 180D, a heavier formulation, ~~180D~~ showed a wider spectrum (4–105 µm). ~~This suggests that~~ Viscosity thus appears to ~~affects~~ affect the width of the droplet spectra, but this ~~aspect however~~ requires ~~further~~ confirmation by ~~repeated~~ additional aerial spray trials under similar weather conditions.

Redundant. You say essentially the same thing later on in the paragraph.

<u>Droplet analysis on glass plate at ground level</u>

From deposit data presented in Tables 7 and 8, it is apparent that the plot mean values obtained by GLC or colorimetry are approximately the same, although individual values ~~varied~~ vary appreciably between samples. This is obviously due to experimental errors in colorimetry which were high because of the low sensitivity of the technique ~~to detect~~ in detecting the extremely low quantities of deposits observed in some cases (minimum detectable level was 0.4 g AI/ha), and also due to the high background readings of the control glass plate eluants. The reason for the latter needs to be investigated for increasing the sensitivity of the technique.

The deposit concentrations at the ground level clearly demonstrate the effect of formulation properties on ground deposition. Among the two volatile formulations, the emulsion spray mix produced the lowest deposits on glass plates. The lighter oil-based spray mix 180FO produced higher deposits whereas the non-volatile heavy spray mix produced the greatest amounts of deposits. This is due to the high viscosity which caused coarser droplets and also due to the non-volatile nature of the spray mix; when large droplets were produced they tend to have high settling velocities and consequently descend rapidly towards the ground level; especially when there is no droplet evaporation, there is little change in droplet sizes and all of the larger ones produced descend downwards resulting in high values for drops/cm^2 and deposit in g AI/ha at the ground level. With the 180FO tank mix however, the diluent I.D.585 is highly volatile resulting in appreciable droplet evaporation in flight. This reduces the drop sizes during descent, and decreases the impaction efficiency on glass plates. The low viscosity of the liquid must have resulted in finer atomization, yielding many times more

This whole paragraph is extremely confusing - it seems to hop from subject to subject and back again, implying comparisons here and there, but leaving the reader with a few nebulous impressions, and wondering exactly what the author is trying to say. It should be re-written and made clearer.

The amount of verbiage must be reduced, repetition and redundant words and phrases avoided, and points made one at a time.

The paragraph referred to here, is the one beginning on line 6 of page 10 and ending on line 16 of page 11.

number of droplets per volume of the tank mix. Therefore more droplets descend ~~downwards~~ and are available for impaction at the ground level. Despite the decrease in drop size and impaction efficiency, the greater number of droplets must have compensated for the low impaction efficiency resulting in a droplet density value similar to that of 180D. However, the fact that the deposit density is low demonstrates clearly the low recovery efficiency of the smaller droplets. With the 180FE on the contrary, the viscosity is very low and this must have caused extremely fine atomization. The droplets are perhaps too small to descend rapidly to the ground level, and therefore must have stayed airborne above or near the tree canopy level for a considerable length of time. This would explain the low droplet and deposit densities observed at the ground level.

The evaporation rates may also have affected droplet deposition. In Table 5, the relatively low evaporation rate ~~of droplets~~ of 180FE, as compared to 180FO, ~~are applicable~~ only ~~for~~ droplets sitting on glass fibre in still air. It is not known whether the engulfing phenomenon (if any) ~~can be extended~~ to droplets in motion. It is highly likely that moving droplets ~~would undergo greater evaporation and at a faster rate~~; thus ~~the~~ 180FE droplets ~~might~~ evaporate more than those of ~~the~~ 180FO ~~in field conditions~~. The present study only indicates the need for further investigations to explore the possible causes of low ground deposition for water-based formulations.

Foliar deposit analysis at the tree canopy level

From Table 6. It is apparent that foliar concentrations of aminocarb varied appreciably between sampling stations, but failed to show a relationship between formulation properties and residue levels (Table 6). The plot mean values were approximately the same. This indicates the role of target-specific drop sizes on foliar deposition. It is known that target geometry has a considerable influence on the collection efficiency of small targets for specific drop size ranges (Himel 1969; Uk 1977). It is highly likely that only certain drop sizes can impact efficiently on balsam fir needles. If the three tank mixes produce even small amounts of those drop sizes, their impaction efficiency, being similar for the similar drop sizes of the three tank mixes, would result in similar foliar concentrations of the A.I. It is known that droplets between 15-50 μm are the ones that are found on spruce needles in aerial applications (Barry and Ekblad 1978; unpublished data of the senior author). Since all three tank mixes produced these drop size ranges to some extent, a similar foliar deposition patterns might be expected for the three formulations, despite the differences noted in ground deposition patterns.

It must also be remembered that all the three tank mixes contained some Sunspray® 6N, a heavy, non-volatile oil present in the aminocarb concentrate (provided by the company). This obviously contributed to the lower evaporation rates of 180FE and 180FO than those of tank mixes that are currently used in forestry spray operations. This is also part of the reason why foliar concentrations were higher than expected for the two lighter formulations.

In brief, it appears that there is no clear-cut relationship between foliar and ground deposits. The amount of chemical that reached the forest floor can however be related to the drop size spectrum; the larger the drops the lower the impaction efficiency on the target and consequently the greater the concentration at the forest floor level. High ground concentration could also mean low efficiency in spray application and wastage of pesticide materials; because of the high rate of sedimentation of larger droplets due to gravitational pull on the larger droplet mass, the droplets would not be readily available either to the fir needles or to the budworm. This is clearly demonstrated by the 180D formulation; in spite of the high droplet and deposit densities observed at the ground level, the foliar concentrations were approximately the same as those for the other two formulations, or in fact were somewhat lower.

CONCLUSIONS

In summary, the present study, under the conditions of spray application and weather parameters measured, indicates the following:

1. A possible inverse relationship exists beween viscosity of the formulation and droplet evaporation rates. The heavy, oil-based formulation was completely non-volatile.

2. The effect of formulation properties was somewhat evident on droplet density observed on Kromekote® cards at the ground level; when viscosity increased, the drops/ cm^2 increased and reached a maximum value for the heavy, non-volatile, oil-based tank mix.

3. The effect of viscosity and evaporation rates was more clearly evident on deposit density observed on glass plates at the ground level; with increasing viscosity values, there was a gradual increase in the deposit densities from 180FE to 180D.

4. The size spectrum of drops collected at the ground-level were also influenced by the formulation properties. The lighter formulations produced finer droplet spectra while the heavy tank mix produced a coarser and wider spectrum. Droplet parameters such as NMD, VMD, D_{max} and number mode were also affected by formulation properties; their values increased with increasing viscosities.

5. It appears that both viscosity and droplet evaporation rates affected the rate of ground deposition. However, the relative contribution of the two properties to the overall ground deposition remains unclear. This aspect requires further investigation with different formulations.

6. The effect of formulation properties on foliar deposition is not clear~~ly apparent;~~; all three formulations ~~showed~~ produced ~~approximately~~ similar foliar concentrations. The reason ~~why lower foliar residues were not observed for~~ the two volatile formulations 180FE and 180FO produced higher foliar residues appears to ~~lie in~~ be the Sunspray® 6N oil present in the aminocarb concentrate; this heavy, non-volatile oil contributed ~~to some extent~~ to the low evaporation rates ~~observed for~~ of 180FE and 180FO.

"similar" means approximately the same; can't say "approximately similar"

redundant! "contributed to", his context, means "was partly to some extent"

7. No direct relationship was observed between foliar and ground deposit~~s~~: the tank mix 180D showed the highest deposit~~s~~ at ~~the~~ ground level, but ~~its~~ foliar residues at ~~the~~ canopy level were about the same as for the other two mixes. This may be due to the coarser droplet spectrum observed with 180D, in addition to ~~Because of~~ the high sedimentation rate ~~due to high gravitational pull~~, which makes the droplets less apt to impact ~~appear to be not readily available for impaction~~ on the balsam fir needles.

"highest deposit" again! Is a "high deposit"? at was high? The volume? number of droplets?

8. High ground deposit~~s~~ could also mean low pesticide efficiency, wastage of pesticide materials and ground contamination. ! It is important to increase droplet deposition ~~at~~ within the tree crown, and this may better be achieved by delivering target-specific drop sizes. ~~i.e., by controlled droplet application.~~

You don't have to add this — it's obvious what you mean.

ACKNOWLEDGEMENTS

The invaluable assistance and cooperation provided by Mr. B.L. Cadogan, and his staff in completing this research project is gratefully acknowledged. Special appreciation is extended to Mr. Cadogan for providing the data listed in Tables 1 to 4.

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