ROLE OF ADDITIVES IN PESTICIDE FORMULATIONS ON FOLIAR DEPOSITION AND PERSISTENCE

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ABSTRACT

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.

INTRODUCTION

In aircraft application of pesticides over forests, four distinct processes influence the dynamics of the sprayed material from the point

of emission to the target level and its deposition on target surface. First, the released spray cloud reaches an approximate equilibirum with the ambient air flow within seconds, by a process referred to as cloud stabilization. Second, the stabilized spray cloud undergoes a downward movement towards the forest tree canopy. This results from three phenomena, gravitational settling, vertical molecular diffusion and downwind transport. The third step involves atmospheric transport and diffusion processes within the forest canopy, which are generally quite different from those above the canopy. This is because the meteorological structure within and below canopy is only very weakly coupled with the above-canopy meteorological structure. The fourth process involves deposition of spray droplets on the biological matrices at the target site. Thus the efficacy of a pesticide is greatly influenced by the above four processes. However, the fourth one, involving foliar deposition, is considered to be of direct relevance to pest control, although this assumption neglects the possible role of the vapour phase on insect mortality.

Following foliar impingement of droplets, the effectiveness of the sprayed pesticide is dependent upon the appropriate residual activity and hence is related to foliar half-life (time for half of the initial amounts to disappear). While the active ingredient is responsible for pesticidal activity, the additives in the formulation can play a significant role in maintaining a desirable half-life in the forest environment. At present little factual information exists in correlating foliar

stability and efficacy of a pesticide. Our present understanding of the role of the additives in efficacy is superficial. Consequently there is a need to investigate the usefulness of some solvents and diluent oils to enhance the half-life of the chemical in foliage thereby increasing its biological activity. This paper presents results obtained under field conditions on the effect of different additives on foliar penetration, persistence and half-life characteristics of fenitrothion and aminocarb in conifer foliage.

MATERIALS AND METHODS

Fenitrothion Formulations

Two types of formulations of the insecticide, oil and emulsion, were investigated. For preparing the oil-based formulations two oils, Arotex® 3470 (Texaco Oil Co. Canada) and fuel oil were used either alone (FF1 and FF2) or in combination (FF3). The emulsion formulation (FF4) was prepared by using the surfactant Atlox® 3409 (Atlas Chemical Industries, Brantford, Ontario, Canada). The composition of the four spray mixtures and the trees treated with them are given in Table 1. All the required amounts of the ingredients in the four spray mixes were weighed individually using stoppered Erlenmeyer flasks to make up to 100 g, a few hours prior to the application and stored at 2°C.

Aminocarb Formulations

With aminocarb, only non-aqueous formulations were studied. The diluents used were acetone, nonylphenol, fuel oil and Arotex® 3470, either alone (AF1 to AF4) or in combination (AF5 to AF7). Technical aminocarb was admixed with various additives as shown in Table 2 to yield a 2%

solution (wt/vol.) of the insecticide. As with fenitrothion, the formulations were prepared a few hours prior to the application and stored at $2^{o}C$.

Experimental Site and Spray Application

The study was conducted in a tree farm near Shawville, Quebec. For spraying fenitrothion formulations, nine white spruce trees, *Picea glauca* (Moench) Voss, of nearly uniform size and shape, ca. 2.8 m in height with abundant foliage and ample growing space, were selected, tagged with plastic ribbon and numbered as FT1 to FT9. Trees FT1 to FT8 were divided into 4 pairs and each pair was sprayed separately with one type of the four fenitrothion formulations shown in Table 1. Tree FT9 served as the untreated check. Prior to application, a portable polyethylene shelter 3 m in height and surrounding a ground surface area 4.6 m^2 was erected around each tree to be treated. A measured 1.5 ml of the formulation was sprayed on each tree using a device and technique developed by Hopewell (1974) for applying measured amounts of simulated aircraft spray to individual small trees.

For spraying aminocarb formulations, eight white spruce trees, *Picea glauca* (Moench) Voss were selected (1.9 to 2.2 m in height and 7.5 to 8.0 cm d.b.h.) and numbered. Trees AT1 to AT7 each received separately 2.0 ml of the formulations AF1 to AF7 listed in Table 2 and tree AT8 served as the untreated check. The spray application was done using the same technique and device reported above.

Sampling and Analysis

a. Fenitrothion treatment. Samples of foliage (7 cm branch from each quadrant of the tree at mid-crown level excluding the new growth tips and buds) were taken 1 day prior to treatment and at 0, 1, 2, 4, 7, 10, 15, 20, 30, 45, 60, 90, 120, 150 and 370 days thereafter. Foliage samples collected from trees treated with similar spray mixes were cut into small pieces, mixed well, put in plastic bags, stored in coolers containing dry ice and transported immediately to the laboratory for analysis.

In the laboratory, fenitrothion present on the surface of the foliage (surface residues) was removed by washing 10 g aliquots of foliage with 4 x 30 ml ethyl acetate in a stoppered measuring jar (250 ml). Fenitrothion residues which penetrated the cuticle and dislodgable by foliar washing (tissue residues) were obtained by Sorvalling the same with 2 x 50 ml of ethyl acetate. The washings and the extracts were separately partitioned, cleaned by adsorption chromatography and quantified by FPD gas-chromatography as described by Sundaram (1974). Foliar samples collected from the untreated check tree (FT9) did not show any detectable levels of fenitrothion (minimum detection limit was 0.1 ppm). The dissipation rates of foliar residues in treated trees and the long range persistence of fenitrothion are presented in Table 3.

b. Aminocarb treatment. Samples of foliage were taken 1 day prior to treatment and at 0, 3, 7, 12, 18, 25, 35, 45 and 60 days thereafter. The surface residues were removed by washing 20 g aliquots of foliage

with 4 x 50 ml acetonitrile. The tissue residues were obtained by Sorvall homogenization of the same foliage followed by extraction with 2 x 100 ml of acetonitrile. The extracts were further cleaned, the residues were quantified by gas-liquid chromatography as described by Sundaram and Hopewell (1977), and the aminocarb concentrations were expressed in ppm of oven-dry foliage weight. Foliar samples collected from the untreated control tree did not show any detectable levels of aminocarb (detection limit was 0.05 ppm). The surface and tissue residues, total foliar concentrations and persistence of aminocarb in conifer foliage is summarized in Table 4.

RESULTS AND DISCUSSION

Fenitrothion Residues In Foliage

The residue data in Table 3 show that the initial concentration of fenitrothion on conifer needles (total residue) ranged from 66.2 to 79.6 ppm; formulation FF1 gave rise to a significantly lower total residue than FF2, FF3 and FF4. This indicates that the appropriate selection of solvent mixtures enhances the foliar deposition and stability of the active ingredient on conifer needles. Among the three oil formulations (FF1 to FF3) studied, the conventional formulation FF3 compared favourably with FF2 in foliar deposition and persistence, although the latter posed some problems in miscibility. Arotex®-fenitrothion mixture (FF1) gave a comparatively low foliar deposition probably due to the low impaction efficiency of the smaller droplets produced (the viscosity of

the mixture was low and therefore the droplets produced were smaller). The two petroleum distillates, Arotex® and fuel oil, were not compatible with fenitrothion when used alone but in combination at the 30:59 weight ratio, they served as an excellent solvent mixture, and yielded high foliar deposits. With the emulsion formulation FF4, the foliar residues were not significantly different from FF2 or FF3.

From the data on the dissipation rates (Table 3), it is obvious that the surface and total foliar concentrations are rapidly lost initially from the foliage. Within the first 24 hr period, ca. 20 to 35 percent of the surface or total residues were lost with all formulations. This rapid loss is primarily due to volatilization of the active ingredient into the surrounding mobile air mass. Such losses are known to occur at all environmental conditions, but the losses are generally high in open tree farms where the wind velocities are high compared to the natural forests (Hartley, 1969). It is evident that the evaporation rate is also influenced to some extent, by the additives in the formulations. Formulation FF1, containing Arotex®, a light petroleum distillate of high volatility, low density and low viscosity, caused a high initial rate of loss (≈30% in 24 h) of the AI. In the case of FF4, the hydrophobic and codistillation factors appeared to have played a combined role in the high rate of initial loss (≈ 35% in 24 h). Formulations FF2 and FF3 showed significantly lower rates of loss (≈ 25% in 24 h), and this can be attributed to the high viscosity of the fuel oil present in the formulations.

From day 1 onwards, foliar deposits (surface and total residues) showed a curvilinear decrease with time. The mechanism of this dissipation seems to involve primarily climatic parameters, rather than metabolic processes. This is evident from the half-lives for the 1 to 150 day interval (Table 1); all formulations showed similar $T_{\frac{1}{2}}$ values (12 to 14 days) except FF2 which showed a significantly higher $T_{\frac{1}{2}}$ value of 17 days. This appears to be the effect of the high fuel oil content in FF2.

Following impaction of droplets on the conifer needles, the tissue concentration of fenitrothion (Table 3) increased with time, reached a maximum value within 24 h and declined gradually over a period of several months. The conifer surface containing the waxy lipophilic cutin (a polymeric material composed of long-chain fatty acids and alcohols) has a strong affinity for the deposited fenitrothion molecules. It is plausible that the active ingredient is slowly partitioned between the solvent and the cutin components, and gradually diffused into the cutin forming tissue deposits. Tissue deposits at the 24 h period for formulations FF2 and FF3 were significantly higher than those with FF1 and FF4. The high viscosity of the fuel oil in FF2 and FF3 appears to have facilitated the penetration process compared to the lighter solvent Arotex® in FF1 and the aqueous component in FF4. The presence of the volatile component (Arotex®) in FF3 slightly decreased the level of tissue deposits (3.7 ppm) compared to the value in FF2 (4.2 ppm) but this decrease is not statistically significant. In the case of the emulsion formulation FF4, the tissue residue at 24 h was about the same as the value observed in FF1.

From day 1 onwards, the tissue deposits showed a gradual decrease with time (Table 3). The half-lives for the 1 to 150 day interval (Table 1) indicate that the high concentration of fuel oil in FF2 significantly contributed to the retention of fenitrothion in tissues for longer periods compared to other formulations.

Results in Table 3 indicate that fenitrothion persisted up to 370 days in small but significant amounts, ranging from 0.3 ppm (FF4) to 1.6 ppm (FF2) depending on the type of formulation used. Usually the oil formulations enhanced the persistence of the chemical compared to the emulsion formulation. The persistent fenitrothion molecules being lipophilic in nature, appear to be stored in cuticular waxes, and resist a rapid loss due to evaporation or foliar leaching. The new foliage which was not exposed to the insecticide spray, contained low but detectable levels of fenitrothion (0.1 to 0.3 ppm), suggesting that the chemical is translocated. This is probably due to the leaching of the foliar residues in the upper canopy by rain wash which has cascaded down and were intercepted by the mid-crown young shoots. Even if translocation is a possibility, the levels involved are extremely low despite the high foliar deposit levels measured. The high dosage rates combined with the spray application technique used in the present study, resulted in deposit levels much higher than those encountered normally in an aerial spray operation involving dosage rates of 0.14 to 0.28 kg AI/ha. Consequently foliar translocation (if any) and persistence levels in a normal spray operation would be very much lower than those observed in the present study.

Aminocarb Residues In Foliage

The residue data in Table 4 show that acetone solutions of aminocarb (AF1) gave poor surface and tissue depositions. The insecticide dissipated rapidly giving a half-life ($T_{\frac{1}{2}}$), of 8.8 days. It appears that acetone being a polar and volatile liquid of low viscosity, is a poor solvent to enhance the dispersability, coverage and retention of aminocarb on foliage.

Nonylphenol, a pale brown viscous liquid, is a mixture of monoalkyl phenols, predominantly para substituted and containing randomly branched nonyl groups as side chains. It is used as an adjuvant in the commercial aminocarb (Matacil®) formulations and also acts as a nonionic surfactant because of the presence of hydrophobic and hydrophilic ends in the molecule. From the residue data (Table 4), it is apparent that apart from the minor difficulties encountered in metering, mixing and spraying (nozzle plugging), the nonylphenol solutions of aminocarb (AF2) gave excellent deposition levels and enhanced the spreading, adhesion, penetration and stability of the active ingredient on the needles. This is evident from the relatively high surface and tissue residues as well as the total foliar residue levels which showed considerable persistence ($T_{\frac{1}{2}}$ 15.3 days) compared to the other solvents and solvent mixtures studied. Our present understanding of the influence of structural requirements of solvents to facilitate and enhance dispersion, foliar penetration and persistence to improve efficacy of an insecticide is still sketchy. However, the present results suggest that the structure of nonylphenol with its hydrophobic and hydrophilic ends and aryl ring, may have considerable influence on insecticide retention, penetration and persistence in conifer

foliage. It is likely that immediately after the spray drop targets on the spruce needle, the solvent molecules, due to their polarity, orient towards the cuticular surface reducing interfacial tension thus facilitating wetting and spreading of spray droplets over the needle. At the same time the solute molecules being apolar uniformly distribute themselves, probably as a monolayer, and diffuse from the spray droplet into the lipophilic cutin forming a solid solution. This process facilitates the penetration through the cuticular layer and incorporation as tissue deposits. Inside the tissue, aminocarb appears to resist a rapid physicochemical degradation resulting in a slow decrease of tissue residues so that a small fraction (0.9 ppm) was persistant even after 60 day interval.

Two petroleum distillates, fuel oil No. 2 (AF3) and Arotex® 3470 (AF4), both showed approximately the same deposition and dissipation characteristics. However, Arotex®, being a more volatile and less viscous fraction, yielded a lower foliar deposit of aminocarb than the heavier fraction, fuel oil No. 2. The fuel oil due to its aromatic content, has some agreeable properties such as increased foliar penetrability, adhesion and resistence, when compared to the latter ($T_{\frac{1}{2}}$ 11.0 vs 9.2 days). With respect to foliar adsorption, spreadability and cuticular diffusion, these two oils exhibited intermediate properties between acetone on one hand and nonylphenol on the other (Table 4). This is probably due to their high paraffinic content and lack of polarity.

Dispersion of aminocarb in a solution of nonylphenol and fuel oil as formulating agent (AF5) gave equally superior deposition concentration on needles compared to the use of pure nonylphenol (AF2). Dominant factors that influenced residual effectiveness ($T_{\frac{1}{2}}$ 14.4 days) in this spray appear to be minimum evaporation loss (authors unpublished data) and foliar leaching due to rain (addition of an oil component further reduces the water-solubility), firm adhesion of the droplets to leaf surface, and penetrability of the toxicant molecules below the cuticular layer of conifer needles. The ingredients used in the formulation are economical and the solvent system considerably increased the penetration and foliar life ($T_{\frac{1}{2}}$ 14.4 days) of aminocarb compared to the use of fuel oil alone. Also the solubility of aminocarb in the solvent mixture was greater than in pure fuel oil.

The solution mixture containing nonylphenol and Arotex® (AF6) was not as effective as the nonylphenol/fuel oil system as evident from a lower $T_{\frac{1}{2}}$ value. Arotex®, being a light petroleum distillate rich in aliphatics, appears to have lacked the adhesion characteristics of fuel oil resulting in evaporation of the targetted formulation, thus reducing the residual effectiveness ($T_{\frac{1}{2}}$ 12.1 days) compared to the nonylphenol/fuel oil ($T_{\frac{1}{2}}$ 14.4 days) solvent system.

The last formulation (AF7) was prepared according to the recipe used for Matacil® in an experimental spray program undertaken previously (Sundaram et al. 1976). The residue pattern, persistence and $T_{\frac{1}{2}}$ (11.5 days) observed for this spray formulation (AF7) were basically the same as nonylphenol/Arotex® mixture. The use of petroleum distillates alone

which are less hydrophobic than nonylphenol, markedly diminished the cuticular penetration and persistence of the active material compared to the formulations containing both the ingredients.

The results of the present investigation indicate a relationship between the chemical nature of the solvents/diluent oils and foliar half-life of the active ingredient. Although only one tree was used to study each formulation, all treatments were done under the same weather conditions. It is assumed that any variation in $T_{\frac{1}{2}}$ due to changes in weather conditions would equally affect all foliage deposits, thus maintaining the relative significant differences between half-lives of different formulations.

CONCLUSION

The present study involves two types of insecticides, on organophosphate (fenitrothion) and a carbamate (aminocarb). Irrespective of these differences in the chemical nature, the physicochemical properties of the diluents/solvents used in the formulations appear to have played a significant role in the efficiency of foliar deposition and persistence characteristics of the active ingredient. The salient points emerging from the study are as follow:

Fenitrothion treatment

1) The solvents and additives in the fenitrothion formulation significantly affected the deposit levels produced in a spray operation.
2) They also influenced to some extent the rate of tissue penetration into the foliar cuticle, the rate of dissipation and foliar persistence.

3) Fuel oil appears to have certain definite advantages over Arotex®, as it yields the desired small droplet spectrum, high droplet density, high foliar deposits (both tissue and total), low rate of dissipation and a high long-term persistence.

4) Irrespective of the nature of additives in the formulation, a large amount of the AI was rapidly lost from the foliage with all formulations. This loss appears to be related to the climatic parameters.

5) Fenitrothion shows a long-term foliar persistence in extremely low concentrations. Generally speaking, oil formulations appear to enhance the persistence.

6) Although some new foliar shoots exhibited low but detectable levels of fenitrothion, it is doubtful whether these resulted from a translocation process or from external contamination due to rain wash of the AI from older leaves. The levels involved are too low to contribute significantly to bio-efficacy.

Aminocarb Treatment

1) Environmental stability of aminocarb was influenced by additives in the formulation.

2) There appears to exist a structure/activity relationship between the solvent type and foliar stability. The chemical nature of the solvents/diluent oils influenced foliar deposition, spreading, wetting, adhesion, penetration and retention of the active ingredient.

3) Tissue deposits decreased more slowly with time than surface residues.
4) Arotex® 3470 appeared to behave similar to acetone with respect to surface and total foliar residues but caused greater foliar penetration and retention resulting in higher tissue residues.
5) Nonylphenol yielded the highest tissue residues among all the additives studied, although the surface and total residues were similar to those found with 1:1 (v/v) mixture of nonylphenol and fuel oil.
6) Formulations AF3, AF6 and AF7 behaved similarly with respect to the half-lives of surface, tissue and total foliar residues of aminocarb. This suggests that these formulations probably had similar physico-chemical properties which played an important role in foliar absorption and retention.

It is evident from the present study that the use of appropriate additives is likely to result in increased efficacy, contributing to reduction in application dose, cost and environmental hazards associated with the release of large quantities of toxicants. Further research should be conducted to explore ways and means by which the fledgling field of formulation science could be exploited fully for the forest pest control programs in Canada.

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TABLE 1. Composition of Fenitrothion Formulations and Half-life Data for Each Application+

Formulation	Composition of formulations (wt%)	Trees sprayed	Residue half-life, $T_{½}$ (days) for 1-150 day interval		
			Surface	Tissue	Total
FF1	Fenitrothion** 10, Arotex®[a] 89, Automate B Red 1	FT1 & FT2	13	12	13
FF2	Fenitrothion 10, Fuel oil[b] 89, Automate B Red 1	FT3 & FT4	17	26	17
FF3	Fenitrothion 10, Arotex® 30, Fuel oil 59, Automate B Red[d] 1	FT5 & FT6	14	14	14
FF4	Fenitrothion 10, Atlox®[c] 1, Arotex® 2, Water 86, Rhodamine B[e] 1	FT7 & FT8	13	10	12
---	Untreated control	FT9	-	-	-

+Application rate = 1.5 g of formulation (density 1.02)/tree corresponding to 330 g AI/ha, i.e., 20% more than the normal application rate of 280 g AI/ha. FF3 and FF4 were the two conventional formulations used in spruce budworm control programs in Canada.

**Technical material supplied by Sumitomo Chemical Company.
*a*Arotex® 3470 supplied by Texaco Oil Company, Canada
*b*Fuel oil No. 2, supplied by Texaco Oil Company, Canada.
*c*Atlox® 3409 emulsifier supplied by Atlas Chemical Industries, Brantford, Ontario, Canada.
*d*Automate B Red supplied by Morton Williams Limited, Ajax, Ontario, Canada.
*e*Rhodamine B supplied by Allied Chemicals, Morristown, New Jersey, United States.

TABLE 2. Composition of Aminocarb Formulations and Half-life Data for Each Application

Formulation	Additive containing 2% (wt/vol.) of aminocarb[a]	Tree sprayed	Residue half-life, $T_{1/2}$ (days) for 0-60 days Surface	Tissue	Total
AF1	Acetone	AT1[f]	8.9	12.3	8.8
AF2	Nonylphenol[b]	AT2[g]	13.0	26.0	15.3
AF3	Fuel oil No. 2[c]	AT3[h]	9.8	17.0	11.0
AF4	Arotex® 3470[d]	AT4[f]	8.2	16.1	9.2
AF5	Nonylphenol:Fuel oil No. 2 1:1 (v/v)	AT5[g]	13.5	17.8	14.4
AF6	Nonylphenol:Arotex 1:1 (v/v)	AT6[h]	10.9	16.1	12.1
AF7	Nonylphenol:Fuel oil:Arotex 1:14:5[e]	AT7[h]	10.6	15.0	11.5
-	Untreated control	AT8	-	-	-

[a]Tech. material supplied by Chemagro Chem. Co.
[b]Fisher Sci. Co. 7956-P.
[c]Supplied by Texaco Oil Co.
[d]Density 0.94; supplied by Texaco Oil Co.
[e]Nearly similar to the operational spray formulation used in early 1974.
[f]Half-life for surface and total residues for trees AT1 and AT4 are not significantly different, whereas for the tissue residues it is different ($P < 0.08$).
[g]Same as above, for trees AT2 and AT5.
[h]No significant difference was found among the three formulations FF3, FF6 and FF7 concerning the half-lives for the three types of residues.

TABLE 3. Fenitrothion Concentration* (ppm) in Spruce Foliage

Time after application	Formulation sprayed											
	FF1			FF2			FF3			FF4		
	Sur.	Tis.	Tot.	Sur.	Tis.	Tot.	Sur.	Tis.	Tot.	Sur.	Tot.	Tis.
0 d	65.5	0.7	66.2	79.1	0.5	79.6	74.2	0.6	74.8	73.8	0.3	74.1
1 d	44.2	2.4	46.6	56.6	4.2	60.8	52.6	3.7	56.3	46.2	2.9	49.1
2 d	39.8	1.9	41.7	49.8	3.8	53.6	47.8	3.4	51.2	42.6	2.6	45.2
4 d	36.4	1.7	38.1	45.2	3.5	48.7	41.9	3.1	45.0	36.8	2.2	39.0
7 d	30.9	1.5	32.4	39.9	3.2	43.1	36.1	2.7	38.8	29.3	1.8	31.1
10 d	26.6	1.2	27.8	35.9	2.9	38.8	31.2	2.5	33.7	28.8	1.3	30.1
15 d	17.6	1.1	17.7	29.6	2.7	32.3	23.9	1.9	25.8	19.6	1.1	20.7
20 d	13.4	1.0	14.4	24.8	2.4	27.2	19.2	1.4	20.6	14.9	0.8	15.7
30 d	10.9	0.8	11.7	19.9	1.9	21.8	16.1	1.0	17.1	11.7	0.7	12.4
45 d	5.7	0.7	6.4	9.8	1.4	11.2	7.7	0.8	8.5	6.4	0.5	6.9
60 d	2.7	0.5	3.2	5.6	1.1	6.7	3.9	0.6	4.5	3.0	0.4	3.4
90 d	2.0	0.3	2.3	3.4	1.0	4.4	2.7	0.4	3.1	2.2	0.3	2.5
120 d	0.6	0.3	0.9	2.8	0.8	3.6	1.8	0.4	2.2	1.4	0.2	1.6
150 d	0.5	0.2	0.7	2.2	0.6	2.8	1.5	0.3	1.8	1.0	0.2	1.2
370 d	0.3	0.1	0.4	1.4	0.2	1.6	0.9	0.2	1.1	0.6	0.1	0.7
370 d**	T	T	T	T	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.3

Sur. - Surface residue
Tis. - Tissue residue
Totl - Total residue
* - MDL 0.1 ppm; mean of two determinations with S.D. < 10%
** - New foliage of the following year

TABLE 4. Aminocarb Concentration* (ppm) in Oven-dry Foliage

Days after spraying	Tree sprayed																				
	AT1			AT2			AT3			AT4			AT5			AT6			AT7		
	Sur.	Tis.	Total	Sur.	Tis.	Total	Sur.	Tis.	Total	Sur.	Tis.	Total	Sur.	Tis.	Total	Sur.	Tis.	Total	Sur.	Tis.	Total
0	14.0	0.7	14.7	25.6	3.2	28.8	19.7	1.5	21.2	17.8	1.1	18.9	23.7	3.0	26.7	21.8	3.1	24.9	21.3	2.2	23.5
3	11.0	1.1	12.1	23.0	4.1	27.1	16.2	1.9	18.1	14.2	1.5	15.7	20.5	3.7	24.2	18.9	3.4	22.3	18.2	3.6	21.8
7	6.9	0.9	7.8	14.9	3.4	18.3	11.2	1.6	12.8	10.8	1.1	11.9	9.9	3.1	13.0	9.4	2.5	11.9	11.4	2.8	14.2
12	3.9	0.8	4.7	9.2	2.7	11.9	7.2	1.2	8.4	6.9	0.7	7.6	8.5	2.2	10.7	7.5	1.7	9.2	8.1	2.0	10.1
18	2.3	0.6	2.9	6.7	2.0	8.7	4.4	0.9	5.3	4.2	0.5	4.7	5.9	1.7	7.6	4.7	1.4	6.1	5.5	1.7	7.2
25	1.2	0.4	1.6	3.4	1.7	5.1	2.3	0.6	2.9	1.9	0.3	2.2	3.3	1.3	4.6	2.8	0.8	3.6	2.9	1.4	4.3
35	0.9	0.2	1.1	3.2	1.3	4.5	1.7	0.4	2.1	1.1	0.3	1.4	3.0	1.0	4.0	2.3	0.6	2.9	2.1	1.0	3.1
45	0.4	0.1	0.5	1.9	1.1	3.0	1.1	0.3	1.4	0.5	0.2	0.7	2.2	0.6	2.8	1.4	0.4	1.8	1.5	0.6	2.1
60	0.1	N.D.	0.1	0.9	0.9	1.8	0.2	0.2	0.4	0.1	0.1	0.2	0.7	0.4	1.1	0.3	0.3	0.6	0.3	0.2	0.5

Sur. = surface residue
Tis. = tissue residue
N.D. = not detectable and the detection limit was 0.05 ppm.
*Values represent the mean of two determinations; for each tree the standard deviation was less than 10%.