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Airborne Drift Residues Collected near Apple Orchard Environments Due to Application of Insecticide Mixtures

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Substantial quantities of agriculturally applied pesticides have been shown to become airborne during and after application operations. This unwanted feature of pesticide usage, referred to as off-site pesticide drift, results not only in loss of pest control but may result in potential exposure to workers and other individuals near agricultural sites (Seiber et al. 1980). This has produced a wave of public concern and in many cases a very negative opinion of pesticide chemicals. The concern of both public and regulatory agencies about the deposition of pesticides outside the target area and the potential health effects due to this exposure situation has been termed "chemical trespass". In the northeastern United States, the problem of chemical trespass has been amplified due to the rather limited areas used for agricultural purposes and to the relatively high population densities which exist around them (Van Driesche et al. 1987).

In response to this situation, application suggestions have been made to reduce the hazards associated with agricultural application of pesticides. In Massachusetts, pesticides are applied by ground means as much as possible, application technology is used that produces large particle sizes (>100μ), pesticides are applied only during low wind velocities (1-5 mph) and early in the day when low temperatures and high humidity conditions exist (Hall 1980). The following is a description of the research which evaluated the effectiveness of these suggestions. Because application of pesticides as mixtures is becoming a widely acceptable practice to suppress the development of resistance in many agriculturally important insects (Georghiou 1983), experiments were included to evaluate the suitability of the sampling techniques to detect multiple residues. Sampling and analytical information of this type is for the most part not available or incomplete but the need for such data is becoming acute. Furthermore, limited research has indicated that the drift characteristics of pesticides applied in combinations can be significantly different from those determined when applied individually (MacCollom et al. 1985).

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MATERIALS AND METHODS

The study site (Massachusetts Horticultural Research Center, University of Massachusetts) consisted of approximately one acre of 220 mature apple trees (Fig. 1). Three commonly used insecticides were applied at their respective field rates; azinphosmethyl (Guthion - 50% WP, 0.5 lb/100 gal, 74.8g/A), fenvalerate (Pydrin - 2.4 EC, 3.5 oz/100 gal, 19.6g/A), and oxamyl (Vydate - 24% L, 1.0 pt/100 gal, 71.8g/A). Applications were made with an air-blast sprayer (Bean model LV320) set at a rate of 6X (66 gal/A), which resulted in an average droplet diameter of 286 + 26 um on film targets placed in the orchard (Prokopy, unpublished results). Four applications were made during the 1984 growing season on June 6, and 26, July 24, and August 22. To insure applications were made during appropriate conditions, wind speed and direction were monitored with a Skyvane W102-P Wind Sensor, WTB102-H4-540 Wind Translator and 338 Recorder. Temperature and relative humidity were monitored with a hygrothermograph (Qualimetrics model 5021, Weather Measure Corp., Sacramento, CA).

Four high volume air samplers (Staplex, Brooklyn, New York) were used to collect airborne residues (1 upwind and 3 downwind). All samplers were repositioned at the start of each collection period to accommodate for shifts in wind direction. Samples were collected for 2 hr periods except during the 30 min application (spray). The air samplers were fitted with glass fiber filters (G.F. Filters, Gelman type A/E, 102 mm diam, 0.3u pore size) to collect drift particulates and 100 ml of Amberlite XAD-4 polystyrene absorbent resin (XAD Resin, Rohn and Haas Chemical Co. Philadelphia, PA) to collect insecticide vapors as described by Kilgore et al. (1984). Air samples were powered by a portable generator and pulled 0.57 m^3 of air/min.

Fallout of airborne insecticides was estimated from residue levels deposited on cellulose collector discs (Whatman 33cm diameter P4 cellulose filters) mounted on foil-covered platforms 0.5 ft above the ground surface. They were placed permanently on north (N), east (E), south (S) and west (W) lines (Fig. 1). Samples were collected as follows; 2 hr pre-spray, during the 30 min spray, and 0-2, 2-8, and 8-24 hr post-application.

Prior to use G.F. filters were soxhlet extracted in acetone for 2 hr (20 cycles). Cellulose discs were rinsed with 75 ml acetone. XAD Resin was acid-washed (pH 5.0 with HCl) for 1 hr, water-rinsed until a neutral pH was obtained, acetone-rinsed and then soxhlet extracted in acetone for 2 hr.

After application, insecticide residues were removed from the XAD resin and cellulose discs by soxhlet extraction (20 cycles) in acetone. The samples were reduced under vacuum and then under nitrogen to a final 10 ml volume for quantification. G.F. filters were extracted with 3 x 50 ml acetone on a wrist-action shaker and reduced as above for quantification.

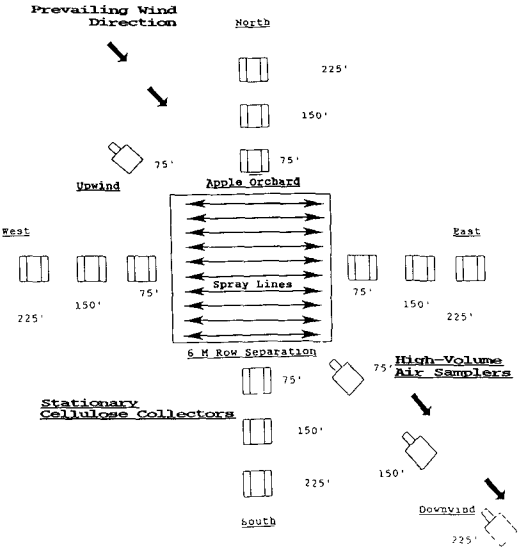

Figure 1. Pesticide Application Site.

Determination of azinphosmethyl was by gas-liquid chromatography (GLC) using a thermionic specific detector and a 12 M, DB-1 capillary column which was temperature programmed from 180°C to 250° C at 10°C/min. Injector and detector temperatures were 250°C and 300°C, respectively. Determination of fenvalerate was by GLC using an electron capture detector and a 15 M DB-1 capillary column programmed from 210°C to 240°C at 25°C/min. Injector and detector temperatures were 250°C and 300°C, respectively. Oxamyl residues were determined by high pressure liquid chromatography with post column derivatization and fluorescence detection (Hill et al. 1984). A 250 x 4.6 mm reversed phase C_{18} analytical column was used with solvent programming of the mobile phase from 15% to 40% methanol in water over 7 min. at a flow rate of 1.0 ml/min.

For every ten samples analyzed, standard curves were obtained using integrated peak areas over the range of 100ppb to 10ppm for azinphosmethyl, and 25ppb to 10ppm for fenvalerate and oxamyl. In each extraction, an appropriate collector was spiked with a standard amount of insecticide to determine variation in extraction efficiencies. Detection limits were 50 ppb for azinphosmethyl and 10 ppb for fenvalerate and oxamyl.

RESULTS AND DISCUSSION

The recoveries of azinphosmethyl, fenvalerate and oxamyl from various substrates used as collectors are presented in Table 1. Mass balance studies were conducted to verify that breakthrough of insecticides from the high volume air samplers did not occur (Table 2). Recoveries were uniformly high indicating little or no

Table 1. Recovery of insecticides from fortified collectors.

Substrate	Fortification Range (ug)	Individual Recovery (N=3)	Mixture Recovery (N=3)
		(percent of total ± S.D.)[a]	
Azinphosmethyl			
Glass-Fiber Filter	1-50	92.9 ± 12.7	78.9 ± 12.1
XAD Resin	0.1-1.0	110.7 ± 17.4	83.7 ± 1.1
Cellulose Disc	0.5-50	77.2 ± 5.5	79.0 ± 6.9
Fenvalerate			
Glass-Fiber Filter	1-100	80.5 ± 3.4	83.7 ± 4.1
XAD Resin	10-100	98.4 ± 6.1	93.9 ± 5.1
Cellulose Disc	10-100	97.6 ± 3.7	90.1 ± 5.4
Oxamyl			
Glass-Fiber Filter	0.1-0.5	86.3 ± 16.9	106.0 ± 2.7[a]
XAD Resin	2-200	89.5 ± 9.6	81.5 ± 4.3
Cellulose Disc	1-50	111.4 ± 9.3	79.9 ± 7.3[a]

[a]Values differ at the $P<0.05$ level of significance.

Table 2. Recovery of insecticides from fortified high volume air samplers[a]

Fortification Level (ug)		Individual Recovery (%)[a]			Mixture Recovery (%)[a]		
Filter	Resin	Filter	Resin	Total	Filter	Resin	Total
Azinphosmethyl							
10	0	103.7	0.0	103.7	80.6	47.1	127.7
0	10	0.0	107.5	107.5	0.0	144.6	144.6
100	0	75.0	0.0	75.0	61.6	60.2	121.8
0	100	0.0	69.0	69.0	0.0	131.5	131.5
Fenvalerate							
10	0	83.1	0.0	83.1	58.4	15.3	73.7
0	10	0.0	96.1	96.1	25.2	67.5	92.7
100	0	98.6	0.0	98.6	84.1	10.9	95.0
0	100	0.0	97.1	97.1	10.1	72.7	82.8
Oxamyl							
10	0	78.3	7.9	86.2	77.3	29.9	107.2
0	10	0.0	104.3	104.3	0.0	92.0	92.0
100	0	98.4	0.0	98.4	70.3	33.6	103.9
0	100	0.0	88.6	88.6	0.0	98.7	98.7

[a]Percentage values of recovered residues have been corrected for extraction efficiencies given in Table 1.

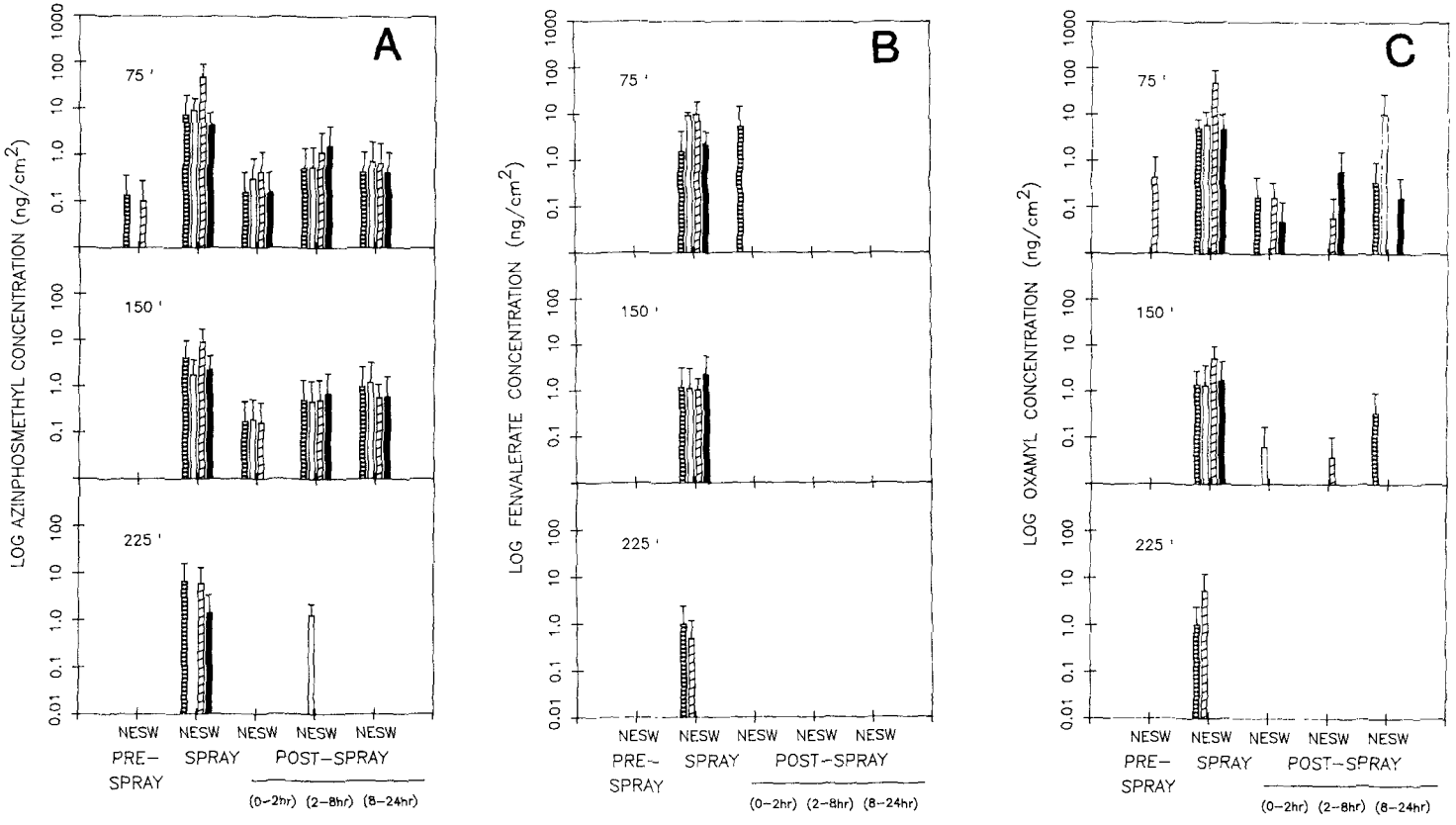

Figure 2. Residues deposited on cellulose discs (N=4).

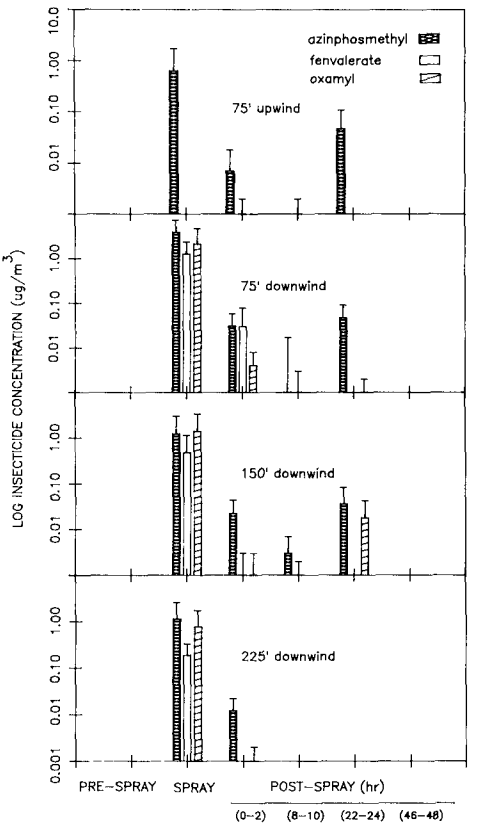

Figure 3. Residues collected by high volume air samplers (N=4).

breakthrough of trapped residues during standard sampler operation (2 hr). Although trapping efficiency appears to fall at the 100ug level of azinphosmethyl, this level of residue was never achieved nor approached during field collections (see Fig. 3).

Insecticide residues collected as a mixture on cellulose discs are illustrated in Figure 2 (A-C). A large proportion of total fallout residues for each insecticide occurred during the spray collection (i.e., 87.3% azinphosmethyl, 80.6% fenvalerate, 98.0% oxamyl). In all cases, the maximum level of residue was deposited at the nearest downwind cellulose disc (i.e., S-75 ft). The maximum residue levels (ng/cm^2) for azinphosmethyl, fenvalerate and oxamyl were 48.24 ± 43.44, 9.82 ± 8.22 and 48.82 ± 42.37, respectively. The relative proportions of total residues for each insecticide deposited over the 0-2 hr post application period were reduced compared to the spray collection (i.e., 1.4% azinphosmethyl, 19.4% fenvalerate, and 0.6% oxamyl). The maximum residue levels (ng/cm^2) deposited on cellulose discs 0-2 hr post application were 0.43 ± 0.74 azinphosmehtyl (S-75 ft), 5.32 ± 9.21 fenvalerate (N-75 ft) and 0.17 ± 0.29 oxamyl (N-75 ft).

Insecticide residues collected as mixtures by high volume air samplers are illustrated in Figure 3. As with the fallout deposition collections, a large proportion of total airborne residues for each insecticide occurred during the spray collection (i.e., 97.1% azinphosmethyl, 98.2% fenvalerate, and 99.4% oxamyl). In all cases, the maximum level of residue was associated with the most proximal downwind air sampler (i.e., 75 ft). The maximum concentrations (ug/m^3) for azinphosmethyl, fenvalerate and oxamyl were 3.87 ± 3.40, 1.28 ± 1.09, and 2.12 ± 2.57, respectively. The relative proportions of total residues for each insecticide collected during the 0-2 hr post application period were dramatically reduced compared to the spray collection (i.e., 1.01% azinphosmethyl, 1.63% fenvalerate, and 0.16% oxamyl). The maximum residue concentration (ug/m^3) for each insecticide during this collection was detected at the 75 ft downwind sampler (0.031+0.027 azinphosmethyl, 0.030+0.048 fenvalerate, 0.004+0.004 oxamyl). Because airborne residues were only detected on the G.F. filters and never on the XAD resin, the majority of the insecticides appeared to be in the particulate form and not as a vapor (Draper et al. 1981).

Because approximately 90% or more of the total off-site drift residues were collected during application and in the period 0-2 hr post application, the maximum residue levels detected during these collections are considered to represent the "worst case" scenarios to estimate potential human exposures. Potential dermal and inhalation exposures were estimated using the calculations and assumptions developed by Draper et al. (1981) (i.e., exposed skin area of a 70kg male $0.29m^3$, $4047m^2/A$ conversion factor, breathing rate $1.8m^3/hr$) and are presented in Table 3.

Table 3. Potential off-site exposure to orchard insecticides.

Dermal Dose at 150 ft (mg)[a]		Inhalation Dose at 150 ft (ug)[b]		
		application	0-2 hr	total
Azinphosmethyl	1.01	1.11	0.08	1.19
Fenvalerate	0.32	0.42	0.004	0.42
Oxamyl	0.56	1.27	0.004	1.27
Mixture	1.89	2.8	0.088	2.88

[a]Intended application rate in g/A (74.8 azinphosmethyl; 19.6 fenvalerate; 71.8 oxamyl). Ratio of maximum residues at 150 ft cellulose discs/residues at 75 ft (e.g., 0.186 azinphosmethyl, 0.227 fenvalerate, 0.107 oxamyl).

[b]Inhaled air (e.g., $0.9m^3$/30 min application, $3.6m^3$/0-2hr post-application period). Maximum residue concentration (ug/m^3) at 150 ft downwind sampler during application (e.g., 1.23 azinphosmethyl, 0.472 fenvalerate, 1.413 oxamyl) and 0-2 hr post-application (e.g., 0.022 azinphosmethyl, 0.001 fenvalerate, 0.001 oxamyl).

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