Distribution and Persistence of Aerially Sprayed Permethrin in Some Terrestrial Components of a Boreal Plantation Forest

Kanth M. S. Sundaram,* Blair V. Helson, and Nicholas J. Payne

Forest Pest Management Institute, Forestry Canada, Box 490,
Sault Ste. Marie, Ontario, Canada P6A 5M7

An aqueous emulsion of permethrin was applied aerially at a dosage rate of 70 g of active ingredient (ai)/ha over a mixed boreal plantation forest near Sault Ste. Marie, ON, Canada. The initial residues after spray in soil and litter were low, 0.025 and 0.033 μg/g, respectively, and dissipated to levels below 0.005 μg/g within 6 days in soil and 16 days in litter. Initial residues (micrograms per gram) in foliage of four tree species were ca. 100 times higher than those in soil and litter. The broad leaves of aspen showed, on average, slightly higher residues than the conifer needles, probably due to a higher surface area-to-mass ratio. The bark samples of all species showed consistently lower residues than the foliage, but the persistence did not differ markedly for the two substrates. Little relationship existed between the initial residues and lipid content of the substrates. Low levels of permethrin overwintered in foliage and bark of all species, but these dissipated to values below 0.005 μg/g at 431 days after spray. The study showed that despite the initial rapid disappearance of the soil and litter residues, some contamination of the environment can still occur from leaf-fall but only with trace amounts of permethrin in the fallen leaves.

INTRODUCTION

Permethrin [3-phenoxybenzyl (1-RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], one of the synthetic pyrethroid insecticides, is used to control various insect pests in agriculture, forestry, horticulture, and stored products, and in animal and human health areas (Elliott et al., 1978). As an insecticide, the chemical has certain desirable properties such as a high knockdown rate against target insects (FMC Corp., 1984), good residual activity with moderate persistence (Chipman, Inc., 1981; Hirano, 1989), low mammalian and bird toxicity (Bradbury and Coats, 1989), absence of toxic metabolites (Menzie, 1980), and a ready availability at a reasonable cost (Watkinson, 1989).

Aerial field trials conducted by DeBoo (1980), Zylstra and Obarymskyj (1981), and Helson et al. (1989) demonstrated the efficacy of permethrin to control forest defoliators such as the eastern spruce budworm, *Choristoneura fumiferana* (Clemens), and the spruce budmoth, *Zeiraphera canadensis* (Mut. and Free.). Permethrin is currently registered for spruce budworm control in Canada by ground application. Before it can be sprayed aerially for plantation pest control in Canada, it must be registered under the Pest Control Products Act for aerial application. To meet this requirement, the environmental safety and ecological acceptability of permethrin need to be examined in field dissipation studies (Forest Pest Management Institute, 1990) under Canadian environmental conditions using the intended maximum dosage. With this objective in mind, an aerial spray trial was conducted in 1989 to investigate the distribution and persistence of permethrin in forest litter, soil, deciduous and conifer foliage, and their respective barks after aerial application at 70 g of active ingredient (ai)/ha. The results of the study are reported here.

EXPERIMENTAL PROCEDURES

Spray Block, Sample Trees, Soil and Litter Plots. The spray block (400 × 400 m) chosen was in a mixed, semimature (trees, 3.5 ± 0.8 m high), and open plantation forest. The block

was located 3 km northwest of Thessalon, ON, Canada, near grid reference 46° 21′ N and 83° 35′ W. Tree species in the sampling site (ca. 280 × 280 m) (Figure 1), approximately in the center of the block, included jack pine (*Pinus banksiana* Lamb.), red pine (*Pinus resinosa* Ait.), white spruce [*Picea glauca* (Moench) Voss] (referred to as spruce hereafter), and trembling aspen (*Populus tremuloides* Michx.) (referred to as aspen), occasionally interspersed with white pine (*Pinus strobus* L.). The ground was nearly flat and largely covered with grass species. The soil was primarily sandy (bulk density 1.25 g/cm³, pH 6.4, moisture content 25%), containing 89% coarse sand, 8% silt, and 3% clay with low organic matter (OM) (<1%) content (Kalra and Maynard, 1991) (it is customary to omit the moisture and organic matter from the total content). The litter layer (bulk density 0.95 g/cm³, pH 6.1, moisture content 19%) had higher OM (9%); otherwise, its composition was very similar to that of the soil.

Six trees each of jack pine, white pine, spruce, and aspen of approximately uniform size, with a height of 3.5 ± 0.5 m, were selected in the sampling site (Figure 1) for foliage collection. Ground vegetation and nearby trees were cleared prior to spraying to enhance exposure of the tree crown to the spray cloud. The intention was to use the "worst case scenario" to obtain the highest amount of deposits.

To collect forest litter, three plots, each 2.0 m², were randomly selected in the open areas of the 8-ha sampling site (Figure 1). All fallen branches, twigs, and stones were removed from the surface to expose the litter layer, and the litter was leveled and packed to the original condition. Similarly, three soil plots of the same size were selected, and in addition to the fallen branches, twigs, and stones, the litter layer was also removed to expose the underlying soil layer. Again, the intention was to obtain maximum possible deposits on soil and litter.

Spray Application. The spray mix consisted of 4.50 g (or 4.05 mL) of Pounce EC (384 g/L of permethrin; Chemagro Ltd., Canada), 0.40 g of Rhodamine dye (in 0.85 mL of ethanol), and 95.10 mL of water. The mix was sprayed at an application rate of 70 g of ai in 4.0 L/ha, on June 24, 1989, over the block using a Cessna 188B aircraft equipped with four Micronair AU3000 atomizers. Marker flags and helium-filled balloons were placed at intervals along the boundaries of the block for aircraft guidance. A meteorological station was established near the edge of the spray block to provide wind speed, wind direction, temperature, and relative humidity. Details are given in Table I.

Sampling and Analysis. At each sampling interval, one branch tip (ca. 25 cm long) from each of the four midcrown

---

2524 *J. Agric. Food Chem.,* Vol. 40, No. 12, 1992

Sundaram et al.
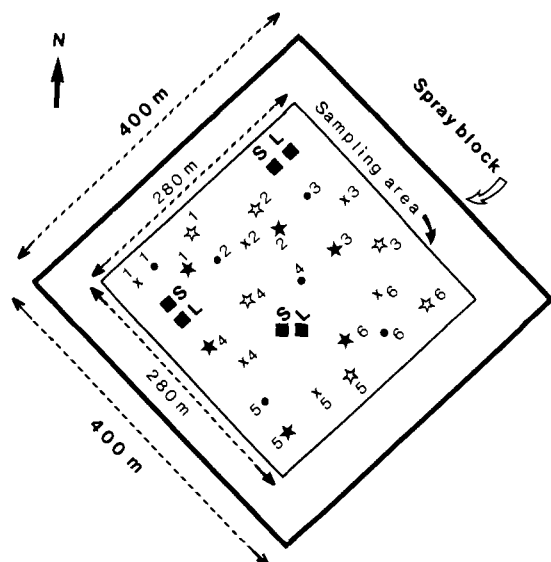
Figure 1. Locations of sample trees of four species, soil and litter plots in the sampling area (280 × 280 m), situated within the spray block (400 × 400 m). (X) Jack pine 1-6; (●) white pine 1-6; (☆) white spruce 1-6; (★) trembling aspen 1-6; (S) soil plots; (L) litter plots. (Foliage from trees 1 and 2 of the same species was pooled to obtain one composite sample. Similarly, samples of trees 3 and 4, and 5 and 6 were pooled to obtain two more composite samples.)

Table I. Meteorological Conditions and Application Parameters in Aerial Spray Trials of Permethrin near Thessalon, Ontario, in June 1989

application date	June 24, 1989
application time	8:35 p.m. (start)–9:00 p.m. (finish)
spray block size, ha	16
sampling plot size, ha	8
aircraft type	Cessna 188B
atomizer units	four Micronair AU3000
blade angle setting, deg	35
aircraft speed,[a] km/h	175
application rate,[a] g of ai	70, in 4 L/ha
emission rate,[a] L/min	30
swath width,[a] m	25
canopy height,[a] m	7
spray height[a]	11 m above canopy
wind speed,[a] m/s	1.0, at 6 m above ground
temp,[b] °C	19 ± 0.6, 6 m above ground
relative humidity, %	52 ± 4, 6 m above ground
cloud cover	1/10
precipitation	nil

[a] Average values are reported.

quadrants of each tree was clipped with a pole pruner. The eight branch tips collected from two of six trees (i.e., trees 1 and 2; 3 and 4; and 5 and 6 in Figure 1) were pooled after the new growth was removed and discarded, to provide one composite sample. In this manner, the 24 branches from the 6 trees of the same species were pooled to provide three composite samples for triplicate analysis of foliar residues. Each sample was packed in aluminum foil, labeled, put in plastic bags, sealed, stored immediately at 0 °C, and transported to the residue laboratory in Sault Ste. Marie. In the laboratory, the 1-year-old conifer needles from each sample were clipped with scissors (cleaned between samples), mixed well, and stored in glass bottles at −20 °C until analysis. The bark of each branch tip corresponding to the sample was carefully removed using sharp blades, pooled, mixed well, and stored as above. For aspen, fully developed leaves were collected from the branch tips for analysis. The bark samples of aspen were collected and stored as described for conifers.

Because of the soil's sandy nature, the conventional soil auger (Sundaram, 1991a) could not be used, and therefore, litter and soil cores, each 19.65 cm² area × 2 cm deep, were collected by driving an inverted cylindrical stainless steel (SS) cup into the ground and lifting the contents carefully with a wide SS spatula. Two soil and litter cores were collected from each plot at each

Table II. Permethrin Residues (μg/g of Wet Weight) in Forest Soil and Litter, following Aerial Spraying at 70 g of Active Ingredient/ha in Ontario, June 1989

time after spray	soil	litter	intermittant rainfall,[m] mm
prespray	ND[a]	ND	nil
1 h	0.025 (0.014)[b]	0.033 (0.012)	nil
15 h	0.023 (0.006)	0.028 (0.008)	nil
36 h	0.014 (0.012)	0.025 (0.010)	0.8
4 days	0.007 (0.007)	0.018 (0.004)	nil
6 days	T[c]	0.014 (0.006)	1.8
10 days	ND	0.008 (0.003)	nil
16 days	ND	T	nil
24 days	NS[k]	ND	nil
rate const (C)[e]	0.3316	0.1373	
coeff detr (R²)[f]	0.978	0.997	
DT₅₀,[g] days	2.1	5.0	
lipid content,[j] %	0.75	1.85	

[a] ND, not detectable (limit of detection is 0.002 μg/g). [b] Total of cis + trans isomers; each value is the mean of triplicate samples (and ± one SD is given in parentheses). Residues were calculated per gram of wet weight of sample. [c] T, trace (0.002 < T < 0.005 μg/g). [e] The constant C is for the exponential equation $B = B_0 e^{-Ct}$. [f] Coefficient of determination R^2 is for the equation $2.303 \log_{10} (B - B_0) = -Ct$. [g] The time required for 50% of the initial residues to dissipate. [j] Lipid content is expressed in w/w % dry weight of substrates. [k] NS, not sampled. [m] Data obtained from Environment Canada for the region containing the spray block.

sampling period, and the two cores were pooled to provide one composite sample. Thus, the six cores of each matrix collected from the three plots provided three composite samples for residue analysis. All samples were wrapped in aluminum foil and brought to the residue laboratory as described previously for foliage. The litter samples were finely chopped using a blender, sieved (2-mm opening), mixed well, and stored at −20 °C until analysis. The soil samples were sieved without further grinding and stored as above.

Samples of soil, litter, foliage, and bark were collected at 1, 15, and 36 h and at 4, 6, 10, 16, and 24 days after permethrin treatment (Table II), with the foliage and bark sampled for a longer period including 30, 40, 51, 60, 73, 93, 110, 125, 363, and 431 days postspray (Tables III–VI).

The stored foliage, bark, forest litter, and soil samples were further processed (Sundaram, 1987), and permethrin residues were analyzed by gas chromatography (GC) after solvent extraction and column cleanup (Sundaram, 1990). An aliquot of each substrate was homogenized in a Polytron with anhydrous Na_2SO_4 (A-SS) and n-hexane (HEX). The pooled extract of each sample was evaporated to dryness under nitrogen, and the residue was dissolved in HEX. The crude extract (Cr-E) was cleaned using a double microcolumn to remove the coextractives. The first column (Fl-C) was packed with A-SS, followed by Florisil and topped with A-SS. The second column (Ch-C) was packed with A-SS, followed by charcoal–cellulose, and topped with A-SS. The columns were prewashed with HEX. An aliquot of the Cr-E was transferred first to the Fl-C column and eluted with dichloromethane (DCM). The eluate was concentrated, transferred to the Ch-C column, and allowed to percolate. The column was washed with DCM/HEX (20:80 by volume), and the washings were discarded. The permethrin was then eluted with DCM, and the eluate was flash-evaporated to dryness under nitrogen. The residue was dissolved in HEX for GC analysis.

Aliquots (2–5 μL) of the cleaned extract were injected into a Hewlett-Packard (HP) Model 5890A gas chromatograph with a ⁶³Ni electron capture detector and a HP3392A electronic integrator. External standards were interspersed among the samples to check consistency of chromatographic response. The minimum detection limit (MDL) for soil and litter samples was 0.002 μg/g and for the plant substrates 0.005 μg/g. The mean ± SD (n = 4) percent recoveries obtained after fortification (prior to the addition of the extracting solvent) of the prespray or control samples at concentration levels (1.0, 0.1, and 0.01 μg/g) relevant for this study were 96 ± 5 for soil and litter and 91 ± 7 for plant substrates. Residue data reported in Tables II–VI include the

Table III. Permethrin Residues (μg/g of Fresh Weight) in Jack Pine Needles and Bark, following Spray Application at 70 g of Active Ingredient/ha in Ontario, 1989

time after spray	needles	amt lost	bark	amt lost	intermittant rainfall,[m] mm
prespray	ND[a]		ND		nil
1 h	3.466 (0.916)[b]		0.818 (0.062)		nil
15 h	3.670 (0.662)	−0.204	0.913 (0.163)	−0.095	nil
36 h	3.120 (0.363)	0.550	0.625 (0.138)	0.288	0.8
4 days	2.449 (0.612)	0.671	0.384 (0.152)	0.241	nil
6 days	2.194 (0.681)	0.255	0.352 (0.038)	0.032	1.8
10 days	1.453 (0.719)	0.741	0.232 (0.037)	0.120	nil
16 days	0.573 (0.216)	0.880	0.090 (0.038)	0.142	nil
24 days	0.497 (0.211)	0.076	0.083 (0.043)	0.007	nil
30 days	0.375 (0.113)	0.122	0.059 (0.020)	0.024	3.4
40 days	0.192 (0.056)	0.183	0.060 (0.022)	−0.001	8.8
51 days	0.078 (0.025)	0.114	0.058 (0.019)	0.002	14.2
60 days	0.044 (0.016)	0.034	0.050 (0.014)	0.008	22.4
73 days	0.038 (0.019)	0.006	0.050 (0.014)	0.000	32.5
93 days	0.037 (0.009)	0.001	0.046 (0.007)	0.004	45.6
110 days	0.036 (0.007)	0.001	0.044 (0.005)	0.002	50.1
125 days	0.034 (0.007)	0.002	0.043 (0.005)	0.001	49.0
363 days	0.037 (0.008)	−0.003	0.048 (0.012)	−0.005	
431 days	ND		T[c]		
rate const (CI)[e]	0.1112		0.1375		
coeff detr (R^2)[f]	0.977		0.975		
DT_{50}-I,[g] days	6.2		5.0		
rate const (CII)[e]	0.0426		0.0082		
coeff detr (R^2)[f]	0.885		0.790		
DT_{50}-II,[g] days	16.3		84.6		
lipid content,[j] %	8.7		11.3		

[a] ND, not detectable (limit of detection is 0.005 μg/g). [b,j,m] See footnote of Table II. [c] T, trace (0.005 < T < 0.010 μg/g). [e,g] The constants CI and DT_{50}-I are for the initial rapid dissipation up to 16 days postspray, whereas CII and DT_{50}-II, are for the slow dissipation during the later stages.

correction for recovery efficiency. Each value represents the mean ± SD of three replicate samples and provides the total of two geometric isomers (cis + trans) of permethrin. None of the prespray or control samples contained permethrin, and there was no evidence of coextracted materials causing interference with the identification and quantification of the chemical. Information on rainfall (obtained from Environment Canada) during the postspray period is given in Tables II and III.

Lipid Contents of Substrates. Literature information suggests the influence of lipid content of substrates on spray deposition and persistence of polar pesticides (Hess, 1987). Permethrin is sparingly soluble in water [0.2 mg/L at 25 °C (Worthing and Walker, 1983)] but is lipophilic (Rawn et al., 1982; NRCC, 1986) (log K_{OW} = 3.5–6.5). Therefore, the lipid contents of substrates would likely provide an indication of their ability to solubilize the chemical within the lipids and retain it for a considerably long time. Consequently, the lipid contents of prespray samples of the substrates were determined according to the method of Wang et al. (1969).

Aliquots of samples were soaked in a mixture of aqueous (1.25%) hydrochloric and hydrofluoric acids for 48 h and filtered, and the filtrate was discarded. The substrate was washed with water until free of acid and shaken with chloroform plus methanol (2 + 1, by volume) solvent for 1 h. The liquid layer was removed by filtration and flash-evaporated to dryness at 40 °C. The residue was taken in n-hexane and centrifuged at 13000g for 20 min. The supernatant liquid containing the lipid components was decanted and evaporated to dryness and the residue weighed. The moisture content of the substrates was determined by drying aliquots of samples at 65 °C in a vacuum desiccator to constant weight. The lipid content was calculated using the dry weight of each substrate (Tables II–VI).

RESULTS AND DISCUSSION

Residues in Forest Litter and Soil. Permethrin residues in forest soil and litter (micrograms per gram of wet weight) at various time intervals after treatment are given in Table II. To minimize variability in results, all residues were measured on a dry weight basis but were

adjusted to the constant, prespray moisture levels of the substrates (soil, 25%; litter, 19%). The initial residues in soil (0.025 μg/g) and litter (0.033 μg/g) were similar to those obtained for a mexacarbate emulsion (0.020 and 0.060 μg/g, respectively) applied at an equivalent dosage rate (70 g of ai/ha) in an earlier study (Sundaram and Nott, 1985).

Analysis of variance (Ryan et al., 1985) of initial deposits on the two substrates (using the three replicate samples analyzed) showed no significant difference (ANOVA $P >$ 0.05) between the two values. The residues in soil degraded more rapidly than those in litter. For example, within 10 days after treatment, the soil residues had dissipated to levels below the detection limit of 0.002 μg/g. In contrast, the residues in litter lingered at 0.008 μg/g until the 10th day after treatment and diminished to nondetectable levels on the 24th day after spray. Contrary to this, Kingsbury and Kreutzweiser (1980) found that at a dosage rate of 17.5 g of ai/ha, initial deposits ranged from 0.04 to 0.07 μg/g (wet wt) in soil and from 0.04 to 0.21 μg/g in litter and were relatively stable over a 58-day period after treatment in both substrates. The shorter persistence observed in the present study could be due to irreversible binding of permethrin to the substrates or its rapid degradation by chemical (Chapman et al., 1981) and/or microbial means (Menzie, 1980).

The dissipation of residues in soil and litter as a function of time was fitted with the exponential equation

$$B = B_0 e^{-Ct} \qquad (1)$$

where B is the amount present at time t (in days), B_0 is the amount initially present, and C is the rate constant. Logarithmic transformation yielded the linear equation

2526 *J. Agric. Food Chem.,* Vol. 40, No. 12, 1992

Sundaram et al.

Table IV. Permethrin Residues (μg/g of Fresh Weight) in White Pine Needles and Bark, following Spray Application at 70 g of Active Ingredient/ha in Ontario, 1989

time after spray	needles	amt lost	bark	amt lost
prespray	ND[a]		ND	
1 h	3.125 (0.322)[b]		0.240 (0.027)	
15 h	3.261 (0.280)	−0.136	0.234 (0.027)	0.006
36 h	2.620 (0.372)	0.641	0.206 (0.042)	0.028
4 days	2.175 (0.118)	0.445	0.178 (0.034)	0.028
6 days	1.685 (0.159)	0.490	0.124 (0.031)	0.054
10 days	0.961 (0.131)	0.724	0.088 (0.021)	0.036
16 days	0.448 (0.129)	0.513	0.043 (0.008)	0.045
24 days	0.415 (0.042)	0.033	0.050 (0.013)	−0.007
30 days	0.186 (0.048)	0.229	0.043 (0.016)	0.007
40 days	0.102 (0.028)	0.084	0.016 (0.017)	0.027
51 days	0.028 (0.016)	0.074	0.015 (0.004)	0.001
60 days	0.035 (0.013)	−0.007	0.012 (0.006)	0.003
73 days	0.031 (0.016)	0.004	0.012 (0.008)	0.000
93 days	0.021 (0.012)	0.010	0.018 (0.009)	−0.006
110 days	0.019 (0.011)	0.002	0.022 (0.014)	−0.004
125 days	0.022 (0.014)	−0.003	0.019 (0.011)	0.003
363 days	0.021 (0.018)	0.001	0.021 (0.015)	−0.002
431 days	ND		ND	
rate const (CI)[e]	0.1244		0.1082	
coeff detr (R^2)[f]	0.994		0.993	
DT_{50}-I,[g] days	5.6		6.4	
rate const (CII)[e]	0.0435		0.0174	
coeff detr (R^2)[f]	0.834		0.558	
DT_{50}-II,[g] days	15.9		40.0	
lipid content,[j] %	7.7		10.2	

[a,e,g] See footnote of Table III. [b,i,j] See footnote of Table II.

$$2.303 \log_{10} (B - B_0) = -Ct \quad (2)$$

Regression analysis of the residues remaining at time t indicated a good fit with R^2 values (the coefficient of determination) >0.97. Values of DT_{50} (i.e., the time required for 50% of the initial deposits to dissipate) were computed (Table II) using

$$DT_{50} = (2.303 \log_{10} 2)/C \quad (3)$$

The DT_{50} values are ca. 2.5 times higher for litter than for soil, indicating a longer persistence in the litter. Nevertheless, permethrin showed shorter persistence in both substrates (residue levels reached below the MDL value in less than 24 days) than in foliage and bark samples (residues persisted up to 363 days) (see Tables III–VI). This is likely due to the higher initial residues (ca. 100 times greater) obtained in foliage and bark than in soil and litter, because a direct relationship has been reported in previous studies (Lichtenstein, 1972; Sundaram, 1991a) between initial residues and duration of persistence.

The difference in persistence between the soil and litter residues observed in the present study could be due to the chemical nature of the two substrates. The higher organic matter (OM) content (ca. 9%) in litter than in soil (<1%), combined with the higher lipid content (more than twice) (Table II), could have caused adsorption and solubilization of permethrin in the litter (Armson, 1977; NRCC, 1986), thus extending its persistence (Demoute, 1989). In a recent study (Sundaram, 1991b), permethrin uptake and persistence in aquatic substrates were shown to be influenced by their lipophilic nature. Alternatively, different levels of microbial activity caused by different moisture contents could explain the difference in persistence (Menzie, 1980).

The rapid dissipation of permethrin from soil and litter is in agreement with findings reported in the literature. Kaufman et al. (1977), Kaneko et al. (1978), and Jordan et al. (1982) demonstrated the role of chemical and microbial action on loss of permethrin from litter and soil.

Table V. Permethrin Residues (μg/g of Fresh Weight) in White Spruce Needles and Bark, following Spray Application at 70 g of Active Ingredient/ha in Ontario, 1989

time after spray	needles	amt lost	bark	amt lost
prespray	ND[a]		ND	
1 h	2.573 (0.435)[b]		0.409 (0.034)	
15 h	2.720 (0.294)	−0.147	0.432 (0.041)	−0.023
36 h	2.300 (0.191)	0.420	0.342 (0.035)	0.090
4 days	1.715 (0.210)	0.585	0.225 (0.049)	0.117
6 days	1.294 (0.241)	0.421	0.170 (0.025)	0.055
10 days	0.699 (0.117)	0.595	0.148 (0.009)	0.022
16 days	0.509 (0.112)	0.190	0.086 (0.026)	0.062
24 days	0.456 (0.110)	0.053	0.083 (0.011)	0.003
30 days	0.281 (0.014)	0.175	0.049 (0.019)	0.034
40 days	0.247 (0.030)	0.034	0.036 (0.012)	0.013
51 days	0.236 (0.034)	0.011	0.024 (0.009)	0.012
60 days	0.215 (0.017)	0.021	0.032 (0.007)	−0.008
73 days	0.172 (0.029)	0.043	0.027 (0.012)	0.005
93 days	0.137 (0.012)	0.035	0.025 (0.005)	0.002
110 days	0.079 (0.008)	0.058	0.022 (0.005)	0.003
125 days	0.050 (0.005)	0.029	0.016 (0.011)	0.006
363 days	0.039 (0.009)	0.011	0.017 (0.015)	0.001
431 days	T[c]		ND	
rate const (CI)[e]	0.1117		0.1000	
coeff detr (R^2)[f]	0.970		0.946	
DT_{50}-I,[g] days	6.2		6.9	
rate const (CII)[e]	0.0162		0.0167	
coeff detr (R^2)[f]	0.899		0.720	
DT_{50}-II,[g] days	42.8		41.5	
lipid content,[j] %	10.3		11.7	

[a,c,e,g] See footnote of Table III. [b,i,j] See footnote of Table II.

Table VI. Permethrin Residues (μg/g of Fresh Weight) in Trembling Aspen Foliage and Bark, following Spray Application at 70 g of Active Ingredient/ha in Ontario, 1989

time after spray	foliage	amt lost	bark	amt lost
prespray	ND[a]		ND	
1 h	4.542 (0.311)[b]		1.646 (0.175)	
15 h	4.565 (0.477)	−0.023	1.672 (0.170)	−0.026
36 h	4.150 (0.301)	0.415	1.046 (0.103)	0.626
4 days	3.172 (0.319)	0.978	0.722 (0.097)	0.324
6 days	2.207 (0.223)	0.965	0.695 (0.106)	0.027
10 days	2.028 (0.324)	0.179	0.563 (0.121)	0.132
16 days	1.108 (0.127)	0.920	0.426 (0.090)	0.137
24 days	0.711 (0.097)	0.397	0.367 (0.071)	0.059
30 days	0.664 (0.089)	0.047	0.325 (0.051)	0.042
40 days	0.590 (0.060)	0.074	0.161 (0.042)	0.164
51 days	0.421 (0.054)	0.169	0.130 (0.021)	0.031
60 days	0.363 (0.024)	0.058	0.056 (0.015)	0.074
73 days	0.344 (0.037)	0.019	0.101 (0.018)	−0.045
93 days	0.210 (0.050)	0.134	0.058 (0.008)	0.043
110 days	0.230 (0.035)[k]	−0.020	0.046 (0.018)	0.012
125 days	0.241 (0.044)[k]	−0.011	0.039 (0.019)	0.007
363 days	0.261 (0.037)[m]	−0.020	0.029 (0.009)	0.010
431 days	ND		ND	
rate const (CI)[e]	0.0894		0.0824	
coeff detr (R^2)[f]	0.971		0.834	
DT_{50}-I,[g] days	7.8		8.4	
rate const (CII)[e]	0.0194		0.0281	
coeff detr (R^2)[f]	0.958		0.832	
DT_{50}-II,[g] days	35.7		24.6	
lipid content,[j] %	4.8		7.2	

[a,e,g] See footnote of Table III. [b,i,j] See footnote of Table II. [k] Dry foliage collected from forest floor around the sampling trees after the autumn leaf-fall. The residue levels were corrected for the moisture content that would be equivalent to that of the fresh foliage collected at 93 days postspray. [m] Foliage samples collected from the forest floor in the late spring of the following year. The residue levels were corrected for the moisture content as described above.

Several reasons have been suggested for this rapid dissipation: Hill (1985) and Demoute (1989) indicated the formation of bound residues (i.e., those tightly bound

Persistence of Permethrin

J. Agric. Food Chem., Vol. 40, No. 12, 1992 **2527**

to the soil and litter matrices and hence unextractable), whereas Ruzo and Casida (1980) pointed out the role of photolytic degradation. Grayson (1975) and Fujie (1975) found that permethrin hydrolyzes in water even at acidic and neutral pH conditions. In the present study, the slightly acidic pH of the soil (6.4) and litter (6.1) could have contributed to some loss by hydrolysis. Volatilization [vapor pressure of permethrin, 261 mPa at 30 °C (Worthing and Walker, 1983)] is also one of the routes of disappearance from the environment (NRCC, 1986). Permethrin is known to be relatively immobile in soils (NRCC, 1986), and therefore the 2.60 mm of intermittent rainfall that occurred during the 15-h–16-day postspray period (Table II) would have contributed little to its dissipation by leaching.

Residues in Foliage and Bark Samples. Permethrin residues (micrograms per gram of fresh weight) in foliage and bark samples of conifers and aspen at various time intervals after treatment are given in Tables III–VI. The residues in plant substrates were much higher than those in soil and litter. The ratio of permethrin residues in foliage to those in bark found at 1 h after spray varied markedly among the tree species studied. For example, the ratios in jack pine, white pine, spruce, and aspen were, respectively, 4.2:1, 13.0:1, 6.3:1, and 2.8:1. This variation could be related to the shape of the tree crown, foliar morphology, canopy density, the open space between trees, or other factors (Sundaram, 1991c). The 15-h-postspray samples of foliage and bark contained slightly higher amounts of permethrin than the 1-h samples, although this increase was not statistically significant (ANOVA $P > 0.05$).

The initial residues found on aspen foliage (mean value of ca. 4.54 μg/g) and bark (ca. 1.65 μg/g) at 1-h postspray were higher than those on conifer needles (mean values of 2.57–3.47 μg/g) and bark (0.24–0.82 μg/g) of the other three species. Analysis of variance showed significant difference between the foliar and bark residues of aspen and conifer species (ANOVA $P < 0.05$). The present observation of higher residues of permethrin in deciduous foliage than in conifers is in agreement with the findings of Kingsbury and McLeod (1979) and Kingsbury and Kreutzweiser (1980). This is likely due to higher surface area-to-mass ratio of the deciduous foliage than that of the conifer needles (NRCC, 1986). Similar findings were reported in previous aerial spray trials with other polar, lipophilic pesticides: in a trial near Searchmont, ON, Sundaram et al. (1989) reported higher fenitrothion residues on birch foliage than on fir needles. Similarly, in another trial near Kaladar, ON, Sundaram (1991a) found higher diflubenzuron residues on maple leaves than on white pine foliage. Furthermore, Sundaram (1991d) found higher residues of phosphamidon on the leaves of white birch and red maple than on the foliage of five conifer species. Several reasons (apart from the higher surface area-to-mass ratio) could be offered for this behavior: (i) the open canopy of broad-leaf trees causes a greater leaf area to be exposed to the spray cloud than the dense canopy of conifers; (ii) the presence of pubescence on the deciduous leaves causes more droplets to be trapped than the smooth surface of the conifer needles; (iii) the different micro-meteorological factors associated with the two types of crown geometrics influence spray deposition (Yates and Akesson, 1973; Cramer and Boyle, 1976); (iv) the deciduous leaves move more along the wind flow than the conifer needles; and (v) differences in the lipid content of the foliar types contribute to differences in droplet interception and retention (Hess, 1987). Among the factors mentioned, only one factor was investigated in the present study, i.e.,

the lipid content of substrates (Tables III–VI). It is evident that little relationship exists between the lipid contents and initial deposits on the substrates, thus indicating the complexity of droplet interception and retention.

Generally, the disappearance of permethrin was slower from foliage than from the bark during the initial stages. For instance, within 4 days after treatment, 30–33% of the initial residues were lost from the foliage, as opposed to the loss from the bark of 45–56%. The only exception was the bark of white pine, which showed a low value of 26%. This could be due to the gradual occlusion of permethrin in the white pine bark, as reported previously by Naumov et al. (1989). After the initial stage, the dissipation of the chemical was gradual, and the percent losses at 10 days after treatment were 55–73 for foliage and 63–72 for bark samples. The residues then tapered off slowly, and at 60 days posttreatment, nearly 99% of the initial deposits were lost from foliage of the two pine species and 92% was lost from spruce and aspen foliage. The corresponding values from the bark samples of the two pine species were 94 and 95% and for spruce and aspen were 92 and 97%, respectively. Kingsbury and Kreutzweiser (1980) reported a similar pattern of persistence in deciduous and conifer foliage: residues were detectable even 57 days after spray application. Low amounts of residues overwintered in the present study and persisted in foliage and bark samples of the three conifer species up to 363 days after treatment (Tables III–V). However, by 431 days only trace (ca. 0.005 μg/g) amounts were present. The aspen leaves, collected from the forest floor after the autumn leaf-fall and the winter, still contained measurable amounts of permethrin, thus indicating a slow rate of dissipation (Table VI).

The disappearance of permethrin from foliage and bark samples appeared to be biphasic, evident from the amount lost between the various time intervals (Tables III–VI). Initially (i.e., during 16 days postspray), the chemical was lost rapidly but underwent a gradual loss during the later stages. Consequently, the residue data were analyzed by using two types of exponential relationships (Sundaram and Sundaram, 1987), viz., eq 4 for the initial stage and eq 5 for the later stages

$$B = B_0 e^{-CIt} \tag{4}$$

$$D = D_0 e^{-CIIt} \tag{5}$$

where CI and CII are the rate constants for the initial rapid loss and for the gradual loss, respectively. Logarithmic transformation and regression analysis yielded numerical values for the constants CI and CII for the foliage and bark samples (Tables III–VI). The dissipation times, DT_{50}-I (the days required for dissipation of 50% of the initial residues during 16 days postspray) and DT_{50}-II (the days required for dissipation of 50% of the residues remaining on the 16th day), were computed using

$$DT_{50}\text{-I} = (2.303 \log_{10} 2)/CI \tag{6}$$

$$DT_{50}\text{-II} = (2.303 \log_{10} 2)/CII \tag{7}$$

The DT_{50}-I values during the initial 16-day period (Tables III–VI) were low for all four species (ranging from 5 to 8.4 days) and indicated similar rates of dissipation from both foliage and bark substrates. In view of the low amount of rainfall (2.6 mm) during the initial period (Table III), the rapid loss could largely be due to photolysis or photoinduced transformation (Leahey, 1985). The present DT_{50}-I

2528 *J. Agric. Food Chem.,* Vol. 40, No. 12, 1992

Sundaram et al.

values are similar to those reported in bean and cotton plants (DT$_{50}$ of 7–9 days) (Ohkawa et al., 1977; Gaughan and Casida, 1978). During the later stages, however, the DT$_{50}$-II values were high (ranging from 15.9 to 84.6 days after the 16-day period), indicating slow rate of dissipation.

Differences were observed in the DT$_{50}$-I values between the conifer and deciduous species. For example, the initial half-lives of disappearance from the foliage and bark samples of the aspen (7.8 and 8.4 days, respectively) were significantly higher than for the three conifer species (5–6.9 days) (ANOVA $P < 0.05$). This could be due to the higher initial residues obtained (Lichtenstein, 1972) on the aspen. In contrast, no significant difference was observed between the DT$_{50}$-II values of the conifer and deciduous species for the later stage of dissipation. This is probably due to the large variability obtained in the data [values ranged from 15.9 to 84.6 (Tables III–VI)], which made it difficult to detect significant differences in the DT$_{50}$-II values. Such large variability in half-lives have been reported in studies where extremely low levels of residues were encountered (Muir et al., 1992), and the authors attributed their findings to the low reproducibility of the analytical methods at very low residue levels.

Permethrin is not a systemic insecticide because little translocation occurs after foliar application or trunk injection (Ohkawa et al., 1977; Gaughan and Casida, 1978). Therefore, the dissipation from foliage can only involve various physicochemical means (Van Middelem, 1966; NRCC, 1986; Demoute, 1989), such as sloughing, codistillation, volatilization, photolysis, hydrolysis, weathering action by wind, rain etc., and/or metabolic or microbial activity. Apart from an occasional light drizzle, no heavy rain occurred during the initial 16 days postspray. However, during the 16–125-day period, the cumulative rainfall was 226 mm (Table III), yet the data show only a gradual loss of residues from foliage and bark. Such a slow dissipation was likely due to volatilization (NRCC, 1986) and metabolic attack (Ohkawa et al., 1977; Gaughan and Casida, 1978) of permethrin that was absorbed and embedded into the lipophilic waxes of the foliage and bark (Schonherr and Riederer, 1989). The lipophilicity of permethrin (NRCC, 1986) seems to facilitate absorption into the lipid components of the substrates, thus resisting dissipation and degradation.

It is worth noting that the total lipid content of the substrates does not seem to influence the persistence during the initial stage. The fresh bark samples, despite their higher lipid contents (Tables III–VI), failed to retain permethrin longer than the foliar samples, which had lower lipid contents (in fact, persistence was lower in bark samples than in foliage of two species). Moreover, within the four foliage types, the spruce needles showed the highest lipid content, while the aspen leaves showed the lowest, yet the persistence was longer in aspen than in conifers. Thus, the present results emphasize the complex phenomenon of spray deposition and ai retention in foliage rather than a simple relationship between lipid contents and ai retention.

In conclusion, the present study indicated that, under the experimental conditions used, permethrin residues were higher and persisted longer in the foliage and bark at the forest tree canopy level than on the soil and litter at the forest ground level. Despite the initial rapid disappearance of the soil and litter residues, some contamination of the environment can still occur from leaf-fall due to the prolonged persistence in foliage. Further investigations are required to determine the toxicological and environmental consequences of persistence in foliage.

LITERATURE CITED

Armson, K. A. *Forest Soils: Properties and Processes,* University of Toronto Press: Toronto, ON, 1977; 390 pp.

Bradbury, S. P.; Coats, J. R. Comparative Toxicology of the Pyrethroid Insecticides. *Rev. Environ. Contam. Toxicol.* **1989,** *108,* 133–177.

Chapman, R. A.; Tu, C. M.; Harris, C. R.; Cole, C. Persistence of Five Pyrethroid Insecticides in Sterile and Natural, Mineral and Organic Soil. *Bull. Environ. Contam. Toxicol.* **1981,** *26,* 513–519.

Chipman, Inc. "Ambush—Experimental Insecticide"; Stoney Creek, ON, Canada, 1981; 10 pp.

Cramer, H. E.; Boyle, D. G. The Micrometeorology and Physics of Spray Particle Behavior. In *Pesticide Spray Application, Behaviour and Assessment,* Workshop Proceedings; U.S. Forest Service, Pacific Southwest Forest Range Experimental Station: Washington, DC, 1976; PSW-15, pp 27–39.

DeBoo, R. F. *Experimental Aerial Applications of Permethrin for Control of Choristoneura fumiferana in Quebec, 1976–1977;* Information Report FPM-X-41; Forest Pest Management Institute, Environment Canada: Sault Ste. Marie, ON, 1980; 24 pp.

Demoute, J-P. A Brief Review of the Environmental Fate and Metabolism of Pyrethroids. *Pestic. Sci.* **1989,** *27,* 375–385.

Elliott, M.; Janes, N. F.; Potter, C. The Future of Pyrethroids in Insect Control. *Annu. Rev. Entomol.* **1978,** *23,* 443–469.

FMC Corp., Agricultural Chemistry Group. "Pounce—Technical Information Report 12 M 10/84"; Philadelphia, PA 1984; 8 pp.

Forest Pest Management Institute. "Pesticide Registration Brief"; Forestry Canada: Sault Ste. Marie, ON, Canada, 1990; 19 pp.

Fujie, G. H. "Hydrolysis of FMC 33297 Insecticide (Phase 1)"; Report P4-FMC 33297; FMC Agricultural Chemical Division, Richmond, CA, 1975 (cited in NRCC, 1986).

Gaughan, L. C.; Casida, J. E. Degradation of *trans-* and *cis-*Permethrin on Cotton and Bean Plants. *J. Agric. Food Chem.* **1978,** *26,* 525–528.

Grayson, B. T. "Physico-chemical and Photochemical Studies of the Pyrethroids WL43467, WL43479, WL43775 and WL42336"; Report WKGR.0071.75; Shell Research: Houston, 1975 (cited in NRCC, 1986).

Helson, B. V.; de Groot, P.; Turgeon, J. J.; Kettela, E. G. Toxicity of Insecticides to First-Instar Larvae of the Spruce Budmoth, *Zeiraphera canadensis* Mut. and Free. (Lepidoptera: Tortricidae): Laboratory and Field Studies. *Can. Entomol.* **1989,** *121,* 81–91.

Hess, F. D. Relationship of Plant Morphology to Herbicide Application and Absorption. In *Methods of Applying Herbicides;* McWhorter, C. G., Gebhardt, M. R., Eds.; Weed Science Society of America: Champaign, IL, 1987; pp 19–35.

Hill, I. R. Effects on Non-Target Organisms in Terrestrial and Aquatic Environments. In *The Pyrethroid Insecticides;* Leahey, J. P., Ed.; Taylor and Francis: London, 1985; pp 151–262.

Hirano, M. Characteristics of Pyrethroids for Insect Pest Control in Agriculture. *Pestic. Sci.* **1989,** *27,* 353–360.

Jordan, E. G.; Kaufman, D. D.; Kayser, A. J. The Effect of Soil Temperature on the Degradation of *cis, trans*-Permethrin in Soil. *J. Environ. Sci. Health* **1982,** *B17* (1), 1–17.

Kalra, Y. P.; Maynard, D. G. "Methods Manual for Forest Soil and Plant Analysis"; Information Report NOR-X-319; Forestry Canada, Northwest Region, Northern Forestry Centre: Edmonton, AB, 1991; 116 pp.

Kaneko, H.; Ohkawa, H.; Miyamoto, J. Degradation and Movement of Permethrin Isomers in Soil. *J. Pestic. Sci.* **1978,** *3,* 43–52.

Kaufman, D. D.; Haynes, S. C.; Jordan, E. G.; Kayser, A. J. Permethrin Degradation in Soil and Microbial Cultures. In

Persistence of Permethrin

J. Agric. Food Chem., Vol. 40, No. 12, 1992 **2529**

Synthetic Pyrethroids; Elliott, M., Ed.; ACS Symposium Series 42; American Chemical Society: Washington, DC, 1977; pp 147–161.

Kingsbury, P. D.; Kreutzweiser, D. P. "Environmental Impact Assessment of a Semi-operational Permethrin Application"; Information Report FPM-X-30; Forest Pest Management Institute: Sault Ste. Marie, ON, 1980; 89 pp.

Kingsbury, P. D.; McLeod, B. B. "Terrestrial Impact Studies in Forest Ecosystems Treated with Double Applications of Permethrin"; Information Report FPM-X-28; Forest Pest Management Institute: Sault Ste. Marie, ON, 1979; 65 pp.

Leahey, J. P. Metabolism and Environmental Degradation. In *The Pyrethroid Insecticides*; Leahey, J. P., Ed.; Taylor and Francis: London, 1985; pp 263–342.

Lichtenstein, E. P. Persistence and Fate of Pesticides in Soils, Water and Crops: Significance to Humans. In *Fate of Pesticides in Environment*; Tahori, A. S., Ed.; Gordon and Breach Science Publishers: London, 1972; pp 1–22.

Menzie, C. M. "Metabolism of Pesticides—Update III"; Special Report, Wildlife 232; U.S. Department of the Interior, Fish and Wildlife Service: Washington, DC, 1980; 477–484.

Muir, D. C. G.; Yarechewski, A. L.; Neal, B. R. Influence of Surface Films on the Fate of Deltamethrin Following Aerial Application to Prairie Ponds. *Environ. Toxicol. Chem.* **1992**, *11*, 581–591.

Naumov, F. V.; Zharkov, A. V.; Basova, Yu. G.; Borozdina, L. K.; Leont'ev, L. L. Permethrin Persistence in Forest Pest Control. *Agrokhimiya* **1989**, *11*, 101–104.

NRCC. *Pyrethroids: Their Effects on Aquatic and Terrestrial Ecosystems*; Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada: Ottawa, ON, 1986; NRCC Publication 24376, 303 pp.

Ohkawa, H.; Kaneco, H.; Miyamoto, J. J. Metabolism of Permethrin in Bean Plants. *J. Pestic. Sci.* **1977**, *2*, 67–76.

Rawn, G. P.; Webster, G. R. B.; Muir, D. C. G. Fate of Permethrin in Model Outdoor Ponds. *J. Environ. Sci. Health* **1982**, *B17*, 463–486.

Ruzo, L. O.; Casida, J. E. Pyrethroid Photochemistry: Mechanistic Aspects in the Reaction of the (Dihalovinyl) Cyclopropanecarboxylate Substituent. *J. Chem. Soc., Perkin Trans.* **1980**, *3*, 728–732.

Ryan, B. F.; Joiner, B. L.; Ryan, T. A., Jr. *Minitab Student Handbook*; Duxbury Press: Boston, MA, 1985; pp 193–217.

Schonherr, J.; Riederer, M. Foliar Penetration and Accumulation of Organic Chemicals in Plant Cuticles. *Rev. Environ. Contam. Toxicol.* **1989**, *108*, 1–70.

Sundaram, K. M. S. Persistence Characteristics of Operationally Sprayed Fenitrothion in Nearby Unsprayed Areas of a Conifer Forest Ecosystem in New Brunswick. *J. Environ. Sci. Health* **1987**, *B22* (4), 413–438.

Sundaram, K. M. S. Gas Chromatographic Method for the Analysis of Permethrin Isomers in Some Forestry Substrates. *J. Environ. Sci. Health* **1990**, *B25* (3), 357–378.

Sundaram, K. M. S. Spray Deposit Patterns and Persistence of Diflubenzuron in Some Terrestrial Components of a Forest Ecosystem after Application at Three Volume Rates under Field and Laboratory Conditions. *Pestic. Sci.* **1991a**, *32*, 275–293.

Sundaram, K. M. S. Fate and Short-Term Persistence of Permethrin Insecticide Injected in a Northern Ontario (Canada) Headwater Stream. *Pestic. Sci.* **1991b**, *31*, 281–294.

Sundaram, K. M. S. Fate of Insecticides in the Forest Environment. In *Control of Forest Insects in Canada*; Armstrong, J. A., Ives, W., Mullins, J., Eds.; Forestry Canada: Ottawa, ON, 1991c; in press.

Sundaram, K. M. S. Influence of Foliar Morphology and Crown Geometry on Insecticide Deposition and Dissipation Following An Aerial Spray over a Mixed Forest. *J. Environ. Sci. Health* **1991d**, *B26*, 601–629.

Sundaram, K. M. S.; Nott, R. Mexacarbate Residues in Selected Components of a Conifer Forest Following Aerial Applications of Oil-based and Aqueous Spray Formulations. *J. Environ. Sci. Health* **1985**, *B20*, 425–444.

Sundaram, K. M. S.; Sundaram, A. Influence of Formulation on Spray Deposit Patterns, Dislodgeable and Penetrated Residues, and Persistence Characteristics of Fenitrothion in Conifer Needles. *Pestic. Sci.* **1987**, *18*, 259–271.

Sundaram, K. M. S.; Millikin, R.; Sundaram, A. Assessment of Canopy and Ground Deposits of Fenitrothion Following Aerial and Ground Application in a Northern Ontario Forest. *Pestic. Sci.* **1989**, *25*, 59–69.

Van Middelem, C. H. Fate and Persistence of Organic Pesticides in the Environment. In *Organic Pesticides in the Environment*; Gould, R. F., Ed.; Advances in Chemistry 60; American Chemical Society: Washington, DC, 1966; pp 228–249.

Wang, T. S. C.; Liang, Y. C.; Shen, W. C. Method of Extraction and Analysis of Higher Fatty Acids and Triglycerides in Soil. *Soil Sci.* **1969**, *107*, 181–187.

Watkinson, I. A. Pyrethroids and the Economics of Pest Management. *Pestic. Sci.* **1989**, *27*, 465–469.

Worthing, C. R., Walker, S. B., Eds. *The Pesticide Manual: A World Compendium*, 7th ed.; The British Crop Protection Council: Croydon, England, 1983; p 427.

Yates, W. E.; Akesson, N. B. Reducing Pesticide Chemical Drift. In *Pesticide Formulations*; Van Valkenburg, W., Ed.; Dekker: New York, 1973; pp 275–341.

Zylstra, B. F.; Obarymskyj, A. "Experimental Aerial Applications of Permethrin, Carbaryl and Chlorpyrifos-methyl for Control of Eastern Spruce Budworm, *Choristoneura fumiferana* (Clem.), in New Brunswick in 1980"; Information Report FPM-X-56; Forest Pest Management Institute: Sault Ste. Marie, ON, 1981; 14 pp.