Persistence, Penetration, and Surface Availability of Cypermethrin and Its Major Degradation Products in Elm Bark

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The initial residues of *cis*-A, *trans*-C, *cis*-B, and *trans*-D cypermethrin in elm bark treated with a 400× aqueous dilution of Ripcord 40 EC (1.0 g of active ingredient/L) to runoff ranged from 29 to 58, from 24 to 53, from 25 to 35, and from 17 to 25 μg/g, respectively. These residues dissipated quickly with half-lives of 1.60−12.0 days for the faster dissipation phase. The dissipation of cypermethrin during the later period became much slower, with dissipation half-lives of 209−365 days. Cypermethrin residues in elm bark remained 100% effective against the native elm bark beetle for ∼60 days after application. Laboratory tests indicated that cypermethrin residues in the bark were 100% effective in preventing elm bark beetles from making overwintering tunnels for up to 627 days (fall application) and 433 days (spring application). No penetration of cypermethrin to the cambium layer or wood tissue was detected during the experimental period of 791 days. Total cypermethrin residue absorbed from treated elm bark during a 1 min contact period did not exceed the acceptable daily intake for humans.

Keywords: *Cypermethrin; degradation products; elm bark; elm bark beetle; residue; effectiveness; penetration; contact availability*

INTRODUCTION

White elm (*Ulmus americana*) is widely distributed in North America. The elm trees in native stands are a source of hardwood and a major component of shelter belts in the Canadian prairie provinces. Its attractive shape has made the elm an important choice in many urban forests. Dutch elm disease, which has destroyed many wild and urban white elms, is caused by the fungus *Ophiostoma (Ceratocystis) ulmi* and is mainly spread by native elm bark beetles (*Hylurgopinus rufipes*). Effective management of the native bark beetle incorporates the application of insecticides as a key component in the integrated management program for Dutch elm disease in recent years in Manitoba and Saskatchewan (Westwood, 1991).

The synthetic pyrethroid insecticide cypermethrin (Figure 1A), (*RS*)-α-cyano-3-phenoxybenzyl (1*RS*)-*cis*-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, first discovered by Elliott and co-workers (Burt et al., 1974; Elliott et al., 1975), was developed by Ciba-Geigy AG, ICI Agrochemicals, Mitchell Cotts, and Shell International Chemical Co. Ltd. Cypermethrin is a racemic mixture of eight isomers resulting from the presence of three chiral carbon atoms in the molecule. The ratio of the *cis*/*trans* isomers in cypermethrin materials is approximately 40:60. The 1*R*, *cis*, α-*S* isomer of cypermethrin is one of the most potent pyrethroids available at the present time (Casida, 1980).

Cypermethrin is both a stomach poison and contact insecticide effective against a wide range of insect pests, particularly Lepidoptera in cereals, citrus, cotton, fruit, rapeseed (canola), soybeans, tobacco, tomatoes, vegetables, and other crops at 20−75 g of active ingredient (ai)/ha. If applied before infestations become well established, cypermethrin also provides protection against plant-sucking Hemiptera in most crops (Worthing and Hance, 1991). Pajares and Lanier (1989) reported that cypermethrin was very effective in killing elm bark beetles when applied to infested elm wood under laboratory conditions and acted more rapidly than chlorpyrifos, the insecticide registered for the control of the elm bark beetle in Canada.

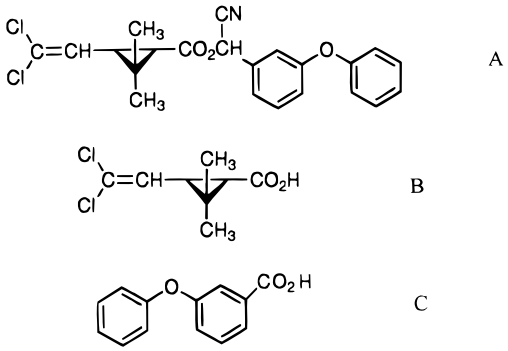

Figure 1. Chemical structures of cypermethrin (A), CCA (B), and PBA (C).

The dissipation of cypermethrin has been studied on cotton leaves (Ware et al., 1983), wheat leaves (Westcott and Reichle, 1987), celery and lettuce (Braun et al., 1987), and cabbages (Furuzawa et al., 1981). The half-life for total cypermethrin in crop plants was several days. Furuzawa et al. (1981) reported different half-lives for *cis*- and *trans*-cypermethrin isomers in cabbage. The initial degradation half-lives of *trans*- and *cis*-cypermethrin on and in treated cabbage leaves were 4−5 and 7−8 days, respectively, indicating that the

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Table 1. Climatic Data for the Two Experimental Sites

site	parameter	Jan	Feb	March	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Glenlea (1967−1990)	daily max *T* (°C)	−13	−10	−2	10	19	23	26	25	19	11	0	−10
	daily min *T* (°C)	−24	−21	−12	−2	4.5	10	13	12	6	0	−9	−19
	daily min *T* (°C)	−18	−15	−7	4	12	17	20	18	12	6	−5	−15
	precipitation (mm)	19	15	23	36	60	84	72	76	51	30	21	19
Beaudry (1938−1990)	daily max *T* (°C)	−13	−10	−2	10	19	23	26	25	19	11	−1	−10
	daily min *T* (°C)	−24	−21	−13	−2	5	10	13	11	6	−1	−10	−20
	daily mean *T* (°C)	−19	−16	−7	4	12	17	19	18	12	5	−5	−15
	precipitation (mm)	29	17	22	30	57	95	71	61	53	38	20	20

trans-isomers degraded approximately twice as quickly as the *cis*-isomers.

Furuzawa et al. (1981) studied the metabolic pathways of (1*R*)-*cis*- and (1*R*)-*trans*-isomer individuals on and in cabbages with ^{14}C preparations labeled separately in the benzyl ring and cyclopropyl ring. They reported that the metabolic pathways of both isomers of cypermethrin included epimerization to (1*S*)-isomers, *cis*/*trans*-isomerization, ester bond cleavage, hydroxylation of the phenoxy group in the alcohol moiety or the geminal methyl group in the acid moiety, hydration of the CN group to the $CONH_2$ group, which subsequently hydrolyzed to the COOH group, and conjugation of the resultant carboxylic acids and alcohols with sugars. The major metabolites were glycoside conjugates of 3-(4-hydroxyphenoxy)benzoic acid and 3-phenoxybenzoic acid from the alcohol moiety and glycoside conjugates of 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid from the acid moiety.

The objectives of the current study were (1) to determine the persistence of individual cypermethrin isomer pairs and their main degradation products, *cis*- and *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (CCA, Figure 1B) and 3-phenoxybenzoic acid (PBA, Figure 1C) in elm bark; (2) to relate the residue levels of total cypermethrin isomers in the elm bark to efficacy against elm bark beetles; (3) to determine the penetration of cypermethrin into the bark and wood tissue where elm bark beetles make their overwintering tunnels; and (4) to evaluate the contact safety of the treated elm bark by measuring the availability of cypermethrin residues on the treated bark surface.

EXPERIMENTAL PROCEDURES

Chemicals and Application Equipment. Ripcord 40 EC (cypermethrin) was obtained from Ciba-Geigy Canada Ltd. (Agricultural Division, Mississauga, ON, Canada). A back-pack sprayer was used to apply the 1.0 g of ai/L aqueous dilution of Ripcord 40 EC.

Field Treatment. The experiments were carried out at two sites containing native elm trees near Winnipeg, MB, Canada: at the Glenlea Research Station of the University of Manitoba, adjacent to the Red River 20 km south of the city, and at Beaudry Provincial Park, adjacent to the Assiniboine River 15 km west of the city. The elm trees used in the experiment grew along the banks of the rivers. The average temperature and precipitation in the individual month of one year at the two experimental sites are presented in Table 1.

Twenty-four healthy elm trees at each site were selected and grouped into eight "plots", with each plot consisting of three trees. Three plots (three replicates) were treated with cypermethrin, and one plot was retained as the untreated control for the application in 1991. The remaining four plots were used for application in 1992 with the same experimental design. The experimental plots used for the 1992 application at each experimental site were located far enough from the 1991 treated plots so that the application of insecticide in 1992 would not contaminate the elm trees treated in 1991. The check treatments were located far enough away to avoid contamination by insecticide drift from the treated plots. The basal 1 m of the trunks of nine elm trees (three replicate plots) at each site was treated to runoff with the 1.0 g of ai/L aqueous dilution of Ripcord 40 EC with the back-pack sprayer on August 15, 1991, or on May 7, 1992.

Sampling. *Residue Determination of Cypermethrin and Its Degradation Products in Elm Bark.* Samples of elm bark including the cambium layer were collected at time 0 (∼1 h after insecticide treatment when the treated bark surface had dried), 4, 11, 32, 62, 279, 341, 427, 627, and 791 days after application on August 15, 1991, and 0, 4, 14, 30, 74, 141, 364, 433, 532 days after application on May 7, 1992, at Glenlea Research Station and at Beaudry Provincial Park, respectively. Three 1.7 × 1.7 cm elm bark samples were taken with a chisel randomly from the insecticide-treated area of each elm tree. The nine pieces of elm bark from the three trees in each plot were combined and ground with a blender prior to extraction.

Determination of Residue Distribution of Cypermethrin in Elm Bark, Cambium, and Wood Tissue. Samples were collected at time 0 (∼1 h after insecticide treatment when the treated bark surface had dried) and 11, 62, 341, 427, and 791 days after application. Elm bark, cambium, and wood tissue were collected separately to determine the penetration of cypermethrin from the treated elm bark surface to cambium and wood tissue at various time intervals after application. This experiment was carried out only at Glenlea Research Station and only for the 1991 application. Outer bark was collected with a 2.6 cm chisel, middle cambium with a 1.7 cm chisel, and inner wood tissue with a 1.3 cm chisel to avoid possible contamination of the cambium and wood layer. The samples of elm bark, cambium, and wood tissue were taken at five points from the cypermethrin-treated elm trees, combined, and ground, respectively, for extraction.

Determination of Availability of Surface Residues of Cypermethrin. Samples were taken at 0, 4, 14, 30, 74, 141, 364, 433, and 532 days after application on May 7, 1992, at Beaudry Provincial Park to determine the availability of cypermethrin on the insecticide-treated bark surface. Samples were collected by pressing glass fiber filter paper (9 cm diameter) against the cypermethrin-treated bark surface for 1 min. One sample was taken from one of the three trees in a plot at each sampling time. Each treatment had three replicates. Samples required no further preparation before extraction.

Biological Effectiveness Persistence Test. Bark disk samples were taken at the same time as the elm bark samples for residue analysis. After the elm trees had been treated with cypermethrin at Beaudry Provincial Park on August 15, 1991, or May 7, 1992, elm bark samples were taken to determine the persistence of insecticidal effectiveness of cypermethrin to kill elm bark beetles. Elm bark disks were collected with a 5.7 cm diameter hole saw (driven by a cordless drill) from the treated bark of one of the three trees in each plot alternately. Each treatment had three samples respectively coming from the three replicate plots.

Soxhlet Extraction Method. Glass fiber filter paper samples taken to determine the availability of cypermethrin surface residues from the elm bark were put into Soxhlet thimbles and the filter paper was extracted with 60 mL of acetone for 3 h. The extracts were concentrated on a rotary evaporator to ∼0.5 mL and then reduced to dryness under a stream of dry nitrogen. Toluene (1 mL) was added to the

Table 2. Recoveries for *cis*-A, *trans*-C, *cis*-B, and *trans*-D Cypermethrin Isomer Pairs in Glass Fiber Filter Paper

analytes	spiked concn ($n = 3$) (μg/m^2)	recoveries (%)	RSD (%)
cis-A	700	92	5.2
	0.1	94	6.1
trans-C	700	93	5.5
	0.1	96	3.2
cis-B	700	94	5.2
	0.1	97	5.5
trans-D	700	94	4.5
	0.1	97	3.1

extracts. Because some extracts were quite concentrated, the toluene solution was further diluted to an appropriate volume to facilitate gas chromatographic analysis.

Analytical Method for Determination of Residues of Cypermethrin and Degradation Products in Bark. Analysis of the residues of cypermethrin and degradation products was performed according to the method of Jin and Webster (1998).

Bioassay Method for Determination of Insecticidal Persistence of Cypermethrin in Elm Bark. Details of the bioassay of residual cypermethrin in bark are contained in Jin et al. (1996).

RESULTS AND DISCUSSION

Analytical Method for Determination of Cypermethrin in Filter Paper. The analytical method for cypermethrin and degradation products (Jin and Webster, 1998) yielded the following recoveries of cypermethrin, *cis*-CCA, *trans*-CCA, and PBA from spiked elm bark: 96−110% (4.1−13% RSD), 88−110% (5.3−9.5% RSD), 86−110% (2.9−5.9% RSD), and 90−95% (2.3−6.1% RSD) for concentrations 2.0−100, 0.5−10 μg/g, 0.5−10 μg/g, and 0.5−10 μg/g, respectively.

The recoveries of cypermethrin isomer pairs from fortified glass fiber filter paper at 0.1 and 700 μg/m^2 are listed in Table 2. Recoveries were 92−97% with standard deviations of 3.1−6.1%.

Dissipation of Cypermethrin and Its Degradation Products in Elm Bark. The residues of four pairs of cypermethrin isomers and their major degradation products in the elm bark for the 1991 and 1992 applications at Glenlea Research Station and Beaudry Provincial Park are shown in Tables 3 and 4. The initial residues of *cis*-A, *trans*-C, *cis*-B, and *trans*-D cypermethrin pairs in the elm bark at both experimental sites and both application times were 29-58, 24−53, 25−35, and 18−25 μg/g, respectively. It took ~50 days for the cypermethrin to dissipate from initial residues to about half these levels. The residues of *cis*-isomers dissipated ~89% after 791 days from the 1991 application and ~85% after 532 days from the 1992 application, whereas the residues of *trans*-isomers degraded ~92% after 791 days from the 1991 application and ~91% after 532 days from the 1992 application, indicating that *trans*-isomers dissipated more readily that their *cis* counterparts. There was no significant difference in the dissipation rate of the four cypermethrin isomeric pairs in the elm bark between the application times or between the experimental sites. Compared to their parent compounds, the residues of the degradation products in elm bark were negligible. The residues of PBA were normally higher than the sum of both *cis*-CCA and *trans*-CCA.

The regression analyses between time after application and the cypermethrin residues in elm bark at the corresponding times indicate that the dissipation of cypermethrin isomer pairs in elm bark with time after application could be well described by the first-order equation

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_t = insecticide residue concentration at time t, C_0 = initial insecticide residue concentration, t = time after application in days, and k = dissipation rate constant. The dissipation half-lives of cypermethrin in elm from bark were calculated from the usual equation

$$t_{1/2} = \ln 2/k \quad (2)$$

The experimental data for the residues of cypermethrin isomer pairs in elm bark at various times after

Table 3. Residues of Four Pairs of Cypermethrin Isomers and Their Major Degradation Products in Elm Bark at Glenlea Research Station at Both Application Times

		cis-CCA		*trans*-CCA		PBA		*cis*-A		*trans*-C		*cis*-B		*trans*-D	
sampling date	days after application	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)
91.08.15[a]	0	0.22	0.08	1.06	0.40	1.10	0.46	52.1	16.9	47.1	13.4	35.2	7.7	24.4	5.7
91.08.19	4	0.35	0.08	1.10	0.33	1.41	0.62	36.7	10.1	34.2	16.3	24.8	8.1	17.2	4.1
91.08.26	11	0.62	0.50	1.80	1.07	2.20	0.53	34.5	9.3	30.1	9.5	22.9	6.2	15.9	7.1
91.09.19	32	0.79	1.03	1.14	0.20	3.39	0.80	30.2	7.3	27.2	7.5	20.5	4.6	14.7	4.1
91.10.16	62	0.35	0.28	0.75	0.50	2.07	1.75	23.1	2.2	20.6	1.9	15.1	2.0	12.6	2.6
92.05.20	279	0.34	0.07	0.55	0.15	1.47	0.81	18.4	3.7	18.6	3.5	12.2	2.0	11.5	1.1
92.07.21	341	0.90	0.67	0.65	0.14	2.01	1.30	14.4	4.9	13.4	2.7	9.2	1.7	8.8	2.1
92.10.15	427	0.05	0.01	0.03	0.02	0.10	0.02	14.0	2.5	10.6	2.7	9.0	2.1	5.5	1.1
93.05.03	627	0.04	0.01	0.09	0.05	0.33	0.14	7.20	1.1	6.3	1.9	5.1	0.6	3.7	1.0
93.10.14	791	0.03	0.01	0.05	0.02	0.06	0.00	5.50	1.0	4.1	1.7	4.0	0.7	2.1	0.8
92.05.07	0	0.00	0.00	0.00	0.00	0.00	0.00	33.4	10.0	28.1	9.2	30.3	10.8	20.5	8.0
92.05.11	4	0.34	0.19	0.55	0.26	1.30	0.58	22.5	9.8	20.5	8.9	21.5	7.7	14.8	8.4
92.05.21	14	0.55	0.07	0.71	0.15	2.14	0.45	20.1	8.0	17.3	0.1	18.3	9.1	12.9	2.7
92.06.15	30	0.42	0.07	0.84	0.07	1.34	0.63	16.1	3.5	14.2	1.7	13.5	2.2	10.3	2.4
92.07.20	74	0.59	0.15	1.09	0.36	1.81	0.89	14.1	2.5	9.4	1.3	11.6	3.0	8.0	0.5
92.09.25	141	0.24	0.16	0.24	0.25	0.99	1.11	11.8	1.9	6.1	0.9	7.6	1.6	5.0	0.7
93.05.06	364	0.12	0.08	0.20	0.16	1.29	0.70	9.1	0.8	5.5	1.1	7.6	0.9	4.2	0.5
93.07.14	433	0.03	0.01	0.03	0.01	0.10	0.11	6.6	1.0	3.8	0.2	5.4	0.9	2.9	0.2
93.10.21	532	0.02	0.01	0.01	0.01	0.08	0.09	5.6	1.0	3.0	0.7	4.7	0.9	2.0	0.4

[a] Application time of cypermethrin (expressed as year.month.date).

Table 4. Residues of Four Pairs of Cypermethrin Isomers and Their Major Degradation Products in Elm Bark at Beaudry Provincial Park at Both Application Times

		cis-CCA		*trans*-CCA		PBA		*cis*-A		*trans*-C		*cis*-B		*trans*-D	
sampling date	days after application	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)	residue (μg/g)	SD (μg/g)
91.08.15[a]	0	0.22	0.08	1.06	0.40	1.10	0.46	52.1	16.9	47.1	13.4	35.2	7.7	24.4	5.7
91.08.19	4	0.35	0.08	1.10	0.33	1.41	0.62	36.7	10.1	34.2	16.3	24.8	8.1	17.2	4.1
91.08.26	11	0.62	0.50	1.80	1.07	2.20	0.53	34.5	9.3	30.1	9.5	22.9	6.2	15.9	7.1
91.09.19	32	0.79	1.03	1.14	0.20	3.39	0.80	30.2	7.3	27.2	7.5	20.5	4.6	14.7	4.1
91.10.16	62	0.35	0.28	0.75	0.50	2.07	1.75	23.1	2.2	20.6	1.9	15.1	2.0	12.6	2.6
92.05.20	279	0.34	0.07	0.55	0.15	1.47	0.81	18.4	3.7	18.6	3.5	12.2	2.0	11.5	1.1
92.07.21	341	0.90	0.67	0.65	0.14	2.01	1.30	14.4	4.9	13.4	2.7	9.2	1.7	8.8	2.1
92.10.15	427	0.05	0.01	0.03	0.02	0.10	0.02	14.0	2.5	10.6	2.7	9.0	2.1	5.5	1.1
93.05.03	627	0.04	0.01	0.09	0.05	0.33	0.14	7.20	1.1	6.3	1.9	5.1	0.6	3.7	1.0
93.10.14	791	0.03	0.01	0.05	0.02	0.06	0.00	5.50	1.0	4.1	1.7	4.0	0.7	2.1	0.8
92.05.07	0	0.00	0.00	0.00	0.00	0.00	0.00	28.8	4.3	24.2	3.9	24.9	5.2	17.7	2.8
92.05.11	4	0.025	0.13	0.50	0.13	0.38	0.22	19.9	7.5	18.5	4.6	17.2	7.6	13.1	2.5
92.05.21	14	0.42	0.19	0.50	0.25	1.64	0.25	17.4	3.8	16.4	1.8	14.6	1.6	12.2	1.1
92.06.15	30	0.38	0.01	0.50	0.13	0.63	0.22	17.0	0.8	15.4	4.4	12.8	3.3	11.1	3.0
92.07.20	74	0.42	0.07	0.63	0.13	0.67	0.32	14.2	1.0	11.0	1.0	11.1	1.0	9.6	1.3
92.09.25	141	0.11	0.01	0.12	0.02	0.27	0.03	13.7	3.6	8.9	2.5	10.1	2.1	6.5	1.5
93.05.06	364	0.07	0.05	0.11	0.10	0.34	0.39	8.6	2.6	6.9	1.7	7.3	2.2	5.4	1.4
93.07.14	433	0.03	0.01	0.03	0.03	0.08	0.07	4.9	0.7	3.6	0.6	4.2	0.6	2.6	0.5
93.10.21	532	0.03	0.02	0.04	0.02	0.10	0.12	3.9	1.2	2.3	0.7	3.7	1.0	1.5	0.6

[a] Application time of cypermethrin (expressed as year.month.date).

Table 5. Models, Half-Lives, and Correlation Coefficients (*r*) for Dissipation of the Four Pairs of Cypermethrin Isomers in Elm Bark

			half-lives (days)		
treatment	analyte	dissipation model	fast	slow	r^a
Glenlea, 1991	*cis*-A	$C_t = 20.7e^{-0.2691850t} + 31.2e^{-0.0021440t}$	2.57	323	0.9911
	trans-C	$C_t = 19.1e^{-0.2358688t} + 27.8e^{-0.0021546t}$	2.94	321	0.9904
	cis-B	$C_t = 14.3e^{-0.2547071t} + 20.7e^{-0.0021423t}$	2.72	324	0.9907
	trans-D	$C_t = 8.56e^{-0.4295456t} + 15.8e^{-0.0020455t}$	1.61	339	0.9855
Glenlea, 1992	*cis*-A	$C_t = 15.4e^{-0.2614109t} + 17.9e^{-0.0022401t}$	2.65	311	0.9915
	trans-C	$C_t = 15.7e^{-0.0577766t} + 10.7e^{-0.0023241t}$	12.0	289	0.9873
	cis-B	$C_t = 16.3e^{-0.0948721t} + 12.8e^{-0.0018985t}$	7.31	365	0.9863
	trans-D	$C_t = 9.59e^{-0.1072493t} + 10.2e^{-0.0030698t}$	6.46	226	0.9876
Beaudry, 1992	*cis*-A	$C_t = 26.5e^{-0.2465597t} + 31.0e^{-0.0022771t}$	2.81	304	0.9873
	trans-C	$C_t = 26.5e^{-0.2465597t} + 31.0e^{-0.0022771t}$	2.19	319	0.9859
	cis-B	$C_t = 14.3e^{-0.1480968t} + 19.9e^{-0.0019493t}$	4.68	356	0.9888
	trans-D	$C_t = 9.10e^{-0.1922431t} + 15.9e^{-0.0019658t}$	3.61	353	0.9920
Beaudry, 1992	*cis*-A	$C_t = 10.6e^{-0.4325324t} + 18.2e^{-0.0025654t}$	1.60	270	0.9942
	trans-C	$C_t = 8.12e^{-0.2529937t} + 16.0e^{-0.0032934t}$	2.74	210	0.9882
	cis-B	$C_t = 10.8e^{-0.2874124t} + 14.1e^{-0.0023736t}$	2.41	292	0.9945
	trans-D	$C_t = 5.42e^{-0.4196228t} + 12.3e^{-0.0033145t}$	1.65	209	0.9885

[a] Significant at the 0.01 level.

application indicate that dissipation of cypermethrin isomer pairs in elm bark was a two-phase process. A two-phase model

$$C_1 = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \quad (3)$$

was used to describe the dissipation of cypermethrin isomer pairs and to calculate the dissipation half-lives in elm bark.

The nonlinear model from the computer program Systat (SPSS Inc., Chicago, IL) was used to solve for C_1, k_1, C_2, and k_2 in eq 3. The dissipation half-lives during the faster and slower phases in elm bark are calculated with eq 2.

The theoretical dissipation models for cypermethrin isomer pairs established from eq 3 through regression between time after application and the corresponding residues in elm bark, the dissipation half-lives for the faster and slower dissipation phases, and the correlation coefficients at Glenlea Research Station and Beaudry Provincial Park for the August 1991 and May 1992 applications are listed in Table 5. Cypermethrin isomer pairs dissipated very quickly in the elm bark, with half-lives ranging from 1.6 to 12 days for the faster dissipation phase. The dissipation rates during the later period became much slower, with the dissipation half-lives ranging from 209 to 365 days.

The difference in the initial residues of cypermethrin isomer pairs at different application times and experimental sites is attributed to experimental error of application and bark texture of the test elm trees used. The rougher bark normally found on the larger trees intercepted larger amounts of insecticide at application and had higher initial residue values when the residual concentration of insecticides in bark was expressed as insecticide weight per unit weight of bark. The initial cypermethrin residues in the bark were higher in the 1991 application than in the 1992 application. The sequence of the tree size in term of the average diameter at breast height (DBH) was 23 cm at Beaudry at 1991 application, 18 cm at Glenlea at 1991 application, 16

Table 6. Residues of Cypermethrin Isomers in Bark, Cambium, and Wood Tissue at Different Time Intervals after Application

sampling time	days after application	residues (μg/g)											
		cis-A			*trans*-C			*cis*-B			*trans*-D		
		wood	cambium	bark	wood	cambium	bark	wood	cambium	bark	wood	cambium	bark
91.08.15[a]	0	ND[b]	ND	120	ND	ND	110	ND	ND	75	ND	ND	50
91.08.26	11	ND	ND	110	ND	ND	96	ND	ND	72	ND	ND	53
91.10.16	62	ND	ND	54	ND	ND	48	ND	ND	35	ND	ND	27
92.07.21	341	ND	ND	34	ND	ND	32	ND	ND	21	ND	ND	21
92.10.15	427	ND	ND	33	ND	ND	25	ND	ND	22	ND	ND	13
93.10.14	791	ND	ND	13	ND	ND	10	ND	ND	9.0	ND	ND	5.0

[a] Application time of the insecticides (expressed as year.month.date). [b] Not detected: detection limit in elm bark was 0.018 μg/g for all four cypermethrin isomer pairs.

cm at Beaudry at 1992 application, and 14 cm at Glenlea at 1992 application.

The experimental residue data revealed that the cypermethrin residues dissipated much more quickly from the elm bark during the initial days after application, presumably due to the loose association of the insecticide residues with the bark and the consequent quick loss of the insecticide from this matrix by natural elements. The dissipation rates of cypermethrin in the elm bark became much lower at the later stage of the experiment. A possible explanation of this phenomenon is that the association of insecticide molecules and the bark became stronger with elapsed time, resulting in less and less cypermethrin being subject to loss by weathering. The dissipation data for the cypermethrin isomers during summer and winter periods presented in Tables 2 and 3 also reveal that the insecticide dissipated more quickly during the summer than during the winter, presumably due to higher temperature and rainfall during the summer, which are favorable for the dissipation of the insecticide from the target matrix.

Considering the facts that the insecticide failed to penetrate to the cambium layer (Table 6) and that the bark sample used in the experiment contained the full thickness of the bark including the cambium layer, the residue concentrations of the insecticide in the surface bark layer must have been several times higher than the whole bark values recorded in Tables 2 and 3.

Table 7 shows the residues of cypermethrin in elm bark and the mortalities of beetles after 24 h of exposure to the treated elm bark at different times following the 1991 and 1992 applications at Beaudry Provincial Park. The experimental results indicate that the effectiveness of cypermethrin in killing the elm bark beetles remained at 100% after 62 days from the 1991 application and 74 days from the 1992 application.

Although the mortality values reflected in the bioassay test according to the mortality-determining criteria declined gradually with time, elm beetles that were not included in the mortality value had been disabled severely by cypermethrin; they could move only very short distances and had lost the ability to make normal overwintering tunnels. The fate of such beetles subjected to cypermethrin under field conditions is not yet known. There is the likelihood that their failure to be able to move normally or to make overwintering tunnels as demonstrated in the bioassays would mean that these beetles would be killed by severe winter conditions. If this were the case, the period of 100% control of the elm bark beetle would be extended to 627 days after application in August or 433 days after application in May. In fact, during the bioassay study, although beetles were not completely killed after the 62/74 (1991/1992) day period from treatment, no tunneling into elm wood tissue (the normal overwintering site) was observed up to 627 days (fall 1991) and 433 days (spring 1992) from application (Jin et al., 1996). After this time, 3−5 of the 20 test beetles were found to have made tunnels into wood tissue. It is thus indicated that effective Dutch elm disease control for almost 2 years could be effected with the cypermethrin application used in this study. Control beetles exposed to untreated bark were fully active and showed 100% survival.

Table 7. Residues of Total Cypermethrin and Mortalities of Elm Bark Beetles on Treated Elm Bark

sampling date	days after application	total residue (μg/g)	mortality (%)
91.08.15[a]	0	170	100
91.08.19	4	120	100
91.08.26	11	110	100
91.09.19	32	110	100
91.10.16	62	55	100
92.05.20	279	51	92
92.05.20	279	51	92
92.07.21	341	54	82
92.10.15	427	44	83
93.05.03	627	25	68
93.10.14	791	16	37
92.05.07	0	96	100
92.05.11	4	73	100
92.05.21	14	64	100
92.06.15	30	58	100
92.07.20	74	46	100
92.09.25	141	39	92
93.05.06	364	28	82
93.07.14	433	15	63
93.10.21	532	11	22

[a] Application time of cypermethrin (expressed as year.month.date).

Availability of Surface Cypermethrin Residues on the Elm Bark. Table 8 lists the residual cypermethrin obtained through direct contact with the bark surface of glass fiber filter paper pressed against the treated elm bark surface for 1 min at various sampling times after treatment. The insecticide residues transferred from the treated bark were 2.3 mg/m^2 for samples taken when the treated bark surface had dried for ∼1 h after application. The availability of the insecticide dropped very quickly to 0.63 mg/m^2 4 days after treatment.

The highest availability of these cypermethrin residues, as expected, occurred just after the application (when the applied insecticide had dried). If it is assumed that the area of a child's hand is approximately 0.01 m^2 (or 10 cm × 10 cm), the dosage available to a child from one such contact with a treated tree would be ∼0.02 mg just after treatment, dropping to 0.006 mg by day 4. These figures also assume that the residue

Table 8. Cypermethrin Available through Direct Contact with the Elm Bark Surface following Treatment

		cis-A		*trans*-C		*cis*-B		*trans*-D	
sampling time	days after application	residue (μg/m^2)	SD (μg/m^2)	residue (μg/m^2)	SD (μg/m^2)	residue (μg/m^2)	SD (μg/m^2)	residue (μg/m^2)	SD (μg/m^2)
92.05.07[a]	0	674	275	641	272	567	237	458	193
92.05.11	4	153	98	184	112	130	87.0	167	97.0
92.05.21	14	115	58	138	74.0	99.0	52.0	117	62.0
92.06.15	30	93.0	9.0	86.0	9.0	77.0	6.8	79.0	9.0
98.07.20	74	12.0	6.0	15.0	6.4	10.	4.9	13.0	6.7
92.09.25	141	7.6	2.1	9.2	1.0	6.7	1.4	8.3	0.7
93.05.06	364	2.9	1.8	3.8	2.1	2.3	1.4	3.4	1.9
93.07.14	433	0.9	0.5	0.8	0.5	0.3	0.1	0.9	0.2
93.10.21	532	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0

[a] Expressed as year.month.date.

was completely absorbed through the skin. The acceptable daily intake (ADI) for humans is 0.05 mg/kg (World Health Organization, 1989) for cypermethrin. A child would weigh ≈15−40 kg; therefore, the dose from a 1 min contact (one hand) with the treated bark would be ∼0.0005−0.001 mg/kg for cypermethrin. The dosage available from one accidental 1 min contact (a relatively long contact time) with a treated elm tree would be well below the level of human toxicological concern, even on the first day after application, and would diminish after that time. Even allowing for increased toxicity to a child compared to an adult, there still appears to be a substantial margin of safety.

Penetration of Cypermethrin from Treated Bark into Cambium and Wood Tissue. Table 6 shows the residue distribution of cypermethrin isomer pairs in the elm bark, cambium, and wood tissue at different time intervals after application. Because the elm bark beetles overwinter between cambium and wood tissues, it is of importance to know if the applied insecticide penetrated to the overwintering area from the treated bark surface. The experimental results reveal that cypermethrin was not detected in the cambium and the wood tissue indicating that cypermethrin lacks the ability to penetrate the bark. Overwintering elm bark beetles encounter the insecticide through contact with the treated bark surface and through the action of making overwintering tunnels. Residues of total cypermethrin in elm bark were still 16 μg/g after 791 days (1991 fall application) and 11 μg/g after 532 days (1992 spring application) (Table 7). Residues at the bark surface would have been considerably greater in view of the evidence that penetration into the bark to the cambium did not occur.

Conclusions. The initial residues of *cis*-A, *trans*-C, *cis*-B, and *trans*-D cypermethrin in elm bark were 29−58, 24−53, 25−35, and 18−25 μg/g, respectively. The residues of cypermethrin isomer pairs dissipated quickly, with half-lives ranging from 1.60 to 12.0 days for the faster dissipation phase; subsequently, dissipation slowed, with the dissipation half-lives ranging from 209 to 365 days during the later period. About 89% of *cis*-isomers had dissipated after 791 days from the 1991 application, and ∼85% after 532 days in the 1992 application, whereas the residues of *trans*-isomers degraded ∼92% after 791 days from the 1991 application and ∼91% after 532 days from the 1992 application.

Bioassay results on the effectiveness of cypermethrin against elm bark beetle indicated that it was still 100% effective in killing bark beetles after 60 days from application. Laboratory tests indicated that cypermethrin residues in bark were 100% effective in preventing the elm bark beetle from making overwintering tunnels for up to 627 days for the fall application and 433 days for the spring application. No penetration of cypermethrin isomer pairs into the cambium layer and wood tissue was found during the whole experimental period of 791 days. Total cypermethrin residues transferred from the treated bark by a single contact (0.01 m^2) for 1 min did not exceed the ADI for humans immediately following drying of the applied insecticide.

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