Persistence, Penetration, and Surface Availability of Chlorpyrifos, Its Oxon, and 3,5,6-Trichloro-2-pyridinol in Elm Bark

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The persistence, penetration, and bark surface contact availability of chlorpyrifos and its main degradation products, the oxon and 3,5,6-trichloro-2-pyridinol, in elm bark were investigated after chlorpyrifos had been applied to the basal 1 m of elm tree trunks for control of overwintering elm bark beetles, the vector of Dutch elm disease, at different application times and sites. The initial residues of chlorpyrifos in elm bark were 388−444 μg/g. The initial chlorpyrifos residues dissipated quickly with half-lives of 1.1−2.9 days for the faster dissipation phase. The dissipation of chlorpyrifos during the later period became much slower, with the dissipation half-lives ranging from 205 to 228 days. No penetration of chlorpyrifos into the cambium layer and wood tissue was found during the experimental period of 791 days. In the contact test, the chlorpyrifos residues transferred from the treated bark during a 1-min contact were below the acceptable daily intake for humans immediately following drying of the treated bark and diminished over the period of the experiment.

Keywords: *Chlorpyrifos; metabolites; residues; elm bark; penetration; contact availability*

1. INTRODUCTION

White elm (*Ulmus americana*) is widely distributed in North America. Elm trees in native stands are a source of hardwood; they have also been used as a component of farm shelter belts. The pleasing aesthetic shape of the tree has also made the elm an important choice in many urban forests. The destruction of wild and urban American elms by Dutch elm disease is of increasing importance in western Canada. The disease is caused by the fungus *Ophiostoma (Ceratocystis) ulmi* and is mainly spread by native elm bark beetles (*Hylurgopinus rufipes*) in the Canadian prairie provinces. Effective management of the native bark beetle by application of insecticide has been a key component in the integrated management program for Dutch elm disease in recent years in Manitoba and Saskatchewan (Westwood, 1991).

Chlorpyrifos (*O*,*O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate) (Figure 1), an organophosphate insecticide, is a broad-spectrum insecticide showing insecticidal activity against many insect and arthropod pests. Chlorpyrifos has been successfully utilized to combat insect and arthropod pests threatening the production of food and fiber and the maintenance of human health. At present, chlorpyrifos is registered for the control of the elm bark beetle.

In most studies, chlorpyrifos has been reported to dissipate very quickly from plant foliar surfaces with dissipation half-lives of several hours to weeks (Leuck *et al*., 1968; Dutta and Goswami, 1982; Abdel-All *et al*., 1990; Kuhr and Tashiro, 1978; Sears and Chapman, 1979; Wetters *et al*., 1985; Goh *et al*., 1986). There were much longer dissipation half-lives when chlorpyrifos was applied to the bark of trees, possibly due to surface sorption to the dead tissue layer or to the higher application rates (Brady *et al*., 1980). For instance, it took 1 month for chlorpyrifos residues to dissipate from initial residues of between 1449 and 3192 μg/g to approximately half these levels on loblolly pine trunks (0−1-cm layer) treated with 1% and 2% (EC) solutions. After the initially rapid dissipation, the rate of dissipation slowed, and 15 months later, 14−18% remained. Berisford *et al*. (1981) applied 1% and 2% solutions to pine trunks, yielding initial residues of 2598−7674 μg/g, depending on the application rate, and found bark dissipation half-lives of 5.0−6.9 months. Research on the dissipation of chlorpyrifos from sand pine bark treated with 2% chlorpyrifos EC drench indicated that initial residues of 24.7−40.8 μg/g in composite tree bark and wood samples did not decline significantly over a 12-month period (Neary *et al*., 1988). Howell and George (1984) examined the dissipation of chlorpyrifos from the twigs of apple trees. The residues of 0.64−6.02 and 0.09−0.19 μg/g were observed 1 and 6 months after up to three cover sprays of EC at 1.2 or 2.4 g/L. The quicker dissipation rate for the surface residues might have been caused by either lower application rates or the different nature of the living twig surface vs dead trunk bark tissue.

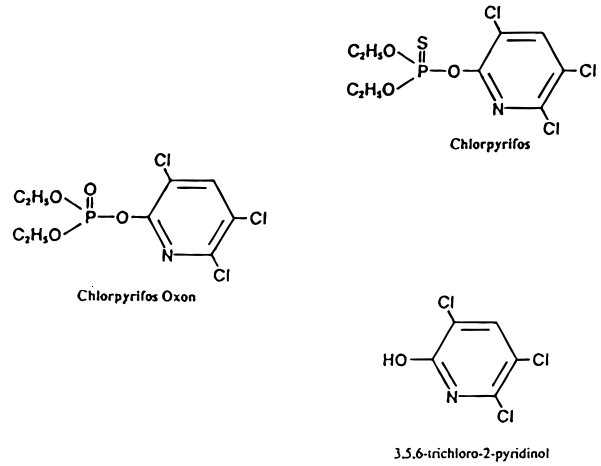

Figure 1. Chemical structures for chlorpyrifos, its oxon, and pyridinol.

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Table 1. Climatic Data for the Two Experimental Sites

sites	parameters	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 mean *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[a] (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

[a] Data from the Winnipeg International Airport, ca. 20 km from the experimental site at Beaudry Provincial Park.

The objectives of the study were to determine the persistence of chlorpyrifos and its main degradation products, the oxon and pyridinol (Figure 1), in elm bark. Further, we were to relate the residue levels of chlorpyrifos in elm bark to the efficacy to elm bark beetles, to determine the penetration of chlorpyrifos into the cambium and the wood tissue where elm bark beetles make their overwintering tunnels, and to evaluate the contact safety of the treated elm bark by measuring the availability of chlorpyrifos residues on the treated bark surface to a representative contact material.

2. EXPERIMENTAL PROCEDURES

2.1. Chemicals and Application Equipment. Dursban 48 EC (chlorpyrifos) was the product of Dow Chemical Canada, Inc. (Sarnia, ON, Canada). A back-pack sprayer was used to apply the 4.8 g of active ingredient (ai)/L aqueous solution of chlorpyrifos.

2.2. Field Treatment. The experiments were carried out at two sites containing American 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 grew in the forest along the banks of the rivers. The average monthly temperature and precipitation data 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 chlorpyrifos, 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 1992 application at each experimental site were located far enough from the 1991 treated plots so that the application of chlorpyrifos in 1992 would not contaminate the elm trees treated in 1991. The check treatments were located far enough away to avoid contamination of the check samples 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 at the recommended dosage of 100× aqueous dilution of 48 EC Dursban(4.8 g of ai/L) with a back-pack sprayer on August 15, 1991, or on May 7, 1992.

2.3. Sampling. *2.3.1. Residue Determination of Chlorpyrifos and Its Degradation Products in Elm Bark.* Samples of elm bark including the cambium layer were collected at time 0 (*ca.* 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, and 532 days after the application on May 7, 1992, at the Glenlea Research Station and at Beaudry Provincial Park. Three 1.7 cm × 1.7-cm elm bark samples with a cambium layer attached were taken randomly with a chisel 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 in a rotary blender prior to extraction.

2.3.2. Distribution of Chlorpyrifos in Elm Bark, Cambium, and Wood Tissues. Samples were collected at time 0 (*ca.* 1 h after insecticide treatment when the treated bark surface had dried), 11, 62, 341, 427, and 791 days after application. Elm bark, cambium, and wood tissue were collected separately to determine the penetration of chlorpyrifos from the treated elm bark surface to the cambium and the wood tissue at various time intervals after it had been applied to the surface of the trees. This experiment was carried out only at the Glenlea Research Station and only for the 1991 application. The outer bark was collected with a 2.6-cm chisel, the middle cambium with a 1.7-cm chisel, and the inner wood tissue with a 1.3-cm chisel to avoid possible contamination of the cambium and the wood layer with the insecticide from the outer layers during sampling. The samples of elm bark, cambium, and wood tissue were taken at five points from the treated elm trees, pooled, and ground in preparation for extraction.

2.3.3. Availability of Bark Surface Residues of Chlorpyrifos. 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 chlorpyrifos from the insecticide-treated bark surface. Samples were collected by pressing glass fiber filter paper (9-cm diameter) against the chlorpyrifos-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.

2.3.4. Biological Effectiveness Persistence Test. Bark disk samples were taken at the same time as the elm bark samples for the residue analysis. After the elm trees had been treated with chlorpyrifos 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 chlorpyrifos against 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 taken from each of the three replicate plots.

2.4. Soxhlet Extraction Method. Glass fiber filter paper samples taken to determine the availability of insecticide surface residues from the elm bark were put into Soxhlet thimbles, and the filter paper was exhaustively extracted with 60 mL of acetone for 3 h. The extracts were concentrated on a rotary evaporator to about 0.5 mL and then evaporated just to dryness under a stream of dry nitrogen. Toluene (1 mL) was added into the extracts. Because some residues were quite concentrated, the toluene solution was further diluted to an appropriate volume to facilitate gas chromatographic analysis.

2.5. Analytical Method for Determination of Residues of Chlorpyrifos, Oxon, and Pyridinol in Bark. Analysis of the residues of chlorpyrifos, oxon, and pyridinol was performed in triplicate by the method of Jin and Webster (1997a).

2.6. Bioassay Method for the Determination of Insecticidal Persistence of Chlorpyrifos in Elm Bark. Details of the bioassay of residual chlorpyrifos in bark are described in Jin *et al.* (1996).

3. RESULTS AND DISCUSSION

3.1. Analytical Method for the Determination of Chlorpyrifos, Its Oxon, and Pyridinol. Recoveries of chlorpyrifos and its oxon and pyridinol from spiked elm bark were in the ranges 94−97% (3.8−5.0% RSD),

Table 2. Recoveries of Chlorpyrifos from Glass Fiber Filter Paper

analyte	fortified concn, $\mu g/m^2$	recovery, %	SD, % ($n = 3$)
chlorpyrifos	1100	93	3.5
	0.5	90	3.1

91−92% (4.9−10.0% RSD), and 91−98% (0.6−1.5% RSD), for concentrations of 5−500, 0.5−5, and 1−30 μg/g, respectively (Jin and Webster, 1997a).

The recoveries of chlorpyrifos from fortified glass fiber paper at 0.5 and 1100 $\mu g/m^2$ are listed in Table 2. Recoveries were 93−96% with standard deviations of 3.1−3.5%.

3.2. Dissipation of Chlorpyrifos, Its Oxon, and Pyridinol in Elm Bark. The residues and standard deviations of chlorpyrifos, oxon, and pyridinol in elm bark after chlorpyrifos treatment at the Glenlea Research Station and Beaudry Provincial Park in 1991 and 1992 are shown in Table 3. The initial residues of chlorpyrifos determined after 1 h from the application (time 0) ranged from 388 $\mu g/g$ following the 1992 application to 444 $\mu g/g$ following the 1991 application at Beaudry Provincial Park. It took about 1 month for chlorpyrifos on the elm bark to dissipate from the initial residues to about half these levels. Approximately 90% of the applied chlorpyrifos dissipated from the treated elm surface after 791 days from the treatments at the two sites.

The regression analyses between the time after application and the chlorpyrifos residues in the elm bark at the corresponding times indicate that the dissipation of chlorpyrifos in the elm bark with time after application could be well approximated 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 chlorpyrifos from elm bark were calculated from the usual equation:

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

The experimental data for the residues of chlorpyrifos in elm bark at various times after application indicate that dissipation of chlorpyrifos in elm bark was a two-phase process. A two-phase model,

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

was used to describe the dissipation of chlorpyrifos and to calculate the dissipation half-lives of chlorpyrifos 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 of chlorpyrifos during the faster and slower phases in elm bark were calculated with eq 2, and the k_1 and k_2 values were obtained by solving eq 3.

The theoretical dissipation models of chlorpyrifos established by eq 3 through regression between the time after application and the corresponding residues in the elm bark, the dissipation half-lives for the faster and slower dissipation phases, and the correlation coefficients at the Glenlea Research Station and Beaudry Provincial Park for the August 1991 and the May 1992 applications are listed in Table 4. Chlorpyrifos dissipated very quickly in the elm bark, with half-lives ranging from 1.1 to 2.9 days for the faster dissipation phase. The dissipation rate of chlorpyrifos during the later period became much slower, with the dissipation half-lives ranging from 205 to 228 days. Dissipation half-lives for chlorpyrifos in the bark showed no significant difference between experimental sites or application times.

The difference in the initial residues of chlorpyrifos at different application times and experimental sites is attributed to the experimental error of application and bark texture of the elm trees used. The rougher bark normally found on the larger trees can intercept larger amounts of chlorpyrifos at application and had higher initial residue values when the residual concentration of the insecticides in the elm bark is expressed as insecticide weight per unit weight of bark. The initial residues of approximately 400 $\mu g/g$ for chlorpyrifos in elm bark are very high compared to the initial residues of 1−10 $\mu g/g$ found in common crops such as corn (Abdel-All *et al*., 1990; Leuck *et al*., 1968) but were considerably lower than the high initial chlorpyrifos residues of 1449−4000 $\mu g/g$ in pine bark reported after pine trunks had been treated with 1% or 2% chlorpyrifos (EC) solutions (Brady *et al*., 1980; Berisford *et al*., 1981). These authors found that the residues dissipated very quickly at the initial time, dropping 50% within the first month; dissipation then slowed in a manner similar to the dissipation pattern seen in our own research. First-order dissipation half-lives of 5.0−6.9 month were calculated. If one-phase first-order kinetics is used, the half-life of chlorpyrifos in elm bark is 37.9−166 days. This experiment did not determine the effect of bark position on the trees on the dissipation of the insecticide on the elm bark, but Page (1983) indicated that there was no significant difference ($P = 0.01$) between the residues of γ-HCH and chlorpyrifos methyl in Ponderosa pine bark (*Pinus ponderosa* Laws.) on the samples from the north or south sides of the trees.

The experimental residue data revealed that the insecticide residues dissipated much more quickly from the elm bark during the initial days after application, presumably due to the loose association of chlorpyrifos residues with the bark and the consequent quick loss of chlorpyrifos from this matrix by the natural elements. The dissipation rates of chlorpyrifos in elm bark became much slower during the later stages of the experiment. The possible explanation of the phenomenon is that the association of insecticide molecules and the bark became stronger and stronger with elapsed time, resulting in less and less insecticide being subject to loss by the action of the natural elements. Chlorpyrifos dissipated approximately 200 times more quickly in the faster than in the slower dissipation phase.

The dissipation data presented in Table 3 also reveal that chlorpyrifos dissipated more quickly during the summer than during the winter, presumably due to higher temperatures. However, rainfall during the summer is favorable for the dissipation of chlorpyrifos from the bark through such processes as molecular decomposition and dislocation of the insecticide from the target area. The dissipation of chlorpyrifos in elm bark became very slow after 341 days from application in 1991, dissipating approximately 36% over the next 450 days. In the case of the 1992 application, chlorpyrifos dissipated approximately 25% over the period from day 364 to day 532 (168 days). The probable tight association between the insecticide molecules and the bark

Table 3. Residues of Chlorpyrifos and Pyridinol in Elm Bark at Both Experimental Sites and Application Times [Oxon Was Not Detected at Any Time (Detection Limit in Elm Bark = 0.048 μg/g)]

		chlorpyrifos				pyridinol			
		Glenlea		Beaudry		Glenlea		Beaudry	
sampling date	days after applicn	residue, μg/g	SD, μg/g	residue, μg/g	SD, μg/g	residue, μg/g	SD, μg/g	residue, μg/g	SD, μg/g
Aug 15, 1991[a]	0	433	43.1	444	59.9	3.7	0.6	3.9	0.4
Aug 19, 1991	4	289	32.2	294	21.2	6.4	0.7	4.2	0.1
Aug 26, 1991	11	288	24.1	273	26.3	10	2.8	6.2	1.9
Sept 19, 1991	32	243	30.9	247	85.4	21	6.4	6.9	1.4
Oct 16, 1991	62	219	36.6	177	36.4	20	3.8	3.6	1.0
May 20, 1992	279	125	10.5	119	37.9	16	2.9	5.9	0.9
July 21, 1992	341	67.4	6.8	59.4	16.5	8.3	3.7	2.6	0.2
Oct 15, 1992	427	57.3	1.70	56.3	2.80	3.1	0.9	0.7	0.6
May 3, 1993	627	46.7	11.8	44.3	10.3	6.1	2.0	4.5	0.7
Oct 14, 1993	791	41.3	6.40	39.7	10.7	8.8	2.5	3.6	1.0
May 7, 1992[a]	0	408	48.6	388	125	3.9	0.5	2.5	0.7
May 11, 1992	4	246	66.1	237	28.3	3.7	0.9	2.5	0.3
May 21, 1992	14	228	11.1	173	14.3	18	6.0	9.9	1.1
June 15, 1992	30	198	33.3	155	27.0	14	3.3	5.7	0.5
July 20, 1992	74	164	25.1	111	28.1	5.4	2.8	1.8	0.9
Sept 25, 1992	141	117	12.9	67.7	13.0	4.6	0.4	1.8	0.4
May 6, 1993	364	69.3	16.4	54.6	11.2	20	6.0	8.2	1.4
July 14, 1993	433	62.0	16.8	54.3	8.00	13	4.8	6.2	1.0
Oct 21, 1993	532	46.8	9.90	42.4	3.80	12	4.8	3.8	0.7

[a] Application time of chlorpyrifos.

Table 4. Models, Half-Lives, and Correlation Coefficients (r) of Chlorpyrifos Dissipation in Elm Bark

		half-lives, days		
treatment	dissipation models	fast	slow	r
Glenlea, 1991	$C_t = 152e^{-0.6257711t} + 281e^{-0.0033782t}$	1.11	205	0.9941[a]
Glenlea, 1992	$C_t = 187e^{-0.4662966t} + 22.1e^{-0.0033103t}$	1.49	209	0.9952[a]
Beaudry, 1991	$C_t = 182e^{-0.3860543t} + 262e^{-0.0034020t}$	1.80	204	0.9903[a]
Beaudry, 1992	$C_t = 232e^{-0.2358654t} + 155e^{-0.0030402t}$	2.94	228	0.9899[a]

[a] Significant at the 0.01 level.

Table 5. Residues of Chlorpyrifos in Elm Bark, Cambium, and Wood Tissue at Different Time Intervals after Application

		residues, μg/g		
sampling time	days after applicn	wood	cambium	bark
Aug 15, 1991[a]	0	ND[b]	ND	1020
Aug 26, 1991	11	ND	ND	633
Oct 16, 1991	62	ND	ND	569
July 21, 1992	341	ND	ND	159
Oct 15, 1992	427	ND	ND	135
Oct 14, 1993	791	ND	ND	97

[a] Application time of chlorpyrifos. [b] The detection limit of chlorpyrifos for this work in elm bark was 0.024 μg/g.

components or probable penetration of the insecticide into inner bark in the later stage might slow down the dissipation processes and decrease the dissipation difference between winter and summer. The dissipation trend observed during the later sampling indicates that effective residues of chlorpyrifos in elm bark may last for a number of years.

Considering the fact that chlorpyrifos failed to penetrate to the cambium layer (Table 5) and that the bark samples used in the experiment contained the full thickness of the bark including the cambium layer, the residue concentration of chlorpyrifos in the thin surface bark layer must have been several times higher than the whole bark values recorded in Table 3.

The chlorpyrifos oxon could not be detected during the experimental period at either site or application time. The residues of the pyridinol in elm bark were initially low and then increased with time (Table 3). The residues of pyridinol detected in the elm bark ranged from 0.7 to 21 μg/g. Higher residual concentrations of pyridinol were found at the Glenlea Research Station

Table 6. Chlorpyrifos Remaining in Elm Bark (Disks) during the 1−2-Year Period following Treatment: All Residues Resulted in 100% Mortality of Elm Bark Beetles (Jin *et al.*, 1996)

sampling date	days after applicn	residue, μg/g
Aug 15, 1991[a]	0	440
Aug 19, 1991	4	290
Aug 26, 1991	11	270
Sept 19, 1991	32	250
Oct 16, 1991	62	180
May 20, 1992	279	120
July 21, 1992	341	59
Oct 15, 1992	427	56
May 3, 1992	627	44
Oct 14, 1993	791	38
May 6, 1992[a]	0	390
May 11, 1992	4	240
May 21, 1992	14	170
June 15, 1992	30	160
July 20, 1992	74	110
Sept 25, 1992	141	68
May 6, 1993	364	55
May 3, 1993	433	54
July 14, 1993	532	42

[a] Application time of chlorpyrifos.

than at Beaudry Provincial Park. The residue concentration of pyridinol in the elm bark could have been influenced by factors such as substrate concentration, microorganism activity, and weather conditions; rainfall was associated with the removal of the pyridinol to the surrounding soil (Jin and Webster, 1997b).

Table 6 shows the residues of chlorpyrifos in the elm bark treated in 1991 and 1992 in Beaudry Provincial Park. The residue levels of chlorpyrifos in the elm bark after 791 days in the 1991 application and 532 days in

Table 7. Chlorpyrifos Available through Direct Contact with the Elm Bark Surface following Treatment

sampling time	days after applicn	residue, $\mu g/m^2$	SD, $\mu g/m^2$ ($n = 3$)
May 7, 1992	0	1900	1000
May 11, 1992	4	230	75
May 21, 1992	14	92	21
June 15, 1992	30	54	14
July 20, 1992	74	24	7.0
Sept 25, 1992	141	15	6.0
May 6, 1993	364	7.8	1.6
July 14, 1993	433	2.0	0.6
Oct 21, 1993	532	0.1	0.0

the 1992 application were 38 and 42 μg/g, respectively, sufficient to be 100% effective in killing elm bark beetles after 24-h exposure to the elm bark surface (Jin *et al.*, 1996). The fact that the detected amount of chlorpyrifos in the elm bark after 791 days was still more than 3 times the initial amounts of chlorpyrifos used on common agricultural crops to control insects and that the residues dissipated very slowly at this time implies that the residual chlorpyrifos in the elm bark might be effective for a further period. Sampling for a longer period than was possible in the current study would be needed to establish the full efficacy period.

3.3. Availability of Chlorpyrifos Surface Residues. Table 7 lists the residual chlorpyrifos 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 1.9 mg/m^2 for samples taken when the treated bark surface had been dried for about 1 h after application. The availability of the insecticides dropped very quickly to 0.23 mg/m^2 4 days after the treatment.

The highest availability of these chlorpyrifos residues, as expected, occurred just after 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 $\times$ 10 cm), the total single dosage available to a child from one such contact with a treated tree would be approximately 0.02 mg just after treatment, dropping to 0.002 mg by day 4. These figures also assume that the residue was completely absorbed through the skin. The acceptable daily intake (ADI) for human is 0.01 mg/kg (Tomlin, 1994) for chlorpyrifos. A child would weigh approximately 15−40 kg; therefore, the dose from a 1-min contact (one hand) with the treated bark would be 0.0001−0.0005 mg/kg. 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. Even allowing for increased toxicity to a child compared to an adult, there still appears to be a substantial margin of safety.

The absorption rates of chlorpyrifos through skin into the human have been reported to be very low. Nolan *et al.* (1984) examined the dermal absorption of chlorpyrifos in human volunteers and reported that only 1.35% of the applied dose (5.0 mg/kg) penetrated the skin during a period of 180 h. Cheng *et al.* (1989) similarly reported minimal dermal absorption of chlorpyrifos in goats, in which a maximum of 0.3% of the applied dose was detected in the goat circulatory system after 12 h.

3.4. Penetration of Chlorpyrifos from the Treated Bark Surface to Cambium and Wood Tissue. Table 5 shows the residue distribution of chlorpyrifos in the elm bark, cambium, and wood tissues taken at different time intervals after application. Because the elm bark beetles overwinter between cambium and wood tissues, it is of importance for the applied insecticide to be able to penetrate to the overwintering area from the treated bark surface. But the experimental results reveal that chlorpyrifos was not detected in cambium and wood tissue, indicating that chlorpyrifos lacks the ability to penetrate the bark. Overwintering elm bark beetles encounter chlorpyrifos on the treated bark surface and when they make overwintering tunnels. The residues of chlorpyrifos in the elm bark layer were still 97 μg/g after 791 days from the initial application of the insecticide. Residues at the bark surface would have been considerably greater in view of the evidence that penetration into the bark to the cambium had not occurred.

4. CONCLUSIONS

The initial residues of chlorpyrifos in elm bark ranged from 388 to 444 μg/g and initially dissipated quickly, with half-lives ranging from 0.3 to 2.9 days for the faster dissipation phase; subsequently, dissipation slowed with half-lives from 173 to 232 days during the later period. Approximately 90% of the applied chlorpyrifos dissipated from the treated elm bark surface after 791 days from treatment. Bioassay results on the effectiveness of chlorpyrifos against the elm bark beetle indicated that it was still 100% effective in killing bark beetles after 791 days (1991 application) and 532 days (1992 application). It is hypothesized that chlorpyrifos would still be effective against the elm bark beetles for a considerable period after 791 days considering the high residues of chlorpyrifos in the bark and the subsequent low dissipation rates at that time.

Chlorpyrifos applied on the bark surface failed to penetrate to the cambium layer and wood tissue during the whole experimental period of 791 days. Chlorpyrifos residues transferred from the treated bark during a single contact (0.01 m^2) for 1 min did not exceed the acceptable daily intake for humans immediately following drying of the applied insecticide.

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