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Applicator Exposure to Airborne Concentrations of a Termiticide Formulation of Chlorpyrifos

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Since chlordane was removed from use, chlorpyrifos (Dursban TC™, Dow Chemical Company, Midland MI) has become one of the major termiticides used throughout the United States. Wright et al (1991) measured airborne concentrations of chlorpyrifos in homes treated for termites over a 4-year period and compared the measured levels detected to that of the National Academy of Sciences (NAS) proposed Guideline Level of 10.0 $\mu g/m^3$. In the working environment, the Threshold Limit Value (TLV) is set at 200 $\mu g/m^3$ for an 8 to 12 hr work day or 40-hr work week (Am. Conf. Govt. Industrial Hygienists 1989). Few data are available on applicator exposure to airborne concentrations of termiticide formulations of chlorpyrifos. Vaccaro (1981) showed applicator exposure levels ranging from 50 to 370 $\mu g/m^3$ (avg 160) when 4-underfloor plenum type houses were treated. Another study by Vacarro (1985), performed to determine exposure levels in home-owners while living in houses of different construction types treated with chlorpyrifos for control of termites, showed levels from ND (0.07) to 8 $\mu g/m^3$. The following study was performed to determine exposure levels to applicators while treating houses of different construction types with chlorpyrifos for the control of termites.

MATERIALS AND METHODS

A 1.0% chlorpyrifos emulsion was applied to 16 single-family houses in North Carolina by pest control firms licensed by the NC Department of Agriculture. Four houses with a crawl space under the entire house and 4 on concrete slabs were selected in the Coastal Plain regions of the state where soils vary from loamy sands to sandy loams. The other eight consisting of 4-crawl space and 4-crawl-slab constructed houses were selected in the Piedmont region whose soils are clay and clay loams. Other conditions, such as the amount of termiticide applied per house, time intervals of air sampling, and temperatures and relative humidities in sampled rooms, were reported by Wright et al. (1988). To determine exposure levels, applicators were fitted with a DuPont Model P4000A Constant Flow Sampling Pump (DuPont Applied Technology Div., Wilmington, DE 1989). A length of Tygon tubing was used to attach a glass sampling cartridge containing a polyurethane foam

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(PUF) plug 3.5 by 2.2 cm O.D. to the pump (Wright et al. 1988). A metal clip was used to attach the sampling cartridge to the applicators shirt at chest level. Pumps were calibrated by a bubble meter before and after each application and pumped an average 0.24 L of air/min. In addition, eight of the crawl-,crawl/slab-constructed houses were monitored for chlorpyrifos residues in the air of the crawl space during application using additional DuPont pumps and PUF traps. A pump was placed level with the bottom of a floor joist near the center of each house. Pumps were started when the application began and shut off upon completion, and the events were timed and recorded. Sampling cartridges were removed and placed in insulated boxes containing solid CO_2 for transport to the laboratory. Samples were stored at -10°C until analyzed.

The extraction method has been described (Wright and Leidy 1988). If cleanup was required, samples were taken up in 10 mL of hexane and transferred to a Florisil Sep Pak prerinsed with 5.0 mL of hexane. The hexane was allowed to drain by gravity and chlorpyrifos was eluted with 12.0 mL of 6% ether in petroleum ether. Samples were concentrated to 0.2 mL under reduced pressure and taken up in hexane for analysis by GLC.

The chromatograph was a Tracor Model 222 equipped with a Flame Photometric Detector operated in the phosphorous mode. The column was U-shaped glass (183 by 0.2 cm i.d.) packed with 4.0% SE-30+ 6.0% QF-1 on Gas Chrom Q (80/100). The carrier gas was nitrogen at a flow rate of 35 mL/min. Temperatures were as follows: oven, 195°C; detector, 185°C; inlet, 200°C. Gases to the detector were hydrogen and air at flow rates of 50 and 80 mL/min, respectively. Data were quantitated by the peak height method using standards of known concentration.

To determine the efficiency of the analytical method, PUF plugs were fortified with varying amounts of analytical grade chlorpyrifos, placed under a hood for 2 h to allow solvent evaporation and then extracted with the samples. Two fortified plugs were extracted with 4 samples. Data were not corrected to reflect recovery values.

RESULTS AND DISCUSSION

Recoveries of chlorpyrifos, put on untreated PUF plugs at rates of 0.25 to 50 µg are shown in Table 1. Recoveries averaged 94.7% for 15 samples.

The amount of termiticide applied varied depending upon construction type and are shown in Table 2. All treatments were done according to label directions for the specific type of construction encountered. The average amount of chlorpyrifos (a.i.) applied to crawl-(clay), crawl-(sandy), crawl-slab (clay) and slab-(sandy) constructed homes was 5.9, 4.4, 6.9, and 9.2 Kg, respectively. It took an average of 231 min to apply the chlorpyrifos under crawl-constructed homes on clay soils, 128 min for

crawl-constructed homes on sandy soils, 290 min for crawl-slab homes on clay soils, and 170 min for slab-constructed homes on sandy soils (Table 3). The different application times and amount of chlorpyrifos applied were influenced by such factors as house size and construction, soil composition and depth of foundation to footing. During house treatment, all applicators were exposed to varyng levels of chlorpyrifos as determined from the amounts found on the PUF plugs (Table 3).

Table 1. Recoveries of chlorpyrifos from untreated PUF plugs[a]

No plugs	Amount added (µg)	Amount recovered (µg)	Range (µg)	Recovery (%)
1	0.25	0.25		100
2	1.00	0.93	0.88 - 0.99	93
1	1.25	1.30		104
1	2.0	1.9		96
1	5.0	4.4		87
1	7.5	6.9		92
3	15.0	14.2	13.9 - 14.4	95
1	20.0	19.7		99
1	25.0	22.8		91
2	30.0	28.7	28.3 - 29.1	96
1	50.0	45.5		91

[a]Varying amounts of chlorpyrifos added to untreated PUF plugs, which were allowed to sit for 2 Hr and extracted. Using the same pipette, equivalent amounts were added to a 12 mL tube which was refrigerated until samples were chromatographed. Recovery values were based upon amount found from fortified plug divided by amount stored under refrigeration.

Termiticide application is quite complex and the work involved in rodding and trenching is strenuous. Thus, the average respiratory rate for applicators was assumed to be 60 L of air/min (heavy work) as reported by Lewis et al. (1980). Based upon this value, the average total volume of inspired air ranged from 7.7 to 17.3 m^3 (Table 3). By dividing the amount of chlorpyrifos found on the PUF plug by the total volume of air inspired during application, the potential applicator respiratory exposure can be determined (Table 3). To determine the percentage of exposure by the application to the TLV of 200 $mg/^3$, the average time to treat the houses (3.42 Hr) and the heavy workload respiratory rate of 60 L/min were used.

The data varied widely with the lowest levels seen from applications to slab-constructed homes. This would be expected since the applicator in these cases did not treat in the crawl-space area. When the levels of exposure are compared to the TLV, they are 0.7% of the TLV which would be expected since these applications were

performed outside. Somewhat higher levels were seen from applications made to crawl-slab-constructed homes. Since some time was spent in an enclosed area, this was expected and the exposure levels was 0.24% of the TLV. Highest concentrations of chlorpyrifos were found on adsorbents worn by applicators treating crawl-space constructed homes.

Table 2. Concentration, construction and soil types for houses treated with chlorpyrifos for termite control[a]

Geographical area	Soil Type	Construction type	House size (M^2)	Amount applied[b] (kg a.i.)
Coastal Plain	Sandy-Sandy Loam	Crawl	100	4.18
			114	5.27
			74	3.63
			114	5.45
		Avg.	100	4.40
		Slab	86	6.72
			145	13.02
			86	4.91
			185	12.18
		Avg.	128	9.20
Piedmont	Clay-Clay loam	Crawl	132	9.09
			96	3.64
			170	6.36
			95	4.36
		Avg.	123	5.85
		Crawl/Slab[c]	121	6.36
			143	9.09
			151	5.64
			150	6.36
		Avg.	141	6.87

[a]From Wright et al. (1988).
[b]Chlorpyrifos applied as a 1.0% emulsion.
[c]House constructed with a portion on a slab and the reminder over a crawl space.

Airborne concentrations of chlorpyrifos were measured in the crawl space of 8 homes (2-crawl-sand, 2-crawl clay; 4-split-clay) to attempt to relate exposure to airborne levels (Table 4). As can be seen, the potentioal exposure levels varies widely when compared to airborne concentrations found in the crawl space. It was observed that some applicators had been splashed with the diluted formulation during application, because dried spots were seen on clothing, respirators, and adsorbent tubes. It was probable that

Table 3. Potential respiratory exposure of applicator to airborne concentrations of chlorpyrifos[a]

Const. type	Soil type	Rep. No.	Treatment time (Min)	Total air[b] inspired (M^3)	Concn[c] (μg)	Potential[d] exposure ($\mu g/m^3$)
Crawl	Clay	A1	365	21.9	32.2	1.5
		A2	94	5.6	0.4	0.1
		A3	244	14.6	136.9	9.4
		A4	221	13.3	8.9	0.7
		Avg	231±111	13.8±6.7	44.6±63.0	2.9±4.4
Crawl-slab	Clay	B1	221	13.3	4.1	0.3
		B2	392	23.5	0.8	0.04
		B3	292	17.5	0.7	0.04
		B4	252	15.1	1.8	0.1
		Avg	289±74	17.3±4.4	1.8±1.6	0.1±0.1
Crawl	Sand	C1	98	5.9	578.4	98.0
		C2	100	6.0	7.6	1.3
		C3	158	9.5	1.3	0.1
		C4	158	9.5	1.8	0.2
		Avg	128±34	7.7±2.0	147.3±287.4	24.9±48.7
Slab	Sand	D1	96	5.8	0.3	0.1
		D2	229	13.7	1.5	0.1
		D3	258	15.5	0.4	0.02
		D4	113	6.8	0.1	0.01
		16	159	9.5	0.3	0.03
		Avg	171±71	10.3±4.2	0.5±0.6	0.05±0.04

[a]Exposures based on actual house application.
[b]Based upon a heavy work load in which an average 60 L/min of air are inspired (Lewis et al. 1980) multiplied by the no. min. required to treat the house.
[c]Amounts found on PUF plug attached to applicator.
[d]Data with an asterisk used in Table 4, Column 4.

some splash back impinged upon the PUF adsorbent and this was assumed to be true for 6 applicators (nos. A1, A3, A4, B1, C1, and C2) (Table 3), based upon the amount of chlorpyrifos found on the sorbent. Thus, it is critical that careful observation be made when tests of this nature are conducted, because the resulting data can be misinterpreted. The exposure levels in crawl-space constructed houses were higher than other construction types, averaging 5.6 and 26.6% of the TLV in houses built on clay and sandy soils, respectively.

The average exposure from all applications averaged 8.1% of the TLV for airborne levels of chlorpyrifos. Thus, even with the 6

elevated values seen in this study, the data indicate a low probability of acute exposure to termiticide formulations when applicators follow label directions and wear the proper respirator.

Table 4. Comparison of applicator exposure to chlorpyrifos in air with concentrations found in crawl space air[a]

Const. type	Soil type		Crawl space Concn ($\mu g/m^3$)	Potential exposure of applicator ($\mu g/m^3$)[b]	(% of TLV-TWA)[c]
Crawl	Clay		36.3	9.4	4.7
			107.5	0.7	0.35
	Sandy		35.0	0.2	0.1
			7.9	0.1	0.05
		Avg.	46.7±52.2	2.6±4.5	1.3±2.25
Crawl-Slab	Clay		3.8	0.04	0.02
			7.6	0.12	0.06
			50.1	0.31	0.16
			7.0	0.04	0.02
		Avg.	17.1±22.0	0.13±0.16	0.065±0.08

[a]8 of 12 houses contained some form of crawl space.
[b]Data taken from Table 3, column 7.
[c]The threshold limit value-time-weighted average of chlorpyrifos is 200 $\mu g/m^3$ of air based on an 8-h workday or 40-h workweek.

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