Chapter 13

Horizontal and Vertical Distribution of Chlorpyrifos Termiticide Applied as Liquid or Foam Emulsions

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Damage due to termites now exceeds $1.7 billion annually in the United States. Termite control presently emphasizes the use of persistent pesticides which either eliminate pest populations directly or prevent their invasion into structures. An evaluation was conducted with liquid and foam formulations of chlorpyrifos termiticide. Horizontal distribution under simulated concrete slabs was enhanced through the use of foam carriers as compared to liquid emulsions applied with a subslab injector system. Vertical penetration within the soil profile was similar for both formulations with 92% and 95% of the total chlorpyrifos recovered from the first 3 cm of soil for liquid and foam emulsions, respectively.

Termites (Order Isoptera) are small, delicate insects that cause tremendous damage to wooden components of structures. While it is difficult to estimate accurately the effects of termite damages, the annual costs for control of termites and repair of their damage exceeds $1.7 billion in the United States. Termites are a problem throughout the world but are primary pests in tropical and subtropical regions which include many areas of the United States. Granovsky *(1)* estimated that termites cost each American $5.16 per year (in 1983 dollars), and do more damage than all tornadoes, hurricanes and wind storms combined *(2, 3)*. He also reported that termites strike over five times as many homes each year as do fires, and that subterranean termites represent the greatest threat of damage to homes of all natural causes. Termites are of particular importance in the southern regions of the United States, where there is a direct correlation between the per cent of infestation and the age of structures. By the time a structure in the coastal regions of Texas is 40 years old, the probability of infestation with one or more of the several species of termites exceeds 90%. In colder climates such as represented by Nebraska *(4)*, it was estimated that 5% of all structures are infested with termites at any point in time.

Termite control and prevention requires a combination of approaches as part of an integrated management system. In addition to the use of pesticides (termiticides), it has been recommended that wood-to-soil contacts be eliminated, moisture sources be reduced

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(repairing water leaks, changes in landscapes, and increased air circulation in structures with crawl spaces) *(5)*, and that regularly scheduled inspections be performed to locate developing infestations.

Termiticides have been used both to prevent and to control termite infestations in structures. They are used both as pre-construction (pretreatment) or post-construction (remedial) applications. The objective of the application of termiticides is to establish a continuous protective barrier between the termite colony (usually in the soil) and the wood within a structure *(6, 7)*. For best results both a horizontal and vertical chemical barrier are recommended. This protective barrier is intended either to kill the invading insects, or to repel them thus preventing their entrance into the structure. In the case of remediation treatments, the chemical is applied to reestablish the termiticide barrier or to kill insects before the infestation increases in size and spreads to other parts of the structure. In order to be most effective as a barrier to invading termites, a continuous contamination zone must be established.

The chlorinated hydrocarbon termiticides were considered ideal for the prevention and control of termite damage due to their wide spectrum of efficacy and persistence *(8)*. Chlordane and heptachlor were used for these purposes from 1952 until 1988-89, when all registrations were discontinued in the United States. It is unlikely that these termiticides will be returned to the market *(9)*. Organophosphate, carbamate, and pyrethroid termiticides are available and effective for both pre- and post construction treatments *(10)*. Results of a survey of professional pest control operators indicated that chlorpyrifos (Dursban TC) was preferred by 65.1% of those responding *(11)*.

At the present time there are questions as to how long the new termiticides will provide protection against termites, and how these products should be applied for best results *(12)*. Evaluations of various application technologies and termiticide distribution have been conducted *(8, 13-23)*. As a result of that research a number of specific recommendations have been made about specific termiticide products, application equipment (pumps, injectors, flow meters), application pressures, application rates, drill hole spacing, trenching procedures, and rodding techniques. Even with all the available information, it still appears that most termiticide applications are made "blindly" when treating beneath concrete slabs *(6)*. In these situations, it has been difficult if not impossible to insure that a continuous protective barrier is established. Different approaches to solving this problem have been taken including the use of termiticide foam formulations *(22, 23)*. These preliminary reports indicate more even distribution of termiticide under construction slabs as compared to conventional liquid injection techniques.

The purpose of this research was to evaluate the horizontal distribution and vertical penetration in soil by chlorpyrifos (Dursban TC) termiticide when applied as a liquid or foam emulsion.

MATERIALS AND METHODS

Study Site. Field studies were conducted at the Center for Urban and Public Health Entomology of the Department of Entomology, Texas A&M University, College Station, Texas. Pine dimensional lumber (5 cm X 15 cm X 4.87 m) was used to construct square soil frames of 1.22 m per side. A total of 24 frames were used in this study with all treatments replicated at least three times. After construction, the frames were placed on top of the existing terrain and leveled. Each frame was filled with soil (Lufkin Series: pH 7.1; 1.2% total organic matter; 53.7% sand; 33.7% silt; 12.5% clay) which was hand tamped and then leveled with a screen. The soil was compacted in the frame to a final depth of 10 cm. The frames were then covered with 20 mm Plexiglass which was used to simulate a concrete slab through which termiticide applications were made. The use of Plexiglass facilitated the visual confirmation of distribution patterns in these tests which were documented through videography and still photography. Injection holes (1.3 mm O.D.) were drilled in the Plexiglass cover in three locations. One hole was drilled in the center of the square (Figure 1), and two other holes were drilled 10.2 cm from one edge, 20 cm apart (Figure 2). A 2.54 cm spacer was used to maintain a gap between the top surface of the soil and the bottom surface of the Plexiglass cover. This space represented the effects of soil settling or shrinkage that takes place after concrete has been poured on grade with standard monolithic slab construction types used typically throughout Texas and surrounding states.

Chemicals. The termiticide used in this study was chlorpyrifos [O,O-Diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] sold as Dursban TC by DowElanco (Indianapolis, Indiana). Concentrate material was mixed with water to make a 1.0% active ingredient (a.i.) emulsion. Two different emulsions were prepared for these tests including a standard 1.0 % liquid which was applied as a liquid emulsion, and a 1.0 % foam emulsion which was prepared from Dursban TC concentrate, mixed with water and to which was added a foaming agent (Flexafoam, Foam Innovations Inc., Pleasanton, California). Sufficient Flexafoam was added to make a foam with an expansion factor of 8-10 (1 l of liquid yielded 8-10 l of foam).

Chemical Applications. Liquid applications were made with a standard sub-slab injector equipped with a straight, open tip (B&G Equipment Co., Model 486). Flow rate was 3.8 l/min at 172.5 kPa using a Hypro 6500NR gas engine roller pump. Foam was made with a Flexafoamer (Foam Innovations Inc.) which was inline with the Hypro 6500NR roller pump. The foam was dispensed through a custom-built sub-slab injector with a shut-off at the tip. Foam and liquid output (flow rate) was measured with an electronic digital flow meter (Digital Flowmeter Model PHL-3, Technology Management, Inc., Kalamazoo, Michigan). All mixing and application of termiticide in this study were done per commercial pest control standards by representatives of Orkin Exterminating Company, Inc., using their equipment and chemicals.

Treatment procedures involved the application of liquid chlorpyrifos at the rate of 5.0 l/m applied against one side of the soil frame (total volume divided between two injection holes). The second treatment was 3.7 l/m followed immediately by the application of 1.2 l/m liquid equivalents of foam (yield=30 l of foam). The total active ingredient applied (37 g/m) was the same for Treatment 1 as it was for Treatment 2, but the application medium (water or water plus foam) differed. Treatment three was 1.2 l/m liquid equivalents of foam which equated to 0.25% of the total chlorpyrifos active ingredient delivered in either Treatments 1 or 2. Treatments 4-6 were made in the center of the soil frame as opposed to the edge (Treatments 1-3). Treatment 4 was 4.1 l/m^2, Treatment 5 was 4.1 l/m^2 liquid equivalent as foam, and Treatment 6 was 16.3 l/m^2.

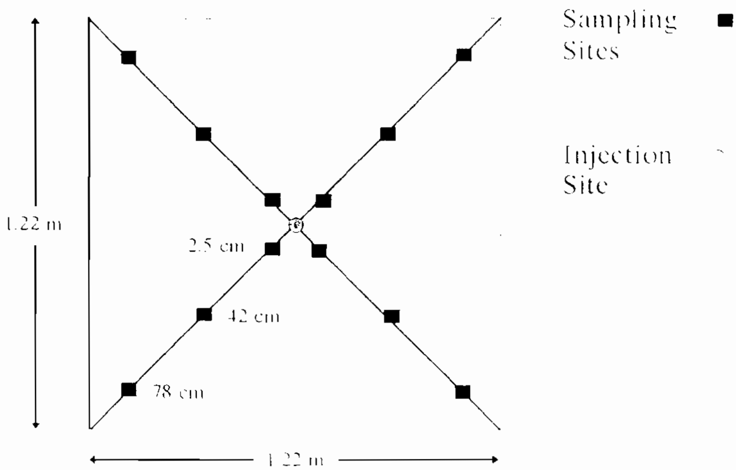

Figure 1. Sampling Scheme for Center Plots

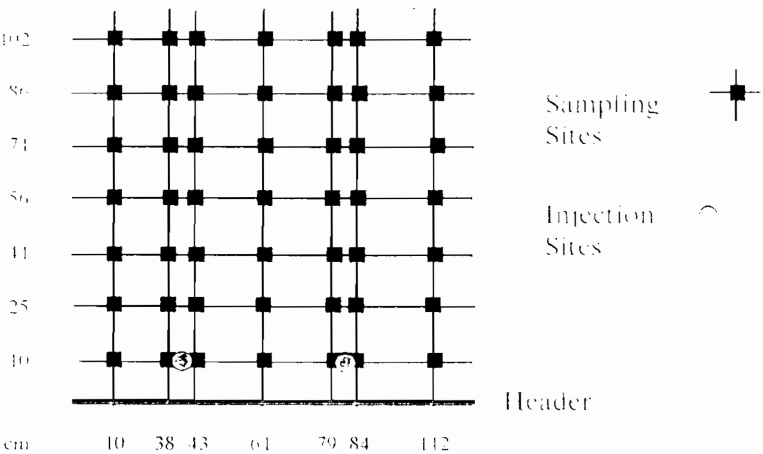

Figure 2. Sampling Scheme for Edge Treatments

Sampling Procedures. Following termiticide applications the plots were covered with plywood and plastic sheeting to minimize the effects of rain. Sampling was initiated 10 days post-treatment. Soil samples were taken by pressing glass shell vials (25 mm diam x 95 mm high), open end down, into the soil, which were then carefully removed. Soil cores were held in these glass vials and stored at -5°C until analysis.

Core samples from the edge treatments (Treatments 1-3) were taken from a grid of seven columns by six rows. The first row was along the row of injection (10 cm from the edge). The successive rows were 15 cm from the previous row. The columns were defines as follows: Column 1 was taken at 10 cm from the left side of the square with the row of injection closest; Columns 2 and 3 were taken approximately 2.5 cm on either side of the injection hole left from the application; Column 4 was midway between the injection holes (61 cm from the left side); Columns 5 and 6 were as in 2 and 3 next to the opposite side of the injection crater; and Column 7 was sampled as was column 1, only from the right side of the square (Figure 2).

For the center injection treatments (Treatments 4-6), core samples were taken along the axes of lines drawn diagonally through the plots. The first and last sample on each diagonal were taken 6 cm from the corners. The third and fourth samples were taken 2.5 cm from the crater in the center of the plots created by the injection process. The second and fifth samples were taken midway along the diagonal from the other samples (Figure 1).

Sample Preparation. Soil samples were prepared for analysis by dividing each sample into levels relating to depth below the soil surface. Each layer weighed approximately 5 g and represented a depth of approximately 1 cm. Each subsample was weighed and put into a 25 ml glass scintillation vial with 20 ml of acetone. The subsamples were shaken and then allowed to sit overnight at room temperature. An aliquot of the initial extraction was then injected into a gas chromatograph(GC).

Chemical Analysis. Analyses were performed using a Lee Scientific Supercritical Fluid Gas Chromatograph (Model 66-D) fitted with a flame ionization detector (Lee Scientific FID-3) operated in a standard GC mode. Conditions for the instrument were as follows: He carrier gas at 30 ml/min, H_2 at 35 ml/min, air at 300 ml/min, N_2 make up gas at 25 ml/min, and a column head pressure at 34.5-68.9 kPa. Temperatures were: injection port, 250°C; detector, 325°C; and oven with a ramp program starting at 75°C for 1 min and increased to 250°C at 50°C/min, held for 7 min and then cooled back to 75°C at -50°C/min. The capillary column was a J&W Scientific DB5, 0.32 mm I.D., 15 m. Autosampler was a Dynatech Precision Sampler (GC-411) with an injection volume of 2µl. Column retention time for chlorpyrifos was 2.67 min with a total run time of 15 min. Performance of the method and instrumentation was monitored through the use of spiked blanks and standardization curves. Recovery rate was 85 $\pm$ 5.3% based on extraction and analysis of replicated spiked soil samples. The limit of detection was 10 ng chlorpyrifos/on column, with an overall methods sensitivity of 5 ppm chlorpyrifos.

RESULTS

Visual Observations. It was possible to see visual evidence of the application and movement of chlorpyrifos in both the liquid and foam treatments. The liquids had a tendency to move to the lowest point in the soil frames, and there was evidence of areas that were not contacted by the chemical. Some areas were not contacted by the termiticide because there was not enough liquid or foam. The foam applications appeared to be much more thorough having fewer missed areas in both the edge and center applications. When the Plexiglass cover was removed from the soil frame, it was evident that the foam had contacted not only the soil and wooden frame, but also the underside of the slab. Applications of the foam took twice as long as the liquid applications, but there was evidence in the center treatments that the foam covered at least twice the area within the space beneath the covered slab as was covered by the equivalent liquid dilutions.

Chemical Analysis. Analysis for chlorpyrifos in the liquids used for treatments yielded an initial concentration of 0.6% a.i. for all liquid applications and 1.6% a.i. for the foams. The findings were confirmed by an independent laboratory (Office of the Texas State Chemist). The data from the applications is expressed in parts per million (ppm) (Figures 3 and 5, and Tables I, III, VI and VIII). Since termiticide concentration differed with treatments, comparisons were made on the per cent of total chlorpyrifos recovered from the soil in both horizontal and vertical dimensions (Figures 4 and 6, and Tables II, IV, V and VII).

Chlorpyrifos residue analysis provided evidence that the application method did make a significant difference in the horizontal distribution of the termiticide (Figure 3) when applied within 10 cm of a header (Figure 1). While the distribution patterns were similar for the 5.0 l/m and the 3.7 l/m plus the 1.2 l foam, there was uniform spread of the 1.2 l foam/m. The chlorpryrifos concentrations (ppm) indicated in Figure 3 were sufficient for effective termite treatments *(10, 24-31)*. When comparisons were made of the percentages of the total amount of chlorpyrifos that was deposited with increasing distances from the header (Figure 4), there were no significant advantages to the use of foams in the edge treatments.

Horizontal movement of termiticide applied in the center of each plot (Figure 2) differed with each of the three treatments (Figure 5) when concentrations (ppm) were considered. The foam only treatment (4.1 l/m^2) provided uniform coverage throughout the plots as did the 16.3 l/m^2 liquid applications. The 4.1 l/m^2 liquid applications provided less horizontal coverage than either of the other application procedures. When the percentage of the total chlorpyrifos deposited was correlated with distance from the point of injection (center treatments) (Figure 6) the 4.1 l/m^2 foam application was as effective as the 16.3 l/m^2 liquid application even though only 25% as much liquid equivalent was applied, thus demonstrating the advantage of the foam formulation in terms of horizontal movement.

Results of the vertical penetration study indicated that chlorpyrifos was effectively applied throughout 7 cm of soil within 25 cm of the header (Table I) for rates of 5.0 l/m and 3.7 l plus 1.2 l foam/m. The 1.2 l foam/m was not as effective in penetrating the soil within the first 25 cm from the header as compared with the other applications. Observations at the time of treatment were that holes (approximately 5 cm across and 7

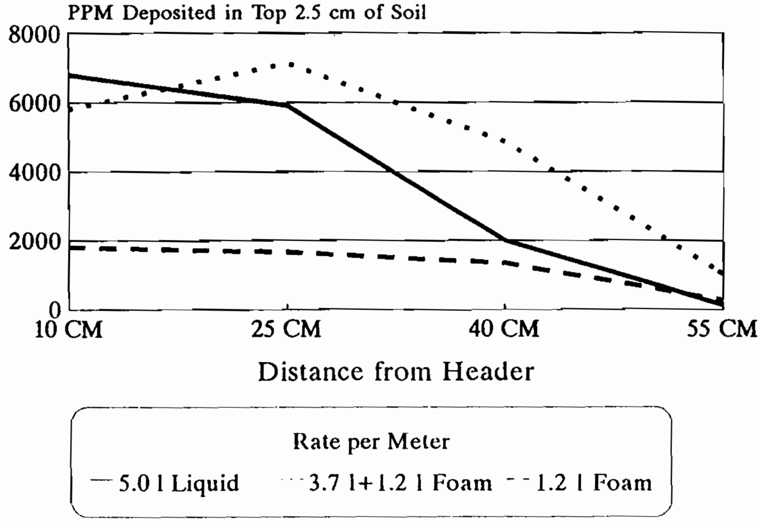

Figure 3. Horizontal Distribution of Termiticide

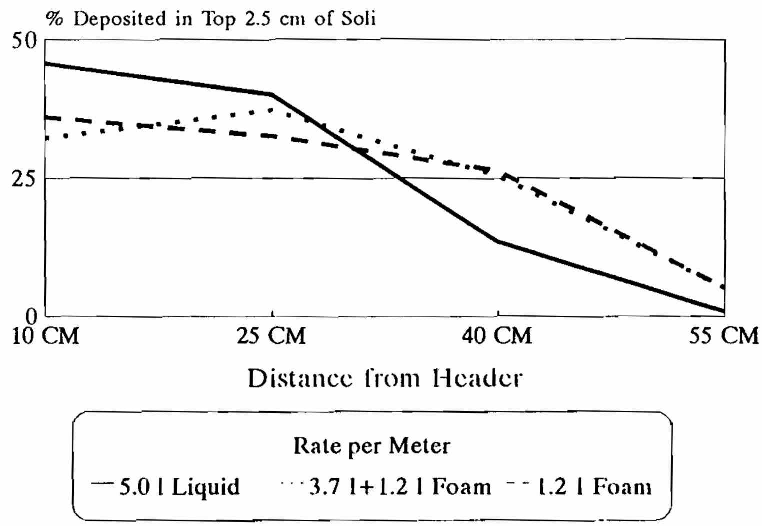

Figure 4. Horizontal Distribution of Termiticide

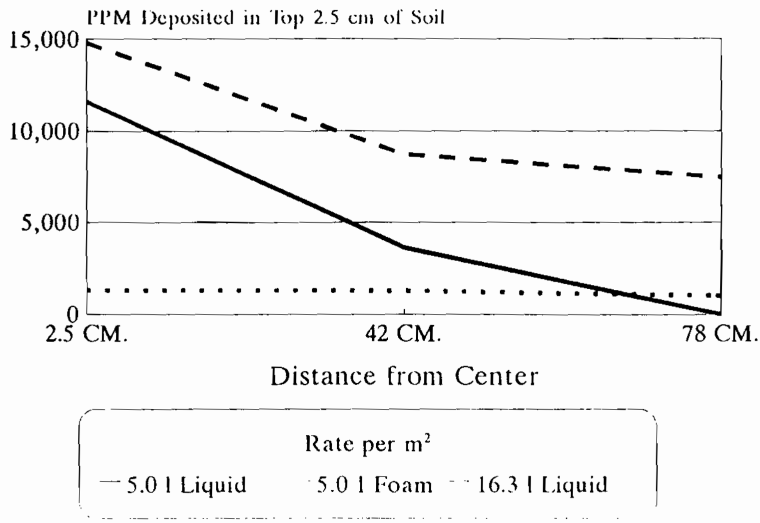

Figure 5. Horizontal Distribution of Termiticide

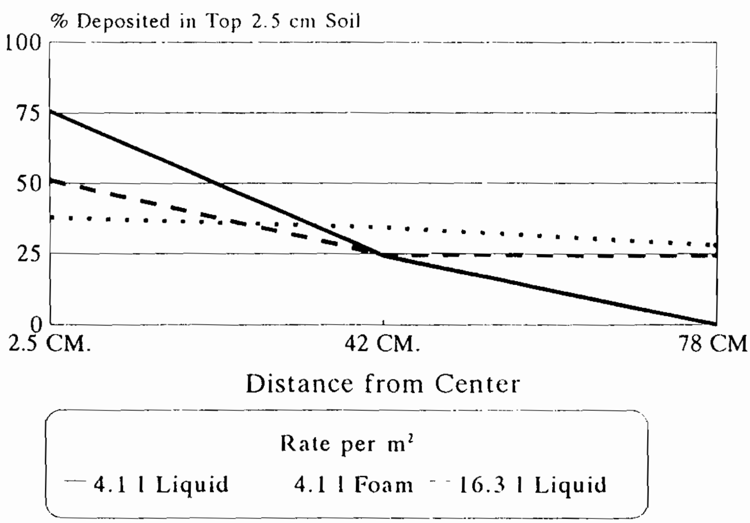

Figure 6. Horizontal Distribution of Termiticide

Table I. Mean Concentrations in ppm of Chlorpyrifos by Formulation, Horizontal Distribution, and Vertical Penetration in Edge Treatments

Distance in cm	Depth in cm	FORMULATION liters/m: 5.0 l Liquid[a]	3.7 l Liquid + 1.2 l Foam	1.2 l Foam[b]
10	0-1	3423	3694	1240
	1-2	2281	1694	425
	2-3	1086	406	139
	3-4	183	176	30
	4-5	47	48	15
	5-6	40	104	0
	6-7	95	205	0
25	0-1	3011	3758	1061
	1-2	2178	2753	459
	2-3	722	622	140
	3-4	129	103	13
	4-5	19	41	0
	5-6	77	15	0
	6-7	135	15	8
40	0-1	1083	2565	789
	1-2	676	4687	461
	2-3	242	613	89
	3-4	94	120	12
	4-5	10	7	0
	5-6	0[c]	0	0
	6-7	0	0	0
55	0-1	87	526	194
	1-2	26	407	55
	2-3	12	94	16
	3-4	11	0	6
	4-5	0	0	0
	5-6	0	0	0
	6-7	0	0	0

[a]0.6% a.i.
[b]1.6% a.i.
[c]Limit of Detection = 5 ppm

Table II. Mean Percent Deposition of Chlorpyrifos by Formulation, Horizontal Distribution, and Vertical Penetration in Edge Treatments

		FORMULATION liters/m		
Distance in cm	Depth in cm	5.0 l Liquid[a]	3.7 l Liquid + 1.2 l Foam	1.2 l Foam[b]
10	0-1	48.9	58.4	66.9
	1-2	31.9	26.8	22.8
	2-3	15.2	6.4	7.5
	3-4	2.6	2.8	0.8
	4-5	0.7	0.8	0.0
	5-6	0.6	1.6	0.0
	6-7	1.3	3.2	0.0
25	0-1	48.0	51.4	62.9
	1-2	34.7	37.7	27.2
	2-3	11.5	8.5	8.3
	3-4	2.1	1.4	0.8
	4-5	0.3	0.6	0.2
	5-6	1.2	0.2	0.2
	6-7	2.2	0.2	0.5
40	0-1	51.3	51.3	58.0
	1-2	32.0	33.8	33.9
	2-3	11.5	12.3	6.5
	3-4	4.5	2.4	0.9
	4-5	0.5	0.1	0.3
	5-6	0.1	0.1	0.1
	6-7	0.2	0.0	0.2
55	0-1	62.6	51.1	71.6
	1-2	18.7	39.6	20.3
	2-3	8.6	9.1	5.9
	3-4	7.9	0.2	2.2
	4-5	2.2	0.0	0.0
	5-6	0.0	0.0	0.0
	6-7	0.0	0.0	0.0

[a] 0.6% a.i.
[b] 1.6% a.i.

Table III. Mean Concentrations in ppm of Chlorpyrifos Deposited by Formulation, Horizontal Distribution, and Vertical Penetration in Center Treatments

Distance in cm	Depth in cm	FORMULATION liters/m² 4.1 l Liquid[a]	4.1 l Foam[b]	16.3 l Liquid
2.5	0-1	3308	1200	3418
	1-2	2418	646	2900
	2-3	1220	253	2554
	3-4	252	114	1652
	4-5	15	50	917
	5-6	0[c]	10	279
	6-7	0	0	139
42	0-1	990	1376	2254
	1-2	778	634	2000
	2-3	409	48	969
	3-4	144	0	377
	4-5	10	0	92
	5-6	0	0	22
	6-7	0	0	0
78	0-1	11	776	1852
	1-2	0	594	1487
	2-3	0	283	1135
	3-4	0	21	730
	4-5	0	0	372
	5-6	0	0	72
	6-7	0	0	14

[a]0.6% a.i.
[b]1.6% a.i.
[c]Limit of detection = 5 ppm

Table IV. Mean Percent Deposition of Chlorpyrifos by Formulation, Horizontal Distribution and Vertical Penetration in Center Treatments

Distance in cm	Depth in cm	FORMULATION liters/m² 4.1 l Liquid[a]	4.1 l Foam[b]	16.3 l Liquid
2.5	0-1	45.9	52.8	28.8
	1-2	33.5	28.4	24.5
	2-3	16.9	11.1	21.5
	3-4	3.5	5.0	13.9
	4-5	0.2	2.2	7.7
	5-6	0.0	0.4	2.4
	6-7	0.0	0.0	1.2
42	0-1	42.5	66.9	39.4
	1-2	33.4	30.8	35.0
	2-3	17.5	2.0	17.0
	3-4	6.2	0.0	6.6
	4-5	0.4	0.0	1.6
	5-6	0.0	0.0	0.4
	6-7	0.0	0.0	0.0
78	0-1	100.0	46.3	32.7
	1-2	0.0	35.4	26.3
	2-3	0.0	16.9	20.0
	3-4	0.0	1.3	12.9
	4-5	0.0	0.2	6.6
	5-6	0.0	0.0	1.3
	6-7	0.0	0.0	0.2

[a]0.6% a.i.
[b]1.6% a.i.

Table V. Mean Percent Deposition of Chlorpyrifos by Formulation and Horizontal Distribution in Edge Treatments

TREATMENT	DISTANCE							
liters/m	10 cm		25 cm		40 cm		55 cm	
	%	S.D.	%	S.D.	%	S.D.	%	S.D.
5.0 Liquid[a]	46.3a[c]	2.4	39.3a	2.1	13.6a	3.9	0.8a	0.72
3.7 Liquid +1.2 Foam	31.8b	9.9	38.5a	5.8	24.5a	15.5	5.2a	4.14
1.2 Foam[b]	35.8ab	3.6	33.3a	1.2	26.0a	2.0	4.7a	1.76

[a] 0.6% a.i.
[b] 1.6% a.i.
[c] Means followed by the same letter not significantly different at 5% level

Table VI. Mean Concentrations of Chlorpyrifos by Formulation and Horizontal Distribution in Edge Treatments

TREATMENT	DISTANCE							
liters/m	10 cm		25 cm		40 cm		55 cm	
	ppm	S.D.	ppm	S.D.	ppm	S.D.	ppm	S.D.
5.0 Liquid[a]	2263a[c]	1332	2088a	1306	1181b	1327	375a	385
3.7 Liquid +1.2 Foam	2028a	1996	2378a	1949	1892a	2620	601a	737
1.2 Foam[b]	625b	831	591b	625	471c	531	221a	312

[a] 0.6% a.i.
[b] 1.6% a.i.
[c] Means followed by the same letter not significantly different at 5% level

Table VII. Mean Percent Deposition of Chlorpyrifos by Formulation and Horizontal Distribution in Center Treatments

TREATMENT liters/m²	2.5 cm		42 cm		78 cm	
	%	S.D.	%	S.D.	%	S.D.
16.3 Liquid[a]	25.2b[c]	7.1	12.2a	7.5	12.5a	8.6
4.1 Liquid	38.5a	4.1	11.4a	10.3	0.1b	0.2
4.1 Foam[b]	18.8b	9.6	17.3a	10.3	13.9a	8.6

[a] 0.6% a.i.
[b] 1.6% a.i.
[c] Means followed by the same letter not significantly different at 5% level

Table VIII. Mean Concentrations of Chlorpyrifos by Formulation and Horizontal Distribution in Center Treatments

TREATMENT liters/m²	2.5 cm		42 cm		78 cm	
	%	S.D.	%	S.D.	%	S.D.
16.3 Liquid[a]	3505 a[c]	1288	2102a	828	3025a	728
4.1 Liquid	2127 b	697	1677a	1191	64b	88
4.1 Foam[b]	601 c	400	555b	414	639b	631

[a] 0.6% a.i.
[b] 1.6% a.i.
[c] Means followed by the same letter not significantly different at 5% level

cm deep) were formed immediately below the point of application. There was evidence of pesticide flow beneath the 7 cm of filled and tamped soil as indicated in Table I for the first 25 cm from the header.

When analysis of the vertical penetration was made based on the per cent of the total chlorpyrifos residue in each of the soil layers for each treatment method and rate (Table II) it was determined that 95% of the termiticide was deposited in the top 3 cm of soil. Whether or not this depth and concentration constitutes an effective barrier to invading termites is not known. Similar results were determined for the center applications (Tables III and IV) with 92% of the chlorpyrifos recovered from the first 3 cm of soil. Both the 4.1 l/m^2 foam and 16.3 l/m^2 liquid were superior to the 4.1 l/m^2 applications both in terms of vertical and horizontal movement of the termiticide.

DISCUSSION

The use of foam formulation for the application of chlorpyrifos termiticide (Dursban TC) had an advantage over liquid applications in situation where the termiticide must be moved beneath concrete slabs to areas that are inaccessible to drill and treat operations. The foam formulation had the advantage of uniformly filling the space between the bottom surface of the concrete slab and the upper surface of the subsoil. In these studies the application of 4.1 l/m^2 (liquid equivalent) foam completely filled a square soil frame of 1.2 m on a side with a 2.5 cm gap between the upper slab and the subsoil. While the horizontal distribution of chlorpyrifos was greatly increased as compared to equivalent liquid applications (4.1 l/m^2), the vertical movement of the termiticide may be insufficient for effective termite control or repulsion. Approximately 92% of the total chlorpyrifos was in the top 3 cm of soil. The paradox is that while the foam formulation may move the termiticide further under the slab, the greater the horizontal distribution the less active ingredient there was per unit area in all dimensions. While it may be advantageous to have the undersurface of the slab treated along with the subsoil and headers, any pesticide not deposited in the soil would not contribute to the barrier, and will not prevent termites from invading the soil under the structure. Research is needed to develop a foam that is dense enough to travel to inaccessible areas, but is wet enough to treat soil to a depth, with a sufficient concentration of termiticide to present an effective barrier to termites. A portion of this problem could be solved through the use of more concentrated (greater than 1% a.i. Dursban TC=present label rate) liquids from which the foams were generated.

Chlorpyrifos is an effective termiticide with LC_{50} values ranging from 1.7-15.4 ppm for various termite species *(10, 24, 26, 27)*. Concentrations of 10-50 ppm caused mortality of subterranean termites within 24 hours and 100 ppm inhibited tunneling activity completely *(30)*. Other reports indicated that chlorpyrifos at 5,000 ppm caused termites to seal off tunnels thus avoiding treated soils *(25)*. Jones *(28, 29)* determined that 500 ppm chlorpyrifos knocked down subterranean termites in 1.25 hrs, but that there was slight tunneling activity at 500 ppm. From this information, it is concluded that chlorpyrifos at between 25-500 ppm will stop tunneling activity of subterranean termites with death of individuals which contact treated soils occurring at much lower levels. Based on this research, concentrations exceeding 500 ppm were obtained within the first 3 cm of soil with all treatments, and it can be concluded that chlorpyrifos would be effective for termite control until such time as application concentrations are degraded to the point that protection is lost. Research into this paradigm is currently underway in our laboratory.

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