Stability of Chlorpyrifos for Termiticidal Control in Six Australian Soils

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Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is the most widely used soil-applied termiticide in Australia. It is relatively stable, has low water solubility, is absorbed by organic matter, and has a high affinity for soil with low partitioning potential from soil matter to soil water. The purpose of this degradation study is to determine the effect of soil alkalinity on the longevity of termite protection when chlorpyrifos is applied as a termiticide in a range of Australian soils, particularly high-pH substrates. The study also examines the effects of initial soil concentration on the degradation of chlorpyrifos in the range of soils. At an initial soil concentration of 1000 mg kg^{-1} for termite control, the degradation rate of chlorpyrifos is very strongly retarded in soils tested when compared with lower soil concentrations of 100 and 10 mg kg^{-1} in the same soils. The degradation data correlated with a logarithmic model of decay, and it was thus possible to produce half-lives and predict likely periods of termite control. Average half-lives for all soils for the three concentrations were 385, 155, and 41 days, respectively. Soil pH had no effect on the rate of degradation at all concentrations tested.

INTRODUCTION

Termites are in abundance in much of Australia with ~300 endemic species. Only ~10 of these 300 species are important pests of timber used in construction service. Almost all of these are subterranean termites that gain access to timber from galleries in adjacent soil. The risk of termite damage across Australia is similar in most states, although Victoria and Tasmania have a lower risk. A recent survey indicated that some 17–19% of houses are infested in Western Australia, Queensland, Northern Territory, New South Wales, South Australia, and Australian Capital Territory (*1*).

The technique most commonly used in Australia to protect timber structures from termites involves the installation of a chemical barrier in the soil either pre- or postconstruction. As many structures have different styles of construction, the installation of soil treatments varies, but essentially the major methods involve (1) preconstruction spraying of soil prior to the laying of a concrete slab; (2) drilling through horizontal concrete surfaces into soil or voids and treating the underslab soil; (3) treating the soil in narrow trenches dug along external and internal walls; (4) rodding and treating the soil around inside walls, piers, and pipes of subfloor crawl space; and (5) drilling through hollow brick or double-brick walls to treat soil that lies beneath, around, or behind the structure.

Chlorpyrifos is a moderately stable organophosphorus insecticide widely used as a soil-applied termiticide in

Australia and throughout the world. It has very low water solubility (1.4 mg L^{-1}), and its octanol–water coefficient (K_{ow}) of 50000 indicates it is strongly sorbed by soil organic matter, providing stability. Its affinity for soil is also indicated by a K_{oc} measurement (6000–8000) indicating a low partitioning by desorption from soil matter to soil water. It has intermediate vapor pressure (2.7 × 10^{-3} Pa at 25 °C) and is immobile in soil, remaining bound to nonpolar colloidal fractions (*2*).

Many studies have shown that major routes of degradation of chlorpyrifos in North American soils are by abiotic mechanisms (hydrolysis resulting from moisture under the influence of temperature, pH, etc.) and microbial degradation. Its major metabolic product is 3,5,6-trichloro-2-pyridinol (TCP), which is further degraded to 3,5,6-trichloro-2-methoxypyridine (TMP) and carbon dioxide (*2*).

A study on the degradation of chlorpyrifos at a termiticidal initial soil concentration of 1000 mg kg^{-1} in several North American soils (*3*) found that chlorpyrifos degradation was retarded at termiticidal initial concentrations of 1000 mg kg^{-1} compared to agricultural concentrations of 100 and 10 mg kg^{-1}.

The main objective of this study was to determine the effect of application rate and soil alkalinity on the degradation of chlorpyrifos when it is applied in a number of Australian soils, particularly alkaline soils. Within industry there has been an assumption that the use of chlorpyrifos in alkaline soils would result in rapid degradation of chlorpyrifos applied to those soils. Starting chlorpyrifos soil concentrations were 1000, 100, and 10 mg kg^{-1}, and soil pH ranged from 5.35 to 9.65.

MATERIALS AND METHODS

Soils. The soils used in this study were chosen to represent a range of soil types, particularly the highly alkaline soils

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Stability of Chlorpyrifos for Termiticidal Control

J. Agric. Food Chem., Vol. 49, No. 6, 2001 **2845**

Table 1. Characteristics of Six Soil/Substrates Studied To Evaluate Stability of Chlorpyrifos at Three Concentrations

soil characteristic	BCRI[a]	RBE	BS	QSD	MBU	LQS
soil type	sandy loam	clay loam	sand	rock part	sand	crushed dust
pH	5.35	7.84	7.94	8.66	9.26	9.65
field moisture capacity (%)	3.16	17.5	0.83	3.6	7.62	1.11
organic C (%)	1.37	1.65	1.32	0.69	0.16	0.09
sand (%)	91.6	48.9	93	45.6	86.5	53.1
silt (%)	2.6	18.3		20	10.6	9.5
clay (%)	3.6	26.9		3.6		6.6

[a] Key to soils' origins: BCRI, Garden soil, NSW Agriculture, Rydalmere; RBE, Red Brown Earth, Adelaide; BS, Bassendean Sand, Perth; QSD, Quarry Sand Dolomite, CSR Readymix; MBU, Maslin Beach Underfill; LQS, Linwood Quarry Sand, Boral.

found in urban areas. Soils were analyzed to determine soil type and physical characteristics (Table 1).

Soil Preparation and Experimentation. All six soils studied were obtained from locations that commonly experience high levels of termite infestation. Three of the soils, Quarry Sand Dolomite, Maslin Beach Underfill, and Linwood Quarry Sand, are of high natural alkalinity and are derived from crushed quarry products, which could be more closely described as substrates than soils. These three are commonly used as subslab substrates in housing construction in Australia. All six soils/substrates studied were initially air-dried by fan at 40 °C for a minimum of 48 h to break up soil clumps and allow sieving through a 2 mm sieve. The Australian Import Guidelines Conditions approved methods for sterilizing soils indicate that soil microbial activity would be unaffected following this air-drying by fan treatment (*4*). However, a soil microbe viability test was not conducted. Any rock particulate content was measured and remixed through the soil prior to experimentation.

The moisture contents of all soils were reconstituted to field moisture capacity (Table 1) with deionized water and mixed homogeneously. The moisture content was maintained throughout the experimentation period, to enable pH effects on the degradation of chlorpyrifos to be investigated. Soils were weighed before and after sampling, and deionized water was added if needed. Jars were opened for sampling but remained sealed in the incubator to help maintain moisture content, minimize aerobic activity, and therefore simulate soil conditions under a concrete slab floor of a building.

Triplicate samples (200 g) of each soil type for each chlorpyrifos treatment were put into prepared storage jars. An untreated sample for each soil type was also prepared. Technical grade chlorpyrifos (99%) in acetone (4 mL of 50000 μg mL^{-1}, 4 mL of 5000 μg mL^{-1}, or 4 mL of 500 μg mL^{-1}) was added volumetrically to each triplicate sample (200 g) according to the required concentration (target = 10, 100, 1000 mg kg^{-1}). After chlorpyrifos had been applied at the required concentration for each soil type, samples were mixed thoroughly and the acetone was allowed to evaporate from the sample through the mixing process. The soils were weighed, and any moisture content loss was restored to field capacity. Samples were analyzed (day 0) and then immediately stored in darkness in an incubator, which was set at a constant temperature of 24 °C ± 0.5 °C and a relative humidity 95%.

Analysis of Chlorpyrifos. Samples were analyzed at 0, 1, 2, 4, 6, 9, 12, 15, 18, 21, and 24 months post-treatment. On each occasion subsamples (5 g) were removed from each triplicate sample jar, spiked with surrogate standard (2 mL of 500 μg mL^{-1} C17, heptadecane), and extracted with acidified acetone (50 mL) containing 1% phosphoric acid (1:1:98, acid/water/acetone) by shaking for 2 h. After settling, an aliquot (5 mL) from each triplicate was measured into a volumetric flask (10 mL), and an internal standard (2 mL of 100 μg mL^{-1}
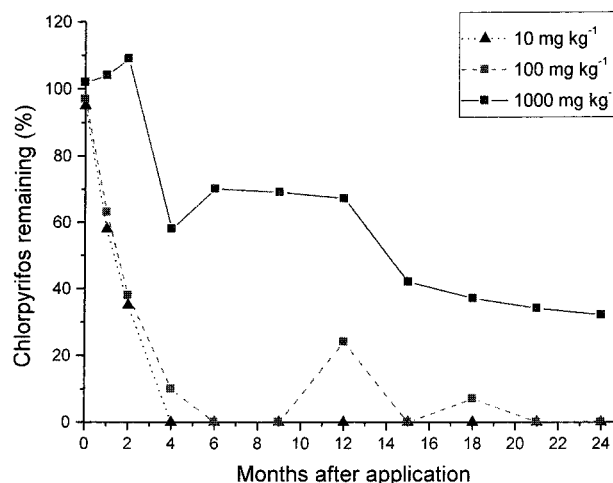
Figure 1. Chlorpyrifos degradation in Quarry Sand Dolomite as affected by application rate.

C21, uneicosane) was added before the mixture was made to volume (10 mL) with AR hexane.

A quality control sample was analyzed as above after a clean soil sample (5 g) had been fortified with chlorpyrifos (2 mL of 2500 μg mL^{-1}).

All extracts were analyzed by GC with FID and diluted or concentrated if necessary to achieve a peak height of 30−60% of total chart deflection. GC consistency was maintained by injecting reference standards after every five samples. Analytical data were corrected for the recovery of chlorpyrifos on the basis of the recovery of the surrogate and internal standard measured in each soil sample.

Statistical Analysis of Data. The data were statistically analyzed, using Excel, Origin (ver. 4.1), and JMP software to calculate the rate of degradation of soil concentrations of chlorpyrifos. Regression equations were fitted on log-transformed data, and statistical estimates including least significant differences (LSD) were estimated. Various predictions of curve shape were selected to establish the best fitting model with the highest regression coefficients. Half-lives were calculated when an exponential decay was found. For each soil, and for the average of all soils, an extrapolation of the time required to reach 5 and 2 mg kg^{-1} levels within 95% confidence limits was made. These reference concentrations were determined by Orton and O'Rourke (*5*) and Su and Scheffrahn (*6*), respectively, to be minimum chlorpyrifos concentrations to provide effective barriers to termite infestation.
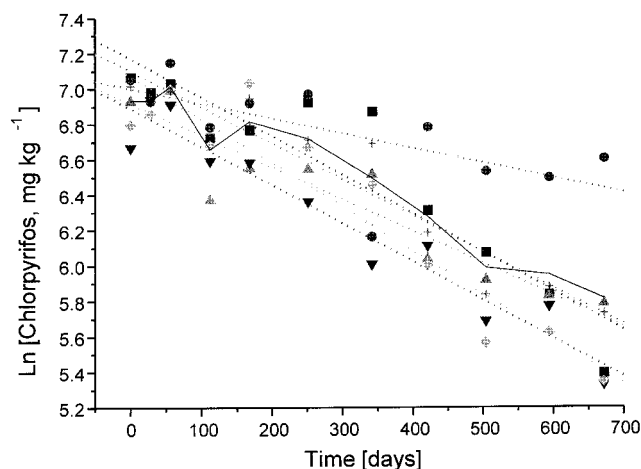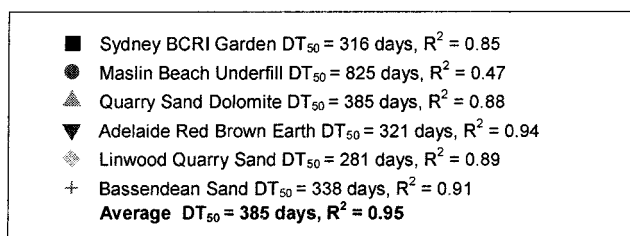
RESULTS

Degradation Pattern in Soil. Degradation data from the soils containing an initial chlorpyrifos concentration of 1000 mg kg^{-1} indicate a steady decline in chlorpyrifos concentration, to a level of 206−324 mg kg^{-1} after 672 days, with one soil (Maslin Beach Underfill) showing residues of 800 mg kg^{-1} after this period (Figure 2). The half-life values for all treatments were estimated from the logarithmic plots of the data and are shown in Table 2. The rate of degradation of chlorpyrifos in the 1000 mg kg^{-1} treatment was observed to be much slower than that for the soils containing 10 and 100 mg kg^{-1} as typified by the pattern shown in Quarry Sand Dolomite (Figure 1).

Figure 2 shows the regression line of the log transformation of the data. The half-lives were calculated from the log transformation (R^2 between 0.85 and 0.94). The fitting from the log transformation was used to calculate the half-lives.

The only soil to behave differently is Maslin Beach Underfill. Chlorpyrifos was more persistent in this

2846 *J. Agric. Food Chem.*, Vol. 49, No. 6, 2001

Murray et al.

Table 2. Half-Life in Days for Chlorpyrifos in Various Soils Following Initial Concentrations of 10, 100, and 1000 mg kg^{-1} Based on Calculations for Line of Best Fit

	soil						
initial concn	BCRI	RBE	BS	QSD	MBU	LQS	av soil
10 mg kg^{-1} half-life (days)	68.8		93.5	39.0	104.5	19.9	40.6
fitting parameters							
intercept	2.40	2.08	2.17	2.25	2.24	2.39	2.38
slope	−0.0101	0.0001	−0.0074	−0.0178	−0.0066	−0.0348	−0.0171
R^2	0.92	0.01	0.59	1.00	0.94	1.00	0.92
100 mg kg^{-1} half-life (days)	249.3	197.5	169.5	183.9	144.4	102.8	155.1
fitting parameters							
intercept	3.84	4.20	4.44	3.95	4.48	4.13	4.12
slope	−0.0028	−0.0035	−0.0041	−0.0038	−0.0048	−0.0067	−0.0045
R^2	0.23	0.44	0.72	0.55	0.83	0.51	0.56
1000 mg kg^{-1} half-life (days)	316.5	320.9	338.1	385.1	825.2	280.6	385.1
fitting parameters							
intercept	7.17	6.89	7.10	6.92	7.00	7.07	7.02
slope	−0.0022	−0.0022	−0.0021	−0.0018	−0.0008	−0.0025	−0.0018
R^2	0.85	0.94	0.91	0.88	0.47	0.89	0.95

■ Sydney BCRI Garden DT$_{50}$ = 316 days, R^2 = 0.85
● Maslin Beach Underfill DT$_{50}$ = 825 days, R^2 = 0.47
▲ Quarry Sand Dolomite DT$_{50}$ = 385 days, R^2 = 0.88
▼ Adelaide Red Brown Earth DT$_{50}$ = 321 days, R^2 = 0.94
◈ Linwood Quarry Sand DT$_{50}$ = 281 days, R^2 = 0.89
+ Bassendean Sand DT$_{50}$ = 338 days, R^2 = 0.91
Average DT$_{50}$ = 385 days, R^2 = 0.95

Figure 2. Fit to logarithmic transformation of chlorpyrifos degradation data (1000 mg kg^{-1}).

soil, with a half-life of double that in the other soils (825 days). However, the data set for this soil is inconsistent and shows a poor correlation coefficient (R^2 = 0.47).

The key finding is that there is no correlation between soil pH and the rate of degradation of chlorpyrifos.

Effect of Degradation on Termite Control. The utilization of a logarithmic model of decay at 1000 mg kg^{-1} enables extrapolation to concentrations of 5 and 2 mg kg^{-1} and the time required for these concentrations to be reached. An Australian study (*5*) determined that 5 mg kg^{-1} chlorpyrifos concentrations in soil will result in 100% mortality of *Coptotermes* spp. Su and Scheffrahn (*6*) found that soil at 2 mg kg^{-1} chlorpyrifos concentration caused 100% mortality of a species of *Coptotermes* and *Reticulitermes*. When extrapolated, average periods of 8.8 and 10.1 years are required for decay to 5 and 2 mg kg^{-1}, respectively (Table 3).

Table 3. Estimated Time To Reach 5 and 2 mg kg^{-1} Levels of Chlorpyrifos in Soil from an Initial Concentration of 1000 mg kg^{-1}

	soil						
	BCRI	RBE	BS	QSD	MBU[a]	LQS	av soil[b]
days to 100 mg kg^{-1}	1050	1066	1123	1278	2740	932	1365 ± 279
days to 5 mg kg^{-1}	2416	2449	2580	2939	6297	2142	3137 ± 641
days to 2 mg kg^{-1}	2827	2866	3020	3440	7370	2507	3672 ± 750
years to 2 mg kg^{-1}	**7.7**	**7.9**	**8.3**	**9.4**	**20.2**	**6.9**	**10.1 ± 2.1**

[a] Poor fitting (R^2 = 0.47). [b] For the average of all soils calculation the standard error is shown.

DISCUSSION

This study supports the finding by Racke et al. (*3*) and demonstrates that the higher the initial soil concentration of chlorpyrifos, the slower the degradation rate (expressed as DT$_{50}$). Racke et al. (*3*) reported that chlorpyrifos displays greater persistence at termiticidal soil concentration (~1000 mg kg^{-1}) than at concentrations that result from typical agricultural applications (0.3−32 mg kg^{-1}). It is clear that agricultural applications do not result in persistent soil residues of chlorpyrifos.

A number of theories have been suggested to explain the increased persistence of chlorpyrifos at high concentration. Racke et al. (*7*) reported noticeable buildup of TCP, the primary metabolite of chlorpyrifos in soil, and TCP's ability to inhibit the degradation of several pesticides in soils. In the same work Racke et al. (*7*) reported that a property of TCP is its ability to inhibit both bacterial and fungal activity and thus inhibit microbial degradation of pesticides. Hance and McKone (*8*) have suggested that system saturation leading to poor availability of a number of abiotic reaction sites (e.g., soil enzyme and soil surface) results in a reduced rate of degradation of pesticide. Racke et al. (*9*) suggest that the access of chlorpyrifos to catalytic soil surface sites is limited by the inactivation of the sites or depletion of the sites in the presence of large concentrations of chlorpyrifos.

Racke et al. (*3*) demonstrated that soil temperature exerted considerable influence on chlorpyrifos degradation rate. Their research showed that the depletion rate approximately doubled for each 10 °C rise in temperature. This finding is supported in Australia, where efficacy trials (*10*) in cooler climates indicate increased stability of chlorpyrifos.

Stability of Chlorpyrifos for Termiticidal Control

J. Agric. Food Chem., Vol. 49, No. 6, 2001 **2847**

The stability of chlorpyrifos under the conditions of this experiment has shown to be unaffected by natural soil alkalinity. A possible explanation for this finding may be due to the very low water solubility of chlorpyrifos (1.4 mg L^{-1}), meaning that only tiny fractions (<0.1%) of applied chlorpyrifos are in the aqueous solution phase. Chemical hydrolysis of chlorpyrifos can occur only in aqueous solution phase, and with the majority of applied chlorpyrifos (>99.9%) in soil existing in the solid phase, it is not subject to hydrolysis by high natural soil pH. It has long been assumed that chlorpyrifos as a soil-applied termiticide was less effective because it would degrade more rapidly under alkaline soil conditions. This study shows that assumption to be incorrect. Other factors such as commercial experience and long-term efficacy trials as reported by Watson et al. (*10*) have demonstrated long-term efficacy of chlorpyrifos as a termiticide in a wide range of Australian soil types.

ACKNOWLEDGMENT

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