

Degradation of bifenthrin, chlorpyrifos and imidacloprid in soil and bedding materials at termiticidal application rates

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Abstract: Organophosphorus, pyrethroid and chloronicotinyl insecticides have been used to control termites in building structures in recent years. We investigated the degradation behaviour of three insecticides (bifenthrin, chlorpyrifos and imidacloprid) at termiticidal application rates under standard laboratory conditions (25 °C, 60% field moisture capacity and darkness) for 24 months. The study was carried out on one soil and two bedding materials (sand-dolomite and quarry sand), which are commonly used under housing in Australia. Experiments were also conducted to examine the effect of soil moisture on the degradation of these insecticides. Insecticide residues in the samples collected at different days after application were measured by high performance liquid chromatography (HPLC). The rate of degradation of bifenthrin and imidacloprid insecticides was adequately described by a first-order kinetic model ($r^2=0.93-0.97$). However, chlorpyrifos degradation was biphasic, showing an initial faster degradation followed by a slower rate. Therefore, the degradation data during the slower phase only (after a two-month period) followed the first-order law ($r^2=0.95$). Soil moisture had little effect on degradation of imidacloprid and bifenthrin. Among the three insecticides, bifenthrin and imidacloprid were most stable and chlorpyrifos the least. Chlorpyrifos showed a major loss (75–90%) of residue during the 24 months incubation period. In the bedding materials, simultaneous accumulation of the primary metabolite of chlorpyrifos, TCP (3,5,6-trichloro-2-pyridinol) was observed. Hydrolysis appeared to have caused the observed rapid loss of chlorpyrifos, especially in the highly alkaline bedding materials (sand-dolomite and quarry sand).

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Keywords: termites; insecticides; persistence; sand-dolomite; quarry sand; bedding materials

1 INTRODUCTION

Termites cause significant damage to the wooden components of building structures in urban areas throughout the world. In the USA alone, the estimated annual damage caused by termites has been reported to be US\$1.7 billion¹ and the corresponding loss is estimated to be more than US\$100 million in Australia. In the past, organochlorine insecticides were widely used to control subterranean termites (eg *Coptotermes* spp, *Mastotermes* spp, *Heterotermes* spp). Owing to the undesirable environmental properties and potential human risks posed by the organochlorine insecticides, they have now been replaced by less hazardous chemicals. Organophosphates (chlorpyrifos and isofenphos), pyrethroids (bifenthrin, cypermethrin, fenvalerate and permethrin) and chloronicotinyl (imidacloprid) insecticides have been used for many years in agriculture for insect pest control.

Several studies have shown the importance of these chemicals to control termites,^{2–5} and consequently they are being used to prevent and to control termite infestation in urban building structures.

Pesticides are normally applied either pre- or post-construction of buildings. For pre-construction treatment, the soil or the bedding materials underneath concrete slabs and around foundation walls is drenched with insecticide. For post-treatment, insecticides are applied through holes drilled in floors and soil surrounding foundation walls. Studies have shown that initial concentration of insecticides in soil for termite control varies from several hundred to over one thousand micrograms per gram. For example, Kard and McDaniel³ reported initial concentrations of 858–990 µg g⁻¹ (0–11.3 cm depth) after a trench application to a Mississippi soil, and Davis and Kamble⁶ reported initial concentrations of chlorpyrifos as high

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Table 1. Selected properties of soil and bedding materials used in this study

| Soil material | pH (H ₂ O) 1:5 | Organic carbon (%) | Sand (%) | Silt (%) | Clay (%) | Moisture content at -10kPa (cm ³ cm ⁻³) |
|-----------------------|------------------------------|-----------------------|-------------|-------------|-------------|--|
| Red brown earth | 7.1 | 1.2 | 59.1 | 28.3 | 10.5 | 0.163 |
| Quarry sand | 9.2 | 0.1 | 80.2 | – | – | 0.026 |
| Redimix/sand-dolomite | 9.6 | 0.2 | 55.0 | – | – | 0.048 |

as 1500 µg g⁻¹ (0–7.6 cm depth) in a Nebraska loamy sand soil.

It has been reported that soil pH, moisture, temperature and pesticide concentration are the most important factors affecting the persistence of termiticides in urban soils. Cink and Coats² showed that soil moisture and pesticide concentration applied had the greatest effect on the degradation of chlorpyrifos in an urban Iowa soil (pH 7.8). They also observed that only 5% of chlorpyrifos remained in the soil 12 weeks after application of 10 µg g⁻¹ (agricultural application rate) in soil, whereas 57% remained in soil when 1000 µg g⁻¹ (urban termite control rate) of chlorpyrifos was applied. This shows that degradation of chlorpyrifos at termiticidal application rates can be much slower and may be concentration-dependent in the urban soil environment. Racke *et al*⁴ reported that soil temperature, moisture and applied concentration had a significant effect on the degradation of chlorpyrifos in five urban soils from the USA. They showed that the degradation half-lives of chlorpyrifos in five soils at 1000 µg g⁻¹ initial concentration ranged from 175 to 1576 days. Recently, Gold *et al*⁵ examined the persistence of six termiticides (bifenthrin, chlorpyrifos, cypermethrin, fenvalerate, permethrin and isofenphos) under field conditions. Among the pesticides studied, isofenphos was the least persistent whereas permethrin and fenvalerate persisted longer. They also reported that soil pH and clay content were the two soil properties greatly affecting the persistence of termiticides.

Considering the varied chemical nature of insecticides and especially the dependence of degradation rate on the initial applied concentration, the actual persistence of these chemicals needs to be determined on soils and bedding materials used under housing developments. Although studies have focused on the persistence and degradation of chlorpyrifos⁴ and bifenthrin⁵ in soils, no published information is available on the persistence of imidacloprid at higher rates used in termite control. Therefore this study was conducted to investigate the degradation of three insecticides in a dominant soil and two bedding materials commonly used in housing developments in Adelaide, South Australia. The objectives of this study were (i) to investigate the persistence of insecticides in soil and bedding materials under laboratory conditions (25 °C, 60% moisture content, darkness) and (ii) to establish the initial rates of

degradation of these insecticides in the soil and bedding materials.

2 MATERIALS AND METHODS

2.1 Soils

One soil (Red brown earth–Natrixeralf) and two bedding materials (Boral quarry sand and CSR redimix/sand-dolomite) varying in their chemical properties were used for the degradation study (Table 1). The soil collected from the housing development around Seaford Rise (urban development area south of Adelaide) belongs to Red Brown Earth group, which is a common soil type around suburban Adelaide. Quarry sand and sand-dolomite are the two commonly used bedding materials in Australia. All materials were passed through a 2-mm sieve prior to use in the degradation studies.

Dehydrogenase activity in the soil and the bedding material was measured by incubating the soil at 37 °C for 24 h with 2,3,5-triphenyltetrazolium chloride for the production of 2,3,5-triphenyltetrazolium formazan, following the method of Casida *et al*.⁷

2.2 Insecticides

Three insecticides varying substantially in their physical and chemical properties were used for the degradation study (Table 2). Analytical grade chlorpyrifos was obtained from Sigma and the primary metabolite of chlorpyrifos, 3,5,6-trichloro-2-pyridinol, (TCP) was kindly donated by DowElanco, USA. Bifenthrin was obtained from FMC Australia and imidacloprid was a gift from Bayer. All insecticides were >98% purity.

2.3 Laboratory degradation study

Standard 1 g litre⁻¹ stock solutions were prepared for each insecticide. Appropriate volumes were mixed with the soil and bedding materials to give 100 mg kg⁻¹ bifenthrin, 50 mg kg⁻¹ imidacloprid or 1000 mg kg⁻¹ chlorpyrifos. The concentration of insecticide was chosen on the basis of recommended rates for termite control in Australia. Uniform mixing in soil was achieved by spreading the soil on a plastic sheet and spraying it with pesticide solution followed by thorough mixing. The uniform mixing of pesticide was checked by removing random samples and analysing for pesticide residues (9 (±3.2)% variation observed between samples).

Table 2. Some important properties of three termiticides

| Property | Bifenthrin | Imidacloprid | Chlorpyrifos |
|--|--|---|---|
| CAS number | 82657-04-3 | 138261-41-3 | 2921-88-2 |
| Chemical class | Pyrethroid | Chloronicotinyl | Organophosphorus |
| Chemical name | (2-Methylbiphenyl)-3-ylmethyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)- 2,2-dimethylcyclopropanecarboxylate | 1-(6-chloro-3-pyridinylmethyl)-N- nitroimidazolidin-2-ylideneamine | O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate |
| Relative Molecular mass | 422.9 | 255.7 | 350.6 |
| Vapour pressure (mPa) | 0.024 | 4×10^{-7} | 2.7 |
| Aqueous solubility (mg litre ⁻¹) | 0.1 | 610 | 2 |
| log K_{ow} | >6 | 0.57 | 4.82 |

The treated soil materials were placed in loosely sealed polythene bags and were maintained at 60% of the maximum water holding capacity (MWHC) determined at -10 kPa and incubated in the dark at 25°C . Water was added once a week to maintain the soil moisture content during the experiment. Duplicate 25 g soil samples were removed from each bag at 0, 1, 2, 3, 6, 9, 12, 18 and 24 months and analysed for pesticide residues by HPLC. The soils in the bags were frequently mixed thoroughly to ensure uniform conditions.

2.4 Effect of moisture on insecticide degradation in soils

The effect of soil moisture on the rate of degradation of imidacloprid and bifenthrin was also investigated. Soil samples treated with bifenthrin or imidacloprid were incubated at one of three soil-water combinations, viz, 40, 60 and 80% MWHC and maintained at 25°C . All the soil samples were incubated in dark. Water was added once a week to maintain the soil moisture content during the experiment. Duplicate 25 g soil samples were removed from each bag at 0, 1, 2, 3, 6, 9, 12, 18 and 24 months, extracted and analysed for imidacloprid and bifenthrin residues by the following HPLC method.

2.5 Extraction and analysis

The soil materials were mixed thoroughly before extraction of pesticide residues. Soil samples (25 g) were weighed in centrifuge tubes and extracted with acetonitrile+water (80+20 by volume; 40 ml) for imidacloprid,⁸ acidified acetone [acetone+water+concentrated phosphoric acid (98+1+1 by volume; 40 ml)] for chlorpyrifos⁹ and acetone (40 ml) for bifenthrin.¹⁰ The suspension was stirred and shaken for 4 h. Following centrifugation (20 min, 8000 rev min⁻¹), the supernatant solution was filtered through a glass fibre filter membrane (0.45 μm) and the shaking and filtration steps repeated. For bifenthrin the extracted solution was passed through a florisil column for sample clean-up before rotary evaporation. The combined extract solution was transferred to a 100 ml round-bottom flask and the extract evaporated using a rotary evaporator at 45°C . The pesticide residue was redissolved in either

acetonitrile+water or methanol+water for HPLC analysis.

All samples were analysed on a Varian HPLC equipped with a Star 9012 ternary gradient pump, Polychrom 9065 diode array detector, Star 9050 programmable variable-wavelength UV detector, an autoinjector, column oven, and a Star 9100 autosampler with electric sample valve. Data were collected and processed on the Star HPLC data system. Instrument conditions for analyses of imidacloprid were as follows: ODS2 C₈ reversed-phase column kept at 25°C using a mobile phase of acetonitrile+water (20+80 by volume) at a flow rate of 1.5 ml min⁻¹.⁸ Bifenthrin was analysed on Radial Pak liquid chromatography C₁₈ cartridges (10 cm \times 5 mm ID, 4 μm particle size) using a mobile phase of methanol+water (80+20 by volume) at a flow rate of 1 ml min⁻¹. For chlorpyrifos, the analyses were conducted under gradient elution conditions with initial solvent conditions of 100% solvent A [water+acetonitrile+glacial acetic acid (80+20+0.5 by volume)] to 100% solvent B [acetonitrile+water+glacial acetic acid (80+20+0.5 by volume)] in 20 min. Sample injection volume was 50 μl . The retention times of chlorpyrifos and TCP under these conditions were 13.3 and 6.5 min, respectively. The detection was performed at 270 nm for imidacloprid, 230 nm for chlorpyrifos and 204 nm for bifenthrin and 0.02 a.u.f.s. External standards of insecticides were run after every 10 samples. The method sensitivity was about 0.5 mg kg⁻¹ for all insecticides.

2.6 Extraction efficiency – recovery test

To address the extraction efficiency and analytical quality control, recovery tests were performed for each insecticide, at different sampling intervals. The soil was sterilised by autoclaving (120°C ; 15 psi (103 kPa); 30 min; on three consecutive days). Sterilised soil (25 g) was placed in a centrifuge tube and spiked with each of three insecticides to a concentration of 25 mg kg⁻¹. These centrifuge tubes were sealed tightly and placed in a constant temperature room at 4°C to prevent further degradation. At each sampling time during the degradation study, three replicate centrifuge tubes were removed from storage at 4°C , and residues determined in the soil. Concentrations in the

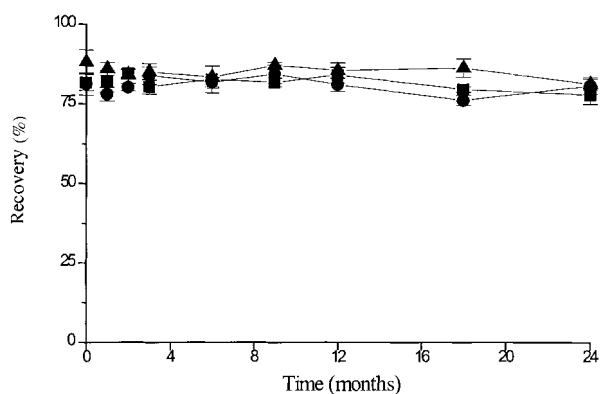


Figure 1. Extraction recovery of insecticides over time. (■) Bifenthrin, (●) chlorpyrifos, (▲) imidacloprid.

spiked soil were compared at each sampling interval and a percentage recovery determined. Analytical results of insecticides were thus corrected for recovery efficiency determined at each sampling date.

3 RESULTS AND DISCUSSION

3.1 Characteristics of soil and bedding materials

Red brown earth is a common soil group and quarry sand and sand-dolomite are the two bedding materials commonly used in the Adelaide area. The red brown earth soil is low in organic carbon content (1.2%) and

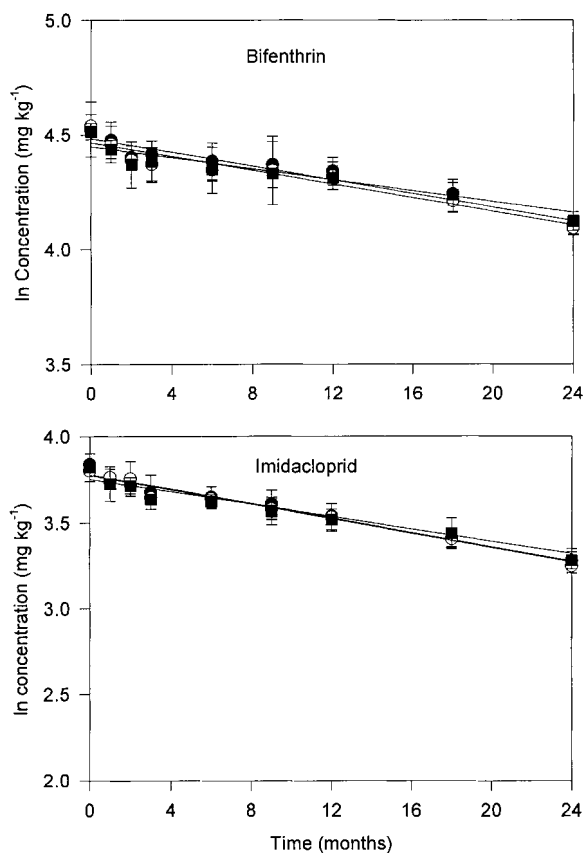


Figure 2. Effect of soil moisture on the degradation of bifenthrin and imidacloprid in red brown earth soil: (●) 40% (○) 60% (■) 80% MWHC. (—) First-order fitted.

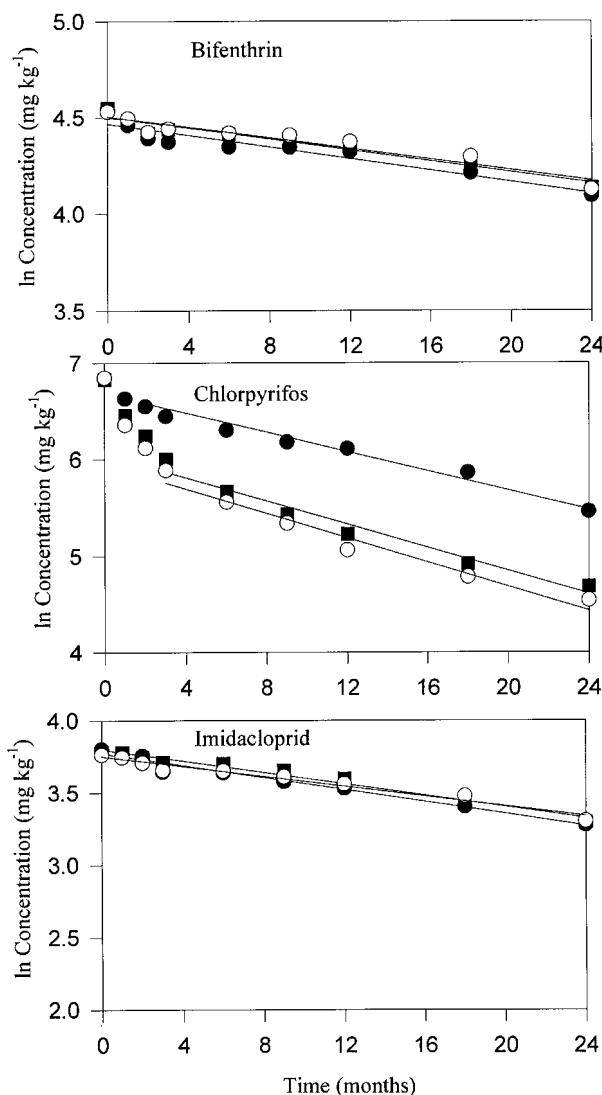


Figure 3. Degradation of pesticides (termiticidal rates) at standard soil moisture (60% MWHC) and temperature (25°C). First-order decay curves were fitted to chlorpyrifos residues after day 60 in soil and after day 90 in the two bedding materials. (●) Red-brown earth, (■) Sand dolomite, (○) Quarry sand. (—) First-order fitted.

has a neutral pH (Table 1). It is sandy loam in texture with high sand content (59%) and low clay content (10.5%). The two bedding materials are low in organic carbon and highly alkaline in nature (pH values 9.2–9.6).

3.2 Extraction recovery

The results of the recovery test conducted for the three insecticides during the study period are presented in Fig 1. This experiment was necessary to establish if the insecticide residue extraction procedure remained effective throughout the study period. Poor recoveries could lead to an overestimation of degradation rates of these insecticides. It is evident that the recovery of three insecticides remained unaffected by time of contact between the soil and the insecticides. Mean recoveries during the study were: 81.6 (± 2.4)% for bifenthrin, 80.8 (± 2.2)% for chlorpyrifos and 85.2 (± 2.4)% for imidacloprid. On this basis it was

Table 3. Degradation rate constants and half-lives of three insecticides in soil and bedding materials at 25°C and 60% MWHC in the dark

| Soil material | Bifenthrin | | | Chlorpyrifos | | | Imidacloprid | | |
|-----------------------|---|-----------------|-------|---|-----------------|-------|---|-----------------|-------|
| | Degradation rate constant (day^{-1}) | Half-life (day) | r^2 | Degradation rate constant (day^{-1}) | Half-life (day) | r^2 | Degradation rate constant (day^{-1}) | Half-life (day) | r^2 |
| Red brown earth | 0.00052 | 1332 | 0.94 | 0.0015 | 462 | 0.97 | 0.0007 | 990 | 0.97 |
| Quarry sand | 0.00049 | 1410 | 0.96 | 0.0021 | 330 | 0.94 | 0.00064 | 1080 | 0.95 |
| Redimix/sand-dolomite | 0.0005 | 1386 | 0.93 | 0.0022 | 315 | 0.95 | 0.0006 | 1230 | 0.96 |

concluded that the data in this study represented real loss due to degradation/transformation and were not influenced by poor recoveries with time, as has been noted in other studies.

3.3 Degradation of insecticides at termiticidal application rates

The effect of soil moisture on the degradation of imidacloprid and bifenthrin in red brown earth is depicted in Fig 2. Clearly soil moisture content had very little or no effect on the degradation of imidacloprid or bifenthrin. The effect of moisture was not studied on chlorpyrifos. Similar degradation trends were also observed in sand-dolomite and quarry sand. The degradation data at a single soil moisture content (at 60% MWHC) and at 25°C have been compared for the three insecticides in Fig 3. The data showed that degradation of bifenthrin and imidacloprid proceeded at a much slower rate than that of chlorpyrifos in the soil, quarry sand and sand-dolomite bedding materials. After 24 months, 31–36% of the applied bifenthrin and 37–40% of the applied imidacloprid had degraded in these materials, in contrast to 75–90% of the applied chlorpyrifos. There was little difference in degradation of bifenthrin and imidacloprid between the soil and bedding materials used in the study, although the degradation appeared to be somewhat faster (non-significant difference) in the case of red brown earth followed by sand-dolomite and quarry sand. The converse was true for chlorpyrifos, where the degradation was considerably slower in the soil than that in the two bedding materials.

3.4 Quantification of degradation kinetics of the insecticides

To quantify the rate of degradation, the data were fitted to a classical first-order rate equation, as shown by log-linear plots in Fig 3. For the soil and bedding materials studied, degradation data for bifenthrin and imidacloprid insecticides were adequately described by the first-order kinetic model (Table 3). The rate coefficients for the two insecticides were of the same order for the soil as well as for the bedding materials. These rate coefficients can be used to determine the half-life of the insecticides, but since the degradation for bifenthrin and imidacloprid was less than 50% in the study period, these half-lives may not be accurate. Assuming that the rate of degradation would continue

to proceed at the same rate beyond the two-year period, the estimated half-lives would range from 1332 to 1410 days for bifenthrin, and from 990 to 1230 days for imidacloprid. It should be noted, however, that often the half-lives of insecticides at termiticidal application rates ($50\text{--}1000\text{ mg kg}^{-1}$) are much higher than those found at normal agricultural rates ($<1\text{--}10\text{ mg kg}^{-1}$).^{4,15}

In the case of chlorpyrifos, a biphasic degradation was evident from the Figure, showing an initial rapid rate followed by a slower rate of degradation. Indeed, within the first 90 days, some 50–60% of chlorpyrifos had disappeared from the two bedding materials. In the case of soil the loss of chlorpyrifos during this period was comparatively smaller (33%). The degradation data in soil followed a first-order rate law (Table 3, $r^2=0.97$) when the data for the first two samples (day 0 and day 30) were excluded from the regression analysis. However, for the two bedding materials, the data fitted well when the first three samples (day 0, day 30 and day 60) data were excluded. The rate coefficients and estimated half-lives are presented in Table 3. A comparison of the rate coefficients of the three insecticides shows that the rate of chlorpyrifos degradation was an order of magnitude faster than those of the other two insecticides.

Our results are consistent with the reported laboratory and field persistence studies on termiticides. For example, Racke *et al*⁴ found from a laboratory study that the degradation of chlorpyrifos at termiticidal application rates ($1000\text{ }\mu\text{g g}^{-1}$ level) was rapid in four soils tested from the USA (half-lives of $c175$ to $c335$ days) and that chlorpyrifos had extended persistence in one of the soils (half-life $c1576$ days). Recently Gold *et al*⁵ studied the persistence of six termiticides for five years under field conditions and ranked the insecticides in the following order based on their persistence: permethrin > fenvalerate > bifenthrin > chlorpyrifos > cypermethrin > isofenphos. In five of the six test locations bifenthrin showed greater persistence than chlorpyrifos. They also observed the rapid degradation of chlorpyrifos in an alkaline soil having a pH of 8.2. In this soil, 95% of the applied chlorpyrifos had degraded within two years. The degradation patterns of bifenthrin and imidacloprid in the soil and bedding materials were essentially the same, whereas that for chlorpyrifos differed markedly. Therefore the effect

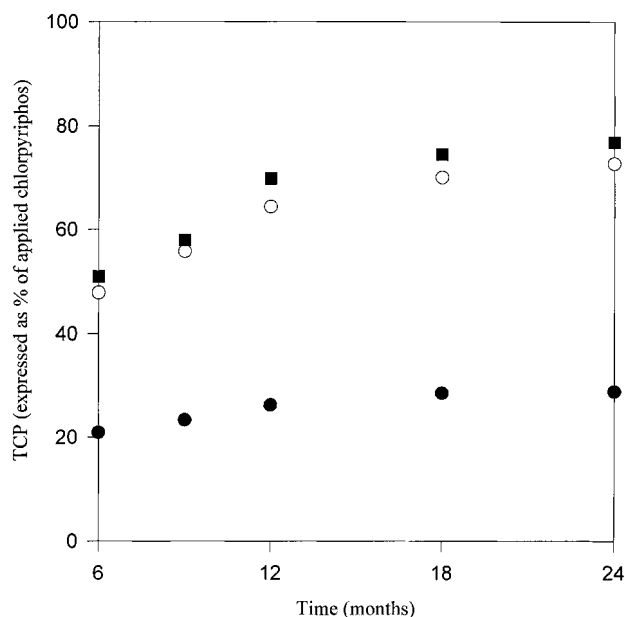


Figure 4. TCP (expressed as % of applied chlorpyrifos) in soil and bedding materials under laboratory condition. (●) Red-brown earth, (○) quarry sand, (■) sand dolomite.

of soil properties on degradation of chlorpyrifos is discussed further in the following section.

3.5 Alkaline hydrolysis of chlorpyrifos

Both biotic and abiotic pathways have been found to be important for chlorpyrifos degradation and/or transformation in soils.¹¹ In the present study, the faster rate of degradation of chlorpyrifos in the two bedding materials than in the biologically more active soil shows that the abiotic pathways such as base-hydrolysis may have been the primary route of chlorpyrifos loss in these materials. The two bedding materials examined were highly alkaline in nature (see Table 1) and had no measurable dehydrogenase activity. Therefore, it is clear that high alkalinity in these materials induced rapid hydrolytic breakdown of chlorpyrifos. Racke *et al*¹¹ examined hydrolysis of chlorpyrifos in 37 soils at agricultural application rates ($10 \mu\text{g g}^{-1}$) and observed that in some alkaline soils hydrolysis indeed constituted the major degradation pathway. In this study soil pH displayed the strongest association with hydrolytic rate constants. However, they also noted that in several soils, with pH values in the range of 7.1 to 8.5, the hydrolytic reaction was inhibited at higher concentrations ($1000 \mu\text{g g}^{-1}$), possibly due to the inhibition of microbial activity and limitation of the number of abiotic reaction sites.^{12,13} This did not occur in the present study, most probably due to (i) lack of inherent microbial activity in soil, and hence no effect of inhibition during degradation, and (ii) much greater alkalinity in the two bedding materials than in the soils previously studied.

It is well-established that the most common pathway of hydrolytic degradation of chlorpyrifos involves formation of 3,5,6-trichloro-2-pyridinol (TCP), which is accelerated under alkaline conditions.¹¹ Therefore

we investigated the formation of TCP with time, in the soil, sand-dolomite and quarry sand materials. The data are presented in Fig 4. The data show that, in the two bedding materials, a large fraction of chlorpyrifos had converted into TCP during the study period. After two years, TCP recoveries were 73% in quarry sand and 76% in sand-dolomite, whereas in the case of the red brown earth soil, only 29% residue was in the form of TCP. This again supports the above observations that in the two bedding materials the primary mechanism of chlorpyrifos loss was alkaline hydrolysis leading to the formation of TCP. Due to there being no microbial activity in the bedding materials (indicated by the total lack of dehydrogenase enzyme activity), neither was the TCP mineralised nor did the TCP accumulation lead to any inhibition of degradation observed in other studies. Such rapid hydrolysis of chlorpyrifos to TCP has also been observed by Baskaran *et al*¹⁴ in organic-matter-deficient alkaline subsoils of Australia.

5 CONCLUSIONS

Laboratory studies were undertaken to examine the degradation of three insecticides (bifenthrin, chlorpyrifos and imidacloprid) at termiticidal application rates in a red brown earth soil and two bedding materials (sand-dolomite and quarry sand) used in construction of buildings in Australia. The three insecticides studied differed widely in their degradation behaviour during the two-year study period. Bifenthrin and imidacloprid degraded at much slower rates (0.00049 – 0.0007 day^{-1}) than chlorpyrifos (0.0015 – 0.0022 day^{-1}) under constant temperature (25°C) and moisture conditions. Soil moisture had no effect on the degradation of bifenthrin and imidacloprid. The rapid rate of degradation of chlorpyrifos resulted in accumulation of TCP, its principal hydrolytic metabolite. In the highly alkaline bedding materials, alkaline hydrolysis appeared to be the dominant transformation pathway for chlorpyrifos.

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REFERENCES

- Gold RE, Howell Jr HN and Jordan EA, Horizontal and vertical distribution of chlorpyrifos termiticide applied as liquid or foam emulsions, in *Pesticides in Urban Environments – Fate and Significance*, ed by Racke KD and Leslie AR, ACS Symposium Series 522, American Chemical Society, Washington, DC. pp 140–155 (1993).
- Cink JH and Coats JR, Effect of concentration, temperature, and soil moisture on the degradation of chlorpyrifos in an Urban

- Iowa soil, in *Pesticides in Urban Environments – Fate and Significance*, ed by Racke KD and Leslie AR, ACS Symposium Series 522, American Chemical Society, Washington, DC. pp 62–70 (1993).
- 3 Kard BM and McDaniel CA, Field evaluation of the persistence and efficacy of pesticides used for termite control, in *Pesticides in Urban Environments – Fate and Significance*, ed by Racke KD and Leslie AR, ACS Symposium Series 522, American Chemical Society: Washington DC. pp 42–62 (1993).
- 4 Racke KD, Fontaine DD, Yoder RN and Miller JR, Chlorpyrifos degradation in soil at termiticidal application rates, *Pestic Sci* 42:43–51 (1994).
- 5 Gold RE, Howell jr HN, Pawson BM, Wright MS and Lutz JC, Persistence and bioavailability of termiticides to subterranean termites (Isoptera: Rhinotermitidae) from five soil types and locations in Texas, *Sociobiology* 28:337–363 (1996).
- 6 Davis RW and Kamble ST, Distribution of sub-slab injected Dursban TC (chlorpyrifos) in a loamy sand soil when used for subterranean termite control, *Bull Environ Contam Toxicol* 48:585–591 (1992).
- 7 Casida Jr LE, Klein D and Santoro T, Soil dehydrogenase activity. *Soil Sci* 98:371–376 (1964).
- 8 Baskaran S, Kookana RS and Naidu R, Determination of the insecticide imidacloprid in water and soil using high-performance liquid chromatography, *J Chrom* 787:271–275 (1997).
- 9 Racke KD, Laskowski DA and Schultz MR, Resistance of chlorpyrifos to enhanced biodegradation in soil, *J Agric Food Chem* 38:1430–1436 (1990).
- 10 Ridler JE, Analytical method for the determination of bifenthrin in various crops and soils, FMC Corporation Agricultural Chemical group project 182CSSR01. pp 1–42 (1989).
- 11 Racke KD, Steele KP, Yoder RN, Dick WA and Avidov E, Factors affecting the hydrolytic degradation of chlorpyrifos in soil, *J Agric Food Chem* 44:1582–1592 (1996).
- 12 Hance RJ and McKone CE, Effect of concentration on the decomposition rates in soil of atrazine, linuron and picloram, *Pestic Sci* 2:31–34 (1971).
- 13 Ou LT, Rothwell DF, Wheeler WB and Davidson JM, The effect of high 2,4-D concentrations on degradation and carbon dioxide evolution in soils. *J Environ Qual* 7:241–246 (1978).
- 14 Baskaran S, Kookana RS and Naidu R, Sorption and degradation of chlorpyrifos and its primary metabolite, TCP (3,5,6-trichloro-2-pyridinol) in surface and sub-surface soils. *Proc ASSSI National Soils Conference*, Brisbane, 27–29 April. pp 213–218 (1998).
- 15 Rouchaud J, Thirion A, Wauters A, Van de Steene F, Benoit F, Ceustermans N, Gillet J, Marchand S and Vanparys L, Effects of fertilisers on insecticide adsorption and biodegradation in crop soils, *Arch Environ Contam Toxicol* 31:98–106 (1996).