

Rapid degradation of termiticides under field conditions

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Abstract Soil testing is used by regulatory agencies to determine the adequacy of termiticide application by pest controllers. Because tests may be carried out years after treatment, an accurate knowledge of termiticide degradation rates is crucial if determinations are to be valid. Degradation of exposed residues of bifenthrin, chlorfenapyr, chlorpyrifos, fipronil and imidacloprid was investigated in a field trial conducted near Narrandera (inland New South Wales) and in Sydney. Samples of soil 75 mm deep were collected immediately after treatment and after 12 months from plots treated with termiticides to a minimum depth of 350 mm and analysed for termiticide residues. Bifenthrin and chlorfenapyr were the most persistent termiticides. Losses of chlorpyrifos exceeded 99% at both locations. Losses of fipronil and imidacloprid were 96% and 94%, respectively, at Narrandera and 67% and 50%, respectively, in Sydney. To explore the fate of chlorpyrifos, fipronil and imidacloprid in the soil profile at Narrandera, samples were collected 15 months after treatment to a depth of 450 mm, in 150 mm increments, from plots treated to a depth of 700 mm. In soil below 150 mm, chlorpyrifos and fipronil content was little changed from time of application whereas major losses of imidacloprid had occurred at all depths. These findings have implications for termite treatment regulation in Australia. Regulatory agencies have relied upon degradation rates observed in laboratory experiments to determine *in situ* treatment adequacy. Results of this field study suggest that termiticides can degrade more rapidly *in situ* than indicated by laboratory experiments.

Key words chemical half-lives, persistence, regulation, soil termiticides.

INTRODUCTION

Termiticidal soil treatments are used throughout mainland Australia to protect buildings from termite infestation. Concentrates are diluted with water and either applied to the soil surface to create a horizontal barrier, or incorporated into the soil to create a vertical barrier (Standards Australia 2000). The concentrations of termiticide in aqueous mixtures are specified on product labels, as are the volumes of mixture required to treat a given area or volume of soil. As with all pesticide usage in Australia, compliance with product label directions (approved by the Australian Pesticides and Veterinary Medicines Authority (APVMA)) is mandatory under State and Commonwealth Government legislation. Termiticide approval by the APVMA is underpinned by the field methods of Lenz *et al.* (1990). When termiticides are used according to label directions, the expectation is that they should achieve levels of efficacy consistent with the claims made on the product label. If insufficient quantities of termiticide are used, premature invasion and infestation is likely to result.

Monitoring of termiticide application by regulatory agencies in most Australian states has been *ad hoc* and few pest controllers have been convicted of breaching product label directions. When investigations do take place, samples of

treated soil may be collected and analysed for termiticide. To determine the adequacy of the treatment, the analytical results are interpreted in terms of application rates described on product labels. Soil tests may be carried out months or years after treatment, and some of the termiticide residues originally applied will have degraded by natural processes. Under these circumstances, knowledge of the rate of degradation of termiticide in soil is critical if determinations are to have any validity. In the past, authorities have used estimates of termiticide half-lives derived from laboratory investigations (Racke *et al.* 1994; Baskaran *et al.* 1999; Murray *et al.* 2001) to determine *in situ* treatment adequacy.

This study was undertaken to provide field validation of the above laboratory observations and to obtain field persistence data for a range of commonly used and experimental termiticides. Whereas the persistence of termiticides in the field has been studied extensively overseas (Kard & McDaniel 1993; Gold *et al.* 1996; Su *et al.* 1999), the amount of corresponding data available from studies conducted in Australia is minimal. Described here are the results of a field investigation of the degradation of termiticides at two different locations in New South Wales (NSW) using bifenthrin, chlorfenapyr, chlorpyrifos, fipronil and imidacloprid. Treated soil was sampled and analysed for residues to determine the extent of degradation over time.

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MATERIALS AND METHODS

Study sites

Investigations of termiticide degradation were undertaken in cleared areas of a managed cypress forest near Narrandera in inland NSW and in the urban western suburbs of Sydney.

During the study Narrandera had mean maximum air temperatures in summer (January) of 33.4°C and winter (July) of 15.4°C, and total precipitation of 625 mm (Forests NSW, Narrandera unpubl. data 2004), while western Sydney had mean maximum air temperatures in summer (January) of 30.6°C and winter (July) of 17.5°C, and total precipitation of 666 mm (Bureau of Meteorology, Sydney unpubl. data 2005).

Termiticides and soil treatment

The five termiticides tested were used in accordance with Australian product labels (or manufacturer's recommendations for an unregistered product). These were: bifenthrin (Biflex) 0.05% volume/volume (v/v), chlorfenapyr (unregistered) 0.125% v/v, chlorpyrifos (Dursban) 1% v/v, fipronil (Termidor) 0.06% v/v and imidacloprid (Premise) 0.05% v/v.

The diluted termiticides were mixed (using cement mixers to ensure even distribution) with a sand/loam (50/50) soil at the rate of 100 L m⁻³. At Narrandera treated soil was placed into pre-drilled holes (diameter 350 mm and depth 700 mm). In Sydney treated soil was placed into trenches (150 mm wide and 350 mm deep) dug from around in-service power poles. Treated soil remained exposed to the elements for the duration of the study.

Soil sampling

At Narrandera and in Sydney, soil samples were collected from three plots of each termiticide immediately after treatment and again after 12 months. Samples were collected to a depth of 75 mm using a steel tube with an internal diameter of 30 mm. At Narrandera more samples were collected 15 months after treatment from plots treated with chlorpyrifos, fipronil and imidacloprid. On this occasion, duplicate samples were collected to a depth of 450 mm in increments of 150 mm (i.e. three samples per core hole).

After collection, soil samples were wrapped in aluminium foil and placed in labelled re-sealable plastic bags. If chemical analysis was delayed for more than 2 days samples were stored at -5°C.

Sample analysis

Soil samples were analysed individually under contract by the Queensland Forestry Research Institute, Brisbane. Laboratory protocols used to analyse each termiticide were: bifenthrin, chlorfenapyr and chlorpyrifos: Sawyer *et al.* (1990); fipronil: Ying and Kookana (2002); imidacloprid: soil samples were extracted with acetonitrile/water (8/2). Extracts were cleaned by liquid-liquid partition on Extube columns, eluting the active ingredient with dichloromethane. The solvent was evaporated and the residue dissolved in acetonitrile/water. Quanti-

fication was by high-performance liquid chromatography with ultraviolet detection (AG Bayer, unpublished method of analysis RA-559/89/1676, 1989). Samples were analysed for the parent molecules of the termiticides. No attempt was made to assay for termiticide metabolites. Mean extraction recoveries (\pm SE) from spiked samples over the course of the study were: bifenthrin 107.0 (\pm 3.3)%, chlorfenapyr 99.0 (\pm 1.0)%, chlorpyrifos 90.8 (\pm 6.7)%, fipronil 107.0 (\pm 3.7)% and imidacloprid 99.2 (\pm 3.5)%. Results are presented uncorrected for recovery efficiency and are expressed as milligrams of active ingredient per air-dried kilogram of soil.

RESULTS

Bifenthrin and chlorfenapyr were the most persistent termiticides. Losses for both termiticides were less than 50% over a 12-month period (Figs 1,2). Chlorpyrifos, fipronil and imidacloprid were the least persistent. Losses of chlorpyrifos exceeded 99% at both locations. Losses of fipronil and imidacloprid were 96% and 95%, respectively, at Narrandera and approximately 67% and 50%, respectively, in Sydney (Figs 1,2).

The very low levels of chlorpyrifos, fipronil and imidacloprid in the 0–75 mm soil layer at Narrandera prompted the

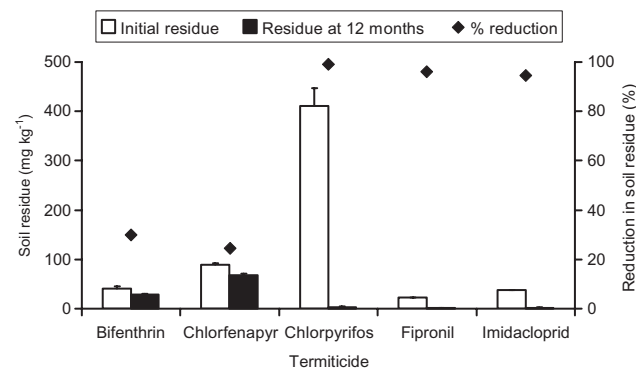


Fig. 1. Mean termiticide concentrations (\pm SE) in soil samples collected to a depth of 75 mm at Narrandera and percentage reductions in concentration over 12 months.

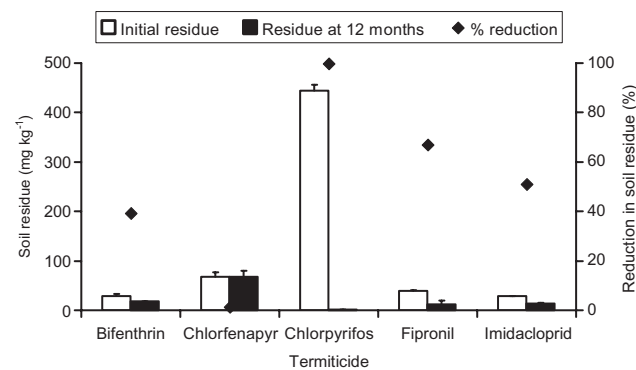


Fig. 2. Mean termiticide concentrations (\pm SE) in soil samples collected to a depth of 75 mm in Sydney, and percentage reductions in concentration over 12 months.

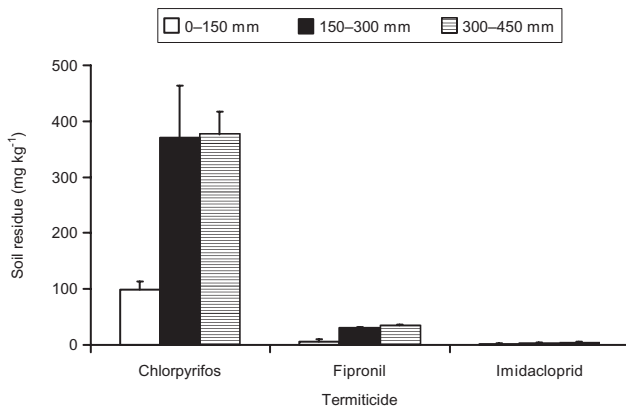


Fig. 3. Mean termiticide concentrations (+SE) in the soil profile to a depth of 450 mm at Narrandera, 15 months after the application of termiticides.

investigation of the concentration of these termiticides at greater depths. Imidacloprid concentration increased with increasing depth (Fig. 3), although at all depths sampled it was very close to the low values found at 12 months in the upper 75 mm layer (Fig. 2). In contrast, concentrations of chlorpyrifos and fipronil were much higher at greater depths. In the top 150 mm soil layer, concentrations of chlorpyrifos and fipronil were down 76% and 72%, respectively, from initial loadings. At greater depths (150–450 mm), concentrations of chlorpyrifos and fipronil were closer to initial loadings, indicating that the termiticides were degrading near the surface.

DISCUSSION

The commonly used termiticides chlorpyrifos, fipronil and imidacloprid, applied under field conditions according to product label directions, suffered major losses in soil close to the surface within 12 months of application. In particular, chlorpyrifos experienced the most pronounced decline, virtually disappearing from the 0–75 mm layer at both test sites. At Narrandera, fipronil and imidacloprid residues also underwent substantial declines. In contrast to chlorpyrifos, residues of imidacloprid and fipronil declined more gradually in Sydney. It is possible that climatic influences, and in particular temperature, played a major part in differences observed at the two study sites. Temperature is a key modulator of insecticidal breakdown (Matsumura 1975). The more rapid breakdown observed at Narrandera may have been a function of higher temperatures experienced at that site. The consistent low level of chlorpyrifos residues at both sites at 12 months indicates that superficial deposits of this chemical are considerably more labile than imidacloprid or fipronil.

In a laboratory study of chlorpyrifos breakdown in the soil profile, Baskaran *et al.* (2003) found that chlorpyrifos degraded more rapidly with increasing depth. Losses were attributed to an associated increase in soil pH found deeper in the soil profile. Quite the opposite pattern of degradation was found for chlorpyrifos, and also for fipronil and imidacloprid

in the present field investigation. Perhaps temperature also played a role in the establishment of an increasing concentration gradient in the soil profile at Narrandera. Changes in soil temperature are rapidly dampened as depth increases (Fluker 1958). Residues deeper in the profile therefore suffer less from extremes of temperature in comparison with residues closer to the surface and thus may degrade more slowly.

Findings reported here about the persistence of chlorpyrifos and imidacloprid residues close to the soil surface appear to vary from the results of a number of laboratory studies of termiticide degradation. For example, Baskaran *et al.* (1999) reported half-lives in three different soil materials ranging between 315 and 462 days for chlorpyrifos and 990 and 1230 days for imidacloprid. Murray *et al.* (2001), investigating chlorpyrifos degradation in six different soils, reported half-lives ranging from 281 to 825 days. In the USA, Racke *et al.* (1994) reported half-lives for chlorpyrifos of between 175 and 1576 days in five different soils. Although termiticide half-lives were not calculated in the present investigation, the results suggest that the half-lives of chlorpyrifos at both sites, and of imidacloprid at Narrandera, were considerably shorter than 12 months (Figs 1,2). Results suggest that the half-life of imidacloprid in Sydney was approximately 12 months (Fig. 2).

Why should the findings of this study differ from those of laboratory studies? One possible explanation is that there were differences in the environmental conditions to which termiticide residues were exposed. The above-mentioned laboratory investigations were carried out under controlled environmental conditions including constant darkness and a constant temperature at or about 25°C, and were thus protected from factors such as sunlight and high temperatures that are likely to have promoted their degradation (Matsumura 1975; Racke *et al.* 1994). It appears that the conditions used in the laboratory experiments were simulated in soil deeper than 150 mm at Narrandera, and may have accounted for the higher concentrations of chlorpyrifos, fipronil and imidacloprid found in soil at these depths. In contrast, termiticides closer to the surface in the present study were exposed to the full gamut of environmental extremes that prevailed at the test site during the term of the study.

A second possible explanation is that there were differences in the initial termiticide soil concentrations. The above-mentioned laboratory studies used initial soil loadings that were considerably higher than those recorded in the present investigation. For example, in the laboratory studies, application rates of chlorpyrifos were 1000 mg kg⁻¹. This contrasts with average initial concentrations of chlorpyrifos of 411 mg kg⁻¹ at Narrandera and 440 mg kg⁻¹ in Sydney, which were applied in accordance with label directions. Application at high concentrations has been found to retard chlorpyrifos degradation, possibly by inhibiting microbial degradation (Racke *et al.* 1994). Inhibited microbial activity may also explain the protracted half-lives observed for other termiticides in the laboratory.

It is proposed that the results of the present study give a more realistic indication of termiticide degradation under field

conditions. Initial soil loadings that were observed better reflect application rates specified on product labels. For example, the so-called 'termiticidal rate' of 1000 mg kg⁻¹ chlorpyrifos used in the laboratory studies is unlikely to be achieved in practice if label directions are followed. The application rate specified on the product label of Dursban (450 g L⁻¹ chlorpyrifos) is 2.2 L (1000 g) per cubic metre. At this rate its expected concentration in soil with a bulk density of 1500 kg m⁻³ will be 667 mg kg⁻¹. Soil used in the present study had a relatively high bulk density of between 1800 and 2000 kg m⁻³. At label application rates a concentration of chlorpyrifos of between 556 and 500 mg kg⁻¹ would be expected. Differences between the observed and expected levels in the present study may be at least partially attributable to inefficient recoveries during analysis.

These findings have important implications for the regulation of termiticide application in Australia. In recent years, regulatory agencies in several states have taken action against pest controllers for applying inadequate amounts of termiticide when doing termite treatments. In some cases charges have been grounded on very low levels of termiticide in soil taken from supposedly treated areas. On occasion, the soil tests were carried out years after treatment. Plaintiffs have argued that, although some degradation during the interval is normal, the levels found were less than expected.

Published estimates of chemical half-lives, such as those of Racke *et al.* (1994), Baskaran *et al.* (1999) and Murray *et al.* (2001), have underpinned the plaintiffs' expectations of the termiticide concentration in soil after periods of time between treatment and testing. For the reasons given above, under certain conditions these expectations may be unrealistically high. The results of this investigation emphasise the need for caution when drawing inferences about the degradation of termiticides in real-life situations.

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