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Effect of Concentration on the Adsorption of Three Termiticides in Soil

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Subterranean termites are commonly controlled by creating a continuous subsoil chemical barrier adjacent to exterior and interior of the building foundation (Kamble 1991, 2001). Historically, the conventional subterranean termite control practices have primarily relied on the use of termiticides (Gold et al. 1994, 1996) that were classified as chlorinated hydrocarbons, organophosphates and carbamates. Recently, new termiticides with novel mode of actions have been introduced. Some of these termiticides such as imidacloprid (chloronicotinyl class), bifenthrin (pyrethroid class), and fipronil (phenyl pyrazole class) are commonly used for termite control because of their low mammalian toxicity. These termiticides have distinct physical and chemical properties as follows: Imidacloprid [1[(6-chloro-3-pyridinyl) methyl]-N-2-imidazolidinimine] is a new systemic chloronicotinyl insecticide. It is moderately soluble in water (0.51 g/L or ~ 510 ppm at 20°C). Imidacloprid acts on the insect nervous system by attaching to the acetylcholine binding sites called nicotinergic receptors on the receiving nerve cells. This mode of action prevents transmission of information at those binding sites, leading to a lasting impairment of the nervous system and eventually the death (Bayer Inc. Premise® Education Training Manual 1997; Ramakrishnan et al. 2000; Sheets 2001). Imidacloprid has K_{oc} values ranging from 80 to 1,600 depending on soil types and concentrations. It does not show leaching potential (Rouchaud et al. 1996). It has a degradation half-life of approximately 40 days in soil under field conditions (Rouchaud et al. 1994). However, the half-life of imidacloprid ranges from 990 to 1,230 days when applied as a termiticide (0.05-0.1% active ingredient [AI]) in different soils (Baskaran et al. 1999).

Fipronil [(±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-trifluoromethyl sulfinyl-pyrazole-3-carbonitrile] belongs to a new class of phenyl pyrazoles. Fipronil interferes with the passage of chloride ions through the gamma-aminobutyric acid (GABA) regulated chloride channel by disrupting the central nervous system (CNS) activity and eventually causes death (Cole et al. 1993). Its water solubility ranges from 1.9 to 2.4 mg/L at 20°C. Fipronil degrades in the environment to its major metabolites via reduction to sulfide, oxidation to sulfone, hydrolysis to amide, and photolysis to des-sulfinyl photodegradate (Hainzl and Casida 1996).

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Bifenthrin [2-methylbiphenyl-3-ylmethyl (Z)-(1RS, RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)2,2-dimethylcyclopropanecarboxylate] belongs to pyrethroid class. Pyrethroids are highly non-polar and lipophilic in nature. Bifenthrin is a white solid with a melting point of 68-70.6°C and a vapor pressure of 1.81 x 10^{-7} mm Hg (0.024 mPa) at 25°C. It has a solubility of 0.1mg/L in water. Bifenthrin is stable in soil over a wide pH range and degrades at a slow rate depending upon soil characteristics. Bifenthrin also persists in aquatic sediments. It has a high Log Kow (>6.0), high affinity for organic matter, and is not mobile in soil (FMC Material Safety Data Sheet 2001). When used as a termiticide, the efficacy of this new generation insecticide depends on its availability to the termites and its persistence in soil. From environmental perspectives, this termiticide has very low leaching potential and therefore it has very high Soil Organic Partition Coefficient (K_{oc}) values. Bifenthrin with low water solubility is able to partition off very easily in the non-polar termite integument. This makes it interesting to study the effect of variable concentrations on K_{oc} values and movement in soil.

The literature review revealed that the performance of termiticides is often influenced by soil type, soil pH, moisture, temperature, microbial organisms, insecticide properties and target insects (Harris 1972; Tashiro and Kuhr 1978; Chapman et al. 1982; Macalady and Wolfe 1983; Felsot and Lew 1989; Davis and Kamble 1992). Similarly, adsorption property affects the distribution of termiticides in the soil and their bioavailability to termites. However, there are no published data available on concentrations affecting the adsorption of termiticide to soil particles and its bioavailability to subterranean termites. This research was undertaken to evaluate the effect of concentration on the adsorption behavior of imidacloprid, fipronil, and bifenthrin in soil.

MATERIALS AND METHODS

Thirty kg of soil was collected from a building site with no history of insecticide applications. This site represents the typical soil type around residential areas in Lincoln, NE. The soil was passed through a 2-mm sieve prior to use and autoclaved (1 hr @ 120^0C and 1 atm) on two successive days. Soil was analyzed for particle size, pH, organic matter content, cation exchange capacity (CEC), phosphorous (Bray-1), and potassium (Table 1) by the Soil and Plant Analytical Laboratory, Department of Agronomy and Horticulture, University of Nebraska, Lincoln, NE.

Five sub-samples (50 g each) were randomly collected from soil stored in 18.9 L plastic buckets in cold storage (5 ± 2.3°C) to determine the water content. Each soil sample was placed in a constant temperature oven (Model no. 1330F, VWR Scientific Products, Cornelius, OR) set at 105 °C for 24 hrs. After drying, the soil samples were cooled in sealed containers and weighed. The percent soil water content was calculated as:

$$\text{\% Soil Water Content} = \frac{\text{Wet Soil Weight (g) - Dry Soil Weight (g)}}{\text{Dry Soil Weight (g)}} \times 100$$

Adsorption isotherms were developed to determine the Soil Partition Coefficient (K_d) and Organic Carbon Partition Coefficient (K_{oc}). Adsorption isotherms allowed to estimate the amount of termiticide adsorbed to soil. All reagents and solvents were HPLC grade. Aqueous dilutions of termiticide were prepared ranging from lowest to highest concentrations allowed on labels. Imidacloprid is registered at 0.05-0.1% (AI) (500 mg/L to 1,000 mg/L, respectively) for termite control. A 1,000 ppm stock solution was prepared from formulated imidacloprid (Premise 75% WSP) by dissolving 333.34 mg of formulated product in 250 mL of 0.01 N $CaCl_2$ solution The stock solution was further diluted to acquire 50 ml each of 500 and 750 ppm of imidacloprid solutions. Fipronil (Termidor 9.1% SC) is registered at 0.06-0.125% AI (600-1250 mg/L) for termite control. Using the previously described procedure, fipronil was diluted to attain 50 ml each of 600, 950 and 1,250 ppm solutions. Bifenthrin (Talstar 7.9% SC) is registered at 0.05-0.12% AI (500-1200 mg/mL) for termite control. Bifenthrin was diluted using above mentioned procedure to attain 50 ml each of 600, 900 and 1,200 ppm solutions. Five grams of oven-dried soil adjusted to 10% water content was placed in 125 mL Erlenmeyer flask and 40 mL of each formulated insecticide solution (0.01 N $CaCl_2$) was added. Flasks were capped with rubber stoppers and mounted on incubator shaker (Model G25, New Brunswick Scientific Co., Edison, NJ) at 250 rpm and 20°C for 24 hrs. After the soil sediment had settled, a 1.5 mL aliquot from each respective insecticide-soil combinations was transferred into a 1.5 mL microcentrifuge tube. Aliquots were centrifuged at 12,000 g for 20 min, and supernatants were transferred to another 1.5 mL microcentrifuge tube. Aliquots were dried by placing them in Eppendorf Vacufuge™ model 5301 (Brinkman Instruments, Inc., Westbury, NY), and by centrifuging them at 3654 g for 12 hrs at 30°C. Residues of imidacloprid and bifenthrin remaining in previous microcentrifuge tubes were resuspended in acetonitrile. Residues of fipronil were resuspended in methanol. The solvents used for resuspension were same as the mobile phase used for analyzing these insecticides. The process of resuspension was repeated 3 times, vortexed, and added to each tube to account for all residues, and it was further confirmed by HPLC analysis of the fourth rinse. One mL from microcentrifuge tube was transferred to 1.5 mL HPLC vials for chemical analysis.

All three insecticides were analyzed using high performance liquid chromatography (HPLC) (Varian® - 9012 pump, 9050 variable length detector UV/VIS, 9100 autosampler). Data collection and peak analysis were performed using Varian® Star (Version 4.5) Chromatography workstation. For imidacloprid a mobile phase 70:30 (Water:Acetonitrile v/v) was used under isocratic conditions at a flow rate of 1.0 mL/min. A reverse phase C-18 (2) column (250 mm x 4.6 mm ID, 5 μ particle size, Luna® - Phenomenex) was used. The UV/VIS detector was set to a wavelength (λ) 270 nm, as described by Placke and Weber (1994), and Baskaran et al. (1999). The methanol:water gradient (78:22 to 72:28 mL/over 12 min flow rate) was used to separate fipronil from the sulfone metabolite (Hainzl and Casida, 1996) and the UV/VIS detector was set at 280 nm wavelength. A reverse phase C-18 (2) column (250 mm x 4.6 mm ID, 5 μ particle size, Luna®-Phenomenex) was used. Bifenthrin samples were analyzed using a reverse phase C-18 column (150 mm x 4.6 mm ID, 5 μ particle size, Luna®-Phenomenex). The mobile phase of acetonitrile:water (95:5) was used at a flow rate of 1.0 mL/min under isocratic conditions. The UV/VIS detector was set at 204 nm wavelength. The HPLC detection sensitivity was 0.5 μg/mL for all there insecticides. The retention times were 6.87, 7.14, and 2.91 min for imidacloprid, fipronil, and bifenthrin, respectively.

The amount of chemical adsorbed to the soil after equilibration was calculated from the difference between initial and equilibrium solution concentrations. Adsorption isotherms were calculated using the linearized form of the Freundlich equation:

$$\log C_{ads} = \log K_f + 1/n \log C_{eq}$$

where, C_{ads} is the amount of chemical adsorbed (mg/Kg of soil), C_{eq} is the equilibrium concentration (mg/L of solution), and K_f and 1/n are the adsorption coefficients expressing adsorption capacity and intensity, respectively (Cox et al. 1997). The natural logarithm of the mass of pesticide adsorbed per mass of soil (mg/Kg of soil) was plotted against the natural logarithm of the pesticide concentration remaining in the solution after equilibration to get the adsorption isotherms.

The difference from initial concentration of termiticide solution was compared to the termiticide solution concentration after 24 hrs equilibration to determine the soil partition coefficient (K_d). The K_d for each termiticide was calculated as:

$$K_d = \frac{\text{Mass of pesticide adsorbed per mass of soil}}{\text{Pesticide concentration remaining in solution}}$$

Because K_d values for pesticides are soil specific and the K_d of one pesticide can differ considerably from soil to soil or with depth in a soil profile, the more widely accepted K_{oc} (organic carbon partition coefficient) was used. The K_{oc} was determined using the formula:

$$K_{oc} = \frac{K_d}{\text{Percent Soil Organic Carbon}} \times 100$$

The Soil and Plant Analytical Laboratory (University of Nebraska, Lincoln, NE) determined the percentage of organic matter in the soil used in this study. The percent organic matter was converted to percent soil organic carbon (OC) by using the Van Bemmelen constant of 1.724. The percent soil OC was determined using the formula:

$$\%\ OC = \frac{\%\ \text{Organic Matter}}{1.724}$$

The extraction efficiency, analytical quality control and recovery rates were tested for each termiticide. Fifty g of sterilized soil was placed in centrifuge tube and technical grade fipronil (98 % pure), imidacloprid (99 % pure), and bifenthrin (99 % pure) were added to yield 100 ppm (100 mg/Kg) concentration of active ingredient in soil (weight/weight). The external standard was used for confirmation and calculation of the total residue because of its accuracy and reproducibility (Poole and Poole 1997).

Each experiment was designed using a complete randomized block design and each treatment was replicated four times. Data were analyzed using Analysis of Variance (ANOVA and PROC GLM (SAS 2000) for testing the slope and concentration interactions.

RESULTS AND DISCUSSION

Soil used in this study was classified as loam based on particle analysis (Table 1). Due to low organic matter content, the non-polar termiticides (e.g., fipronil and bifenthrin) have low affinity for tightly binding with soil particles but these termiticides can still be adsorbed fairly well as compared to relatively polar imidacloprid.

Table 1. Particle size and elemental analysis of the soil used in concentration dependent adsorption study of Premise 75® WSP, Termidor® 9.1% SC, and Talstar® 7.9%SC.

Sand	Coarse Silt	Fine Silt	Very Fine Silt	Clay	Water pH	Buffered pH	P (ppm)	K (ppm)	CEC[1]	OM[2] (%)
Percent										
25.95	23.10	19.8	4.40	26.76	7.41	7.00	17.23	178	22.80	0.91

[1]Cation Exchange Capacity.
[2]Percent Organic Matter.

For imidacloprid (Premise® 75% WSP), the adsorption coefficient K_f and slope 1/n (describing the sorption capacity and sorption intensity, respectively) were obtained from linearized form of the Freundlich equation which are presented in Fig.1. The slope of the adsorption was <1 indicating that isotherm was L-type. The L-isotherms correspond to a decrease in adsorption site availability as the solution concentration increases, suggesting that the molecules are more likely to be adsorbed in flat position and that they do not experience strong competition from solvent molecules for adsorption sites (Cox et al. 1997, 1998). The impact of concentration dependence on adsorption was also evident from the data provided in Table 2. K_{oc} values corresponding to 500 to 1,000 ppm suggest that K_d and K_{oc} decreased with increasing imidacloprid concentrations. These results correspond with the trend reported by Cox et al. (1998) in a similar soil for K_d values (Table 2). K_{oc} values are also consistent with results of Cox et al. (1997) (Table 2).

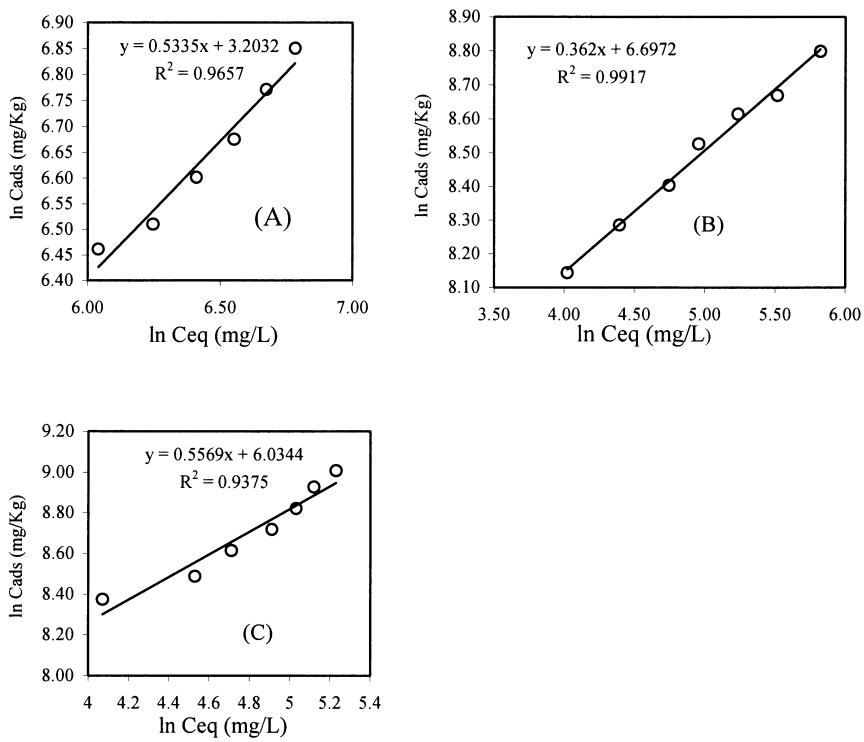

Figure 1. Adsorption Isotherms for imidacloprid (A), fipronil (B), and bifenthrin (C)

The fipronil (Termidor® 9.1% SC) adsorption isotherm had a slope of <1 (1/n) indicating that this isotherm was L-type and there was a decrease in adsorption site availability as the solution concentration increased. Fipronil K_d and K_{oc} values (Table 2) clearly indicated a concentration dependent adsorption trend.

The slope of adsorption for bifenthrin (Talstar® 9.1% SC) was <1 indicating that the adsorption isotherm was L-type. The adsorption isotherm showed similar concentration dependent trend as indicated for imidacloprid and fipronil. The calculated K_d and K_{oc} values decreased with increasing bifenthrin concentrations (Table 2).

The calculated K_{oc} values for Premise® 75 WSP were much lower than Termidor® 9.1% SC or Talstar® 7.9% SC for all concentrations used in this study. The lower K_{oc} values are directly related to the higher water solubility of imidacloprid (0.51mg/L water) when compared to its solubility with either fipronil (1.9 mg/L water at 20°C) or bifenthrin (0.1 mg/L water). The higher water solubility of imidacloprid (0.51g/L) indicates a leaching potential in soil but field trials did not

Table 2. Adsorption Coefficient (K_d) and Organic Carbon Partition Coefficient (K_{oc}) for imidacloprid, fipronil and bifenthrin.

Termiticide	Concentration ppm (mg/L)	K_d (L/Kg)	K_{oc} (L/Kg)
Imidacloprid (Premise® 75%WSP)	500	1.54 ± 0.17	295.24 ± 2.37
	750	1.37 ± 0.19	262.90 ± 2.74
	1,000	1.05 ± 0.19	202.15 ± 2.72
Fipronil (Termidor® 9.1% SC)	600	62.06 ± 0.53	11,934.68 ± 5.51
	950	30.81 ± 0.38	5,925.51 ± 5.32
	1,250	19.69 ± 0.14	3,787.34 ± 1.75
Bifenthrin (Talstar® 7.9% SC)	600	74.53 ± 0.60	14,332.42 ± 8.35
	900	45.22 ± 0.42	8,695.29 ± 5.87
	1,200	43.61 ± 0.22	8,387.37 ± 2.95

support the leaching behavior in soil (Oi 1999). Regardless of high water solubility, the lack of leaching for imidacloprid could be a larger adsorption potential at lower concentration compared to higher concentration range. The other explanation for lack of leaching may be an increase in the adsorption of imidacloprid with time in soil (Oi 1999).

K_{oc} values for the different concentrations of Termidor® 9.1% and Talstar® 7.9%, suggest that both of these termiticides can be categorized as immobile (K_{oc} >2,000). Based on the calculated K_{oc} values for Premise® 75 WP at different concentrations in similar soil type, it can be categorized as having an intermediate mobility (K_{oc} 150-500) (Comfort et al. 1994). Calculated K_{oc} values derived in this experiment are consistent with reported K_{oc} values (Cox et al. 1997, 1998; Baskaran et al. 1999), especially for soils with similar textural characteristics.

The insecticide efficacy in soil is influenced by many complex factors such as soil type, pH, insecticide type, moisture, and organic matter (Forschler and Townsend 1996). Each active ingredient-formulation must be tested individually because efficacy in different soil types can not be extrapolated from chemical structure alone (Harris 1972). Therefore, it was necessary to observe the behavior of three different formulated termiticides in the soil. This research provided adsorption values to generalize the trend for bioavailability of termiticides in soil. Adsorption can be perceived as stable process but studies indicated that adsorption values may change with time (Oi 1999). Imidacloprid is adsorbed to outer positions of the soil aggregates and later within the soil aggregates. Other options are the consolidation of initially weak bonds, a change of mechanism of adsorption/binding, and a steric inclusion of the ingredient molecule into clay/humic matter complexes (Oi 1999). The K_d and K_{oc} values are the two most widely used indicators to evaluate insecticide behavior in soil. Insecticides currently registered as termiticides have soil adsorption coefficients (K_{oc} values) that place them in the immobile classification (Forschler and Townsend 1996). This indicates the potential for interactions between insecticide and components of the soil matrix that could affect the biological activity. Thus, studying the adsorption behavior of termiticide in soil is essential to predict the fate and bioavailability to termites. This paper provides the first record of differing K_d and K_{oc} values for different class of termiticides and their concentrations.

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