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Author(s): T. Chris Keefer and Roger E. Gold
Source: Southwestern Entomologist, 39(4):705-716.
Published By: Society of Southwestern Entomologists
DOI: http://dx.doi.org/10.3958/059.039.0402
URL: http://www.bioone.org/doi/full/10.3958/059.039.0402

Recovery from Leachate and Soil Samples of Fipronil at Termiticide Concentration

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Abstract. Longevity, mobility, and dissipation of Termidor® SC termiticide/ insecticide (fipronil) at the highest recommended label rate (0.125%) was applied to sandy loam soil in greenhouse experiments to simulate field application. High-performance liquid chromatography was used to analyze soil and leachate samples at regular intervals for 12 months after treatment. The mean concentrations of fipronil from initial treated soil and leachate samples were 1,101.75 ± 24.21 µg/g and 0.00 ± 0.00 µl/liter, respectively. Fipronil was recovered from all soil samples throughout the study; however, no fipronil was found in leachate samples. At all post-treatment analyses the highest concentration of fipronil recovered was in the middle soil profile. Results of this study indicated that fipronil was bound to the soil, and there was little movement of the active ingredient within the soil profile.

Introduction

Fipronil was registered in the United States by Rhone Poluenc in 1996 for use on several species of agricultural, turf, and urban insect pests (Konwick et al. 2005, Kumar et al. 2012). The compound is a pyrazole insecticide that acts on gamma-aminobutyric acid receptors and disrupts the passage of chloride ions, which interferes with the central nervous system, resulting in death of the insect (Cole et al. 1993, Hu 2005, Kavallieratos et al. 2010). Fipronil is a non-repellent, slow-acting termiticide, so it is not detected by subterranean termites when used to protect structures. The result is that termites tunnel into the treated structure and die (Su et al. 1982, 1987). In recent years, use of non-repellent insecticide has increased over repellent termiticides detected and avoided by termites (Shelton and Grace 2003). The slow action of non-repellent termiticide can lead to transfer of the active ingredient through grooming and trophallaxis of unexposed nest mates (Thorne and Breisch 2001, Keefer et al. 2010), thereby killing more in the colony than does repellent termiticide (Kard 2001, Bagneres et al. 2009).

Many factors, such as degradation by microorganisms, hydrolysis, and photodegradation, can play a role in the longevity of effectiveness of a termiticide applied to soil to protect a structure (Peterson 2010). The application rate, formulation, systemic properties, and water solubility of a termiticide; soil type and properties; and environmental conditions also can affect the success of a termite treatment (Su and Scheffrahn 1990, Gold et al. 1996, Bobe et al. 1997, Wiltz 2010).

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All factors combined affect the longevity and effectiveness of termiticide in the soil and complicate the goal of protecting a structure from subterranean termites.

There are approximately 2,300 species of termites worldwide, 183 of which damage structures, trees, and agricultural crops (Su and Scheffrahn 1998). Globally, termites are estimated to be responsible for more than $22 billion in damage, repair, and treatment costs annually (Su 2002). In the United States, termites are estimated to cost property owners $11 billion annually. Therefore, it is important to analyze the longevity of effectiveness of termiticides used to treat soil to protect structures from subterranean termites. The objectives of this study were to determine longevity, mobility, and dissipation of fipronil in simulated field studies with sandy-loam soil and plants commonly grown in urban environments.

Materials and Methods

Soil Preparation. Nineteen-liter buckets (Letica Corporation, Rochester, MI) had five 2.54cm-diameter holes drilled in a circular pattern in the bottom for collection of leachate. Fiberglass silver-gray window screen (Phifer Incorporated, Tuscaloosa, AL) was cut into a circle 24 cm in diameter and attached with adhesive (Liquid Nails, Strongsville, OH) over the interior bottom of each bucket. The adhesive was allowed to dry for 24 hours, after which 7.64 cm (weighing approximately 7.14 kg) of washed play sand (Quikrete® International, Inc., Atlanta, GA) was added to the bottom of the bucket.

To determine the amount of soil to be treated and added to each experimental unit (individual bucket), a simulated trench was formed of Southern yellow pine lumber. The 3.05-m-long by 15.24-cm-wide and 15.24-cm-deep lumber form simulated a soil treatment trench that would hold 15 liters of finished dilution of termiticide per 3.05 linear meters per 0.30 m of depth the manufacturer recommended next to a structure. The soil in this part of the study was commercially available sandy loam with pH 5.9, 72% sand, 18% silt, 10% clay, and 1.0% organic matter from the College Station, TX area. It required 84.6 kg of soil to fill the form, and this weight was used when calculating the amount of Termidor SC needed for the label-recommended soil-application rate of 14.8 liters (0.125% fipronil) per 3.1 m. The result was soil with (1,250) µg of fipronil per kilogram of soil.

A total of 84.6 kg of soil was added to the drum of a cement mixer (Model 59020CF, Gilco Incorporated, Grafton, WI). Termidor SC finished dilution (3.6 liters) was added at the greatest labeled application rate of 0.125% AI. A hand-held pump sprayer (B&G Equipment, Jackson, GA) with coarse jet fan spray was used to slowly add termiticide to the soil. The sandy loam soil was mixed for 20 minutes at a constant rate of 20 revolutions per minute. After mixing, 20.32 cm (depth) (weighing 21.05 kg) of treated soil was placed on top of the sand previously placed in each 19-liter bucket. In each bucket, one of the following plant types had one plant that was planted or transplanted: St. Augustine grass, *Stenotaphrum secundatum* (Walter) Kuntze; Bermudagrass, *Cynodon dactylon* (L.); Mexican heather, *Cuphea hyssopifolia* Kunth; and red-tip photinia, *Photina fraseri* Dress. Bermudagrass was grown from seed (Pennington Seed, Inc., Madison, GA), and the other three kinds of plants were transplanted as mature vegetation. A thin layer of sphagnum peat moss (Miracle Gro, Marysville, OH) was added to promote growth of Mexican heather and red-tip photinia. All replications were watered at regular intervals throughout the study to promote healthy plant growth. During the summer, each replication received 1 liter of water two or three times a week. In the

fall, spring, and winter, the amount of water was reduced to 1 liter once or twice a week. There were three replications of each plant species, for a total of 12 buckets. The checks in the study were: 1) soil without termiticide or plants (n = 3); 2) soil with termiticide and no plants, for no plant data and horizon data (n = 3); and 3) soil with each of the four plant species but no termiticide (n = 12) for a total of 18 check buckets. Thirty test-unit buckets were used in the study. The study was done during one calendar year and maintained under greenhouse conditions at College Station, TX.

Soil Extraction and Sampling. Immediately after application of termiticide and establishment of experimental units (Time Zero), three samples were taken from the fipronil-treated soil and analyzed to ensure the target concentration of 1,250 µg/g was achieved. A stainless steel T-bar probe with 25 x 2.5-cm plastic sleeve insert to capture the soil core was used to sample the soil in the buckets at 1, 3, 6, 9, and 12 months post-treatment. The sleeve with the soil core was labeled, and a red cap was placed over the top and a blue cap over the bottom. All soil samples were stored at -5°C in a freezer. All sampling holes in the buckets were filled with Quikrete Premium Play Sand (white color) immediately after sampling to keep the structure of the soil in place and avoid sampling sequentially from the same location in respective replications, because sampling was random.

To prepare soil samples for analysis by high-performance liquid chromatography, the cores were separated into top, middle, and bottom sections. The top cap (red) of the sleeve was removed and approximately 15 g (8 cm) of soil (top) was placed in a 5.5-cm weigh-boat, labeled, and allowed to air dry overnight at 25 ± 2°C in the dark. The next 15 g (8 cm) of soil was removed from the sleeve and labeled as the middle. The last 15 g (8 cm) of soil was pushed from the sleeve and labeled as the bottom. After drying, 5 g of soil from each of the sections was removed from each weigh-boat, placed into a separate 40-ml vial, and 15 ml of acetonitrile was added. The vial was agitated by hand for 20 seconds and allowed to settle for 24 hours after which 1 ml of supernatant was taken with a micropipette and put into a 1.5-ml scintillation vial (National Scientific Company, Rockwood, TN). The subsamples were kept at -5°C in a freezer until analyzed.

Leachate Sampling. Leachate (1 liter) was sampled at 0, 1, 3, 6, 9, and 12 months after treatment. The plant and soil were irrigated with 2 liters of water sufficient to fill a 1-liter Nalgene bottle (Rochester, NY) with leachate during each sampling period. All replications were watered throughout the study to ensure positive continuous plant growth. Samples were collected by placing a funnel inserted into the 1-liter Nalgene bottle under the bucket suspended by two hollow-block bricks (Fig. 1). One-liter leachate samples were prepared using a vacuum pump (Model L-79200-00, 115 v, 60 HZ, Cole Parmer, Vernon Hills, IL). A piece of 0.5-m long, 0.31-cm inside diameter, by 0.16-cm-thick walled Tygon® tubing was attached to the vacuum pump, and the other end was attached to a Resprep™ 12-port Solid Phase Extraction Manifold (Restek, Bellefonte, PA). Pressure on the vacuum pump (-103.4 kPa) was set so activation of the cartridge occurred within 10 minutes. A Resprep™ 60 ml C18 cartridge had a mixture of 50 ml of 60% acetonitrile/40% high-performance liquid chromatography-grade water pulled through it by the vacuum pump to activate the column beads within the C18 cartridge. Then, 150 ml of high-performance liquid chromatography-grade water was pulled through to wash the solvent solution from the C18 column matrix (beads), after which 100 ml of leachate sample was passed through the column, and fipronil if present attached to the activated beads. The fipronil was released

Fig. 1. Leachate was collected by placing a funnel inserted into a 1-liter Nalgene bottle under a bucket suspended by two hollow-block bricks.

from the beads when 100 ml of 60% acetonitrile/40% high-performance liquid chromatography-grade water solvent was passed through the column and collected in a 120-ml Nalgene bottle. A 1.0-ml subsample of the elute was pipetted and placed into a 1.5-ml scintillation vial and stored at -5°C until analysis by high-performance liquid chromatography.

High-Performance Liquid Chromatography. The termiticide in soil and leachate samples were analyzed on a 1200-series Agilent high-performance liquid chromatography system (Waldbronn, Germany) equipped with an ultraviolet-visible photodiode array detector that registered the data as total milli-absorbance units arrayed under a chromatographic curve, the area of which was directly correlated to the concentration (µg/g or µl/liter) of fipronil in each of the samples based on a standard dilution curve. Standard curves were prepared with technical-grade fipronil at 99.5% purity and purchased from Chem Service (West Chester, PA) to make serial dilutions. The only pesticide analyzed was fipronil; no metabolites were assessed. To make the stock solution for each serial dilution, 0.12 g of technical-grade fipronil was mixed in 100 ml of acetonitrile to make a 1,000 µl/liter solution. From that stock solution, a 10-fold dilution series was made of 0.1, 1.0, 10, 100, and 1,000 µl/liter of fipronil. To help quantify the serial dilutions, a best-fit line was generated and used to estimate the concentration of fipronil in samples after analysis by high-performance liquid chromatography. The concentrations were

correlated to an intersection point of the best-fit line (Fig. 2) wherein the mean number of milli-absorbance units reported was proportionately correlated on the curve, by the integrator. This method was used to quantify the amount of termiticide concentrations in the soil and leachate samples throughout the study.

The detector wavelength was 280 nm, analysis time ~12 minutes for each sample, using a Zorbax Eclipse XDB-C18 analytical 4.6 x 150 mm 5-micron column. High-performance liquid chromatography separation used an aliquot-injection volume of 1.0 µl via an autosampler (Agilent 1200 Model G1329A). The high-performance liquid chromatography analysis in this study was similar to that described by Ibrahim (1999) and Kamble and Saran (2005). Mobile phase was a uniform elution of 60% ACN:40% H_2O. The column temperature was maintained at 22°C. Solvents used to extract the termiticide from soil and water samples were Fischer Scientific (Fair Lawn, NJ) HPLC grade. The data were arrayed by an integrator (model #dc7600S, HP Compaq, Palo Alto, CA), which read in the range of 200-300 nm. Samples of finished dilution (40 ml) used to treat soil were collected at the time of treatment to analyze and ensure accurate mixture according to the target of 0.12% = 1,200 ppm µl/liter of fipronil in finished solutions. The samples were analyzed with the same process as the non-quantified samples. The limit of detection of fipronil was 0.1µl/liter (Fig. 2).

One-way analysis of variance (ANOVA) (SPSS 2007) was used to compare the concentration of active ingredient recovered from soils associated with the different plant species and all post-treatment observations. Means were separated using Tukey's honest significant difference test ($\alpha < 0.05$).

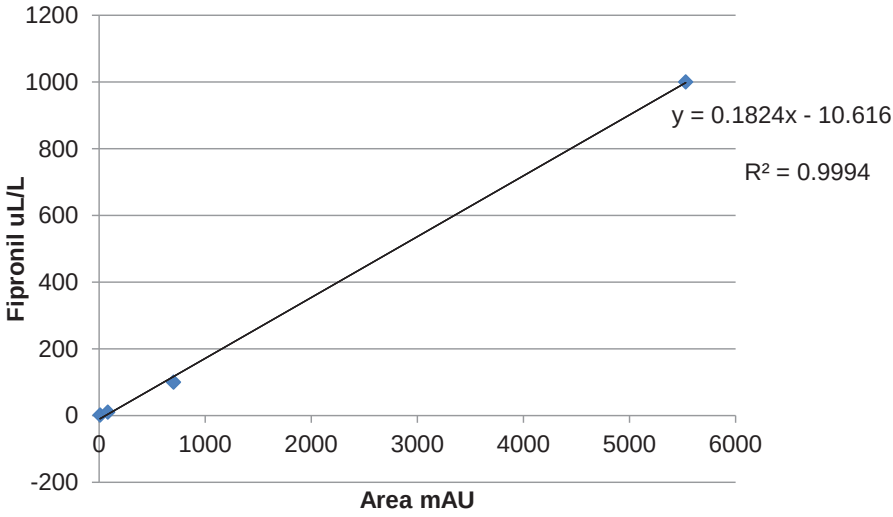

Fig. 2. Detector linearity of Agilent (Model 1200 series) high-performance liquid chromatograph equipped with an ultraviolet diode array detector; λ = 280, eluted by a Zorbax Eclipse XDB-C18 analytical 4.6 x 150 mm 5-micron column; limit of quantification was 0.01µl/liter.

Results

High-Performance Liquid Chromatography. Before samples were analyzed by high-performance liquid chromatography, a serial dilution of known concentration of fipronil was prepared and analyzed to calibrate the instrument and ensure detector linearity. The mean retention time for the fipronil dilutions across all concentrations and sampling periods was 4.80 ± 0.05 minutes. The mean percentage milli-absorbance unit across concentrations in the serial dilutions of fipronil ranked low to high was 7.72 ± 7.76 (0.1 µl/liter), 18.44 ± 8.86 (1.0 µl/liter), 62.55 ± 8.57 (10.0 µl/liter), 466.02 ± 28.21 (100.0 µl/liter), and 4,098.95 ± 345.65 (1,000.0 µl/liter), respectively. In this case, milli-absorbance unit was defined as a logarithmic unit to measure optical density which had a direct relationship to the area under the peak in the chromatogram. The R^2 value for the serial dilutions was 0.9994. The values used to calculate the previous means were used to determine the amount of fipronil in the leachate and soil samples during the study.

Leachate. The mean recovery of fipronil in the leachate samples at Time Zero was 0.00 ± 0.00 µl/liter (treated soil only, no plants). No fipronil was recovered from any leachate sample (plant or no plant) during any post-treatment sampling period.

Soil. The mean recovery concentration of fipronil was 1,101.75 ± 24.21 µg/g (soil only, no plants) in samples at Time Zero. The mean fipronil recovery concentration 1 month after treatment in soil samples associated with plants ranged from 42-73 µg/g (Table 1). There were no significant differences in recovery of fipronil at 1 month between replications with and without plants. The mean amount of fipronil recovered 3 months after treatment was 29-52 µg/g in soil samples with plants and 33 µg/g with no plants. At 6 months after treatment, the mean recovery concentration ranged was 21-37 µg/g in soil with plants and 23 µg/g in soil with no plants. Fipronil was detected by high-performance liquid chromatography in soil samples at 9 months after treatment and ranged from 21-29 in soil samples with plants, 28 µg/g with no plants and at 12 months after treatment, 12-27 µg/g and 40 µg/g with no plants (Table 1). At 12 months after treatment there were significant differences in recovery of fipronil between replications with and without plants (Table 1).

Table 1. Mean (±SE) Concentration (µg/g) of Fipronil 0.12% AI Detected in Soil (All Horizons) via High-Performance Liquid Chromatography in Association with Various Plants through Time

MAT[a]	Red tip photinia	St. Augustine grass	Bermuda-grass	Mexican heather	No plant
1	50.47±10.34a1	59.71±11.61a1	73.27±10.23a1	42.92±10.48a1	36.59±11.67a1
3	51.90±15.22a1	29.65±7.57a1,2	34.61±7.98a2	29.15±6.31a1,2	33.26±9.36a1
6	36.24±6.84a1	20.79±7.26a2	31.79±6.89a2	37.27±7.65a1,2	23.30±6.26a1
9	20.60±5.18a1	26.46±4.21a2	29.37±5.75a2	25.66±6.13a1,2	28.39±5.67a1
12	22.07±5.70ab1	27.08±6.78ab2	27.22±6.21ab2	11.68±4.65b2	40.20±8.60a1

Means followed by the same letter in the same row and means followed by the same number in the same column are not significantly different ($p < 0.05$) per Tukey's HSD (Honest Significant Difference).

[a]MAT = months after treatment.

At 1 month after treatment in fipronil-treated soils separated by horizon, the mean amounts of detectable fipronil were 59.38 ± 8.27 µg/g (top), 82.10 ± 6.55 µg/g (middle), and 17.66 ± 6.39 µg/g (bottom) (Table 2). Fipronil in soils separated by horizon at 3 months after treatment were 45.43 ± 4.91 µg/g (top), 56.79 ± 9.80 µg/g (middle), and 5.41 ± 2.74 µg/g (bottom). Fipronil was detected by high-performance liquid chromatography at 6, 9, and 12 months after treatment in soil separated by horizon and ranged from 8-49 µg/g (Table 2).

Table 2. Mean (±SE) Concentration (µg/g) of Fipronil 0.12% AI Detected in Soil Horizons via High-Performance Liquid Chromatography through Time

	Soil horizon		
MAT[a]	Top	Middle	Bottom
1	59.38 ± 8.27a1	82.10 ± 6.55a1	17.66 ± 6.39b1
3	45.43 ± 4.91a1,2	56.79 ± 9.80a1,2	5.41 ± 2.74b1
6	31.43 ± 4.94b2,3	48.93 ± 5.24a2	10.36 ± 3.64c1
9	26.86 ± 3.53a2,3	43.28 ± 3.97b2	8.43 ± 2.44c1
12	21.15 ± 4.05b3	44.28 ± 5.57a2	11.53 ± 4.07b1

Means followed by the same letter in the same row and means followed by the same number in the same column are not significantly different ($p < 0.05$) per Tukey's HSD (Honest Significant Difference).
[a]MAT = months after treatment.

Discussion

The mean yields of fipronil at Time Zero were 1,101.75 ± 24.21 µg/g and 0.00 ± 0.00 µl/liter in soil and leachate, respectively. High-performance liquid chromatography was used by Kamble and Saran (2005) and Saran and Kamble (2008) to separate and detect fipronil by methods similar to those of this study. A reversed-phase high-performance liquid chromatography method following extraction of samples with acetonitrile/water (3/2, v/v) and cleanup using a silica gel column was developed for water and soil samples for fipronil (Ibrahim 1999, Kamble and Saran 2005). The limit of detection by the high-performance liquid chromatography method was 0.01 µg/mg for fipronil (Hadjmohammadi et al. 2006), which is consistent with the current study. The results of our study agree with those of Hadjmohammadi (2006) who used high-performance liquid chromatography to recover fipronil in 90% of soil samples; the recovery rate in our study was 88%.

The environmental fate of fipronil has been investigated previously. The half-life of fipronil in soil was 124-132 days (Ying and Kookana 2001), depending on groundcover and organic material (Scholz and Spiteller 1992, Rouchard et al. 1994). The U.S. Environmental Protection Agency (1996) reported the half-life of fipronil in soil to range from 102-122 days. The water solubility value of fipronil was 0.0024 g/liter and organic carbon partition coefficient (K_{oc}) was 803 (Mede and Rhone-Poulenc Agricultural Limited 1997, Mize et al. 2008), indicating that fipronil adsorbs to soil particles which reduces the probability that the compound will leach, and that it can provide long-term protection against subterranean termites (Keefer et al. 2012). The water solubility and soil organic carbon-water partitioning coefficient values of fipronil are important in longevity and movement of the chemical in soil.

These factors may influence adsorption to soil and mobility of fipronil in the environment.

A large K_{oc} value coupled with low water solubility suggests that fipronil is not likely to move through the soil and out of the treatment zone. The results of our research supported this statement as indicated by the amounts of fipronil recovered in leachate and soil samples (Tables 1-2). The soil horizon data also showed that fipronil was not very mobile in the environment (Table 2). Low mobility of fipronil in soil was noted by Chatterjee and Gupta (2010). In our study, the amount of fipronil recovered had a larger decrease at 3 months than at 6, 9, or 12 months after treatment which was in contrast to studies by Masutti and Mermut (2007) who observed the largest decrease in fipronil after 90 days. As in our study, Peterson (2010) found vegetation did not affect degradation, mobility, or longevity of fipronil. The amount of fipronil in soil samples in replications with no plants was generally the same for all inspection periods. This suggests the fipronil had bound to the soil and not moving out of the treatment zone (Table 2) which is consistent with studies by Peterson (2010).

The current study indicated that fipronil did not show much potential to leach or run off and contaminate groundwater which is consistent with results by the US EPA (1996) and Burr (1997). Sorption of fipronil to soils has been linked to organic carbon content (Ying and Kookana 2001). The soil in this study had an organic carbon content of 1.0%. In contrast, Reilly et al. (2012) determined that fipronil was capable of leaching into groundwater at 2.2 ng liter^{-1}; the concentration of fipronil detected was <0.01 to 1.0 ppb. It is our opinion that the subsoil in this study was influential in exacerbating the loss/breakdown of fipronil from the treatment zones, given the ample watering required to maintain healthy plant growth throughout the study. Additionally, had more time been allotted to insecticide-soil treatments before the first wash of insecticide, greater adsorbance (to soil) might have occurred because adsorbance to soil is often greater with time (Kamble and Saran 2005).

Fipronil was detected in the soil at all sampling periods (Tables 1-2). If fipronil is detectable at a minimal amount of 0.05 ppm, it is thought the compound applied at termiticidal rates offers continued long-term protection to structures for several years (Peterson 2010). In topical assays, the LD_{50} of fipronil for *Coptotermes formosanus* Shiraki (Formosan subterranean termite) is <0.05 ppm and 0.1-1.6 ng for *Coptotermes formosanus* and *Reticulitermes flavipes* Kollar (eastern subterranean termite) (Mao et al. 2011). In our study, fipronil was recovered 12 months after treatment at amounts greater than the listed LD_{50} (Table 1) for the two prevalent species of subterranean termites in the United States.

The environment of the study was important. All plants were in a greenhouse with warm temperatures during the summer. The environment also had sunlight available to the plants during all daylight hours. The warm temperatures and sunlight led to necessity of copiously watering the plants in the summer and spring to maintain vigor. All plants received 1 liter of water two or three times a week during the summer and 1 liter of water once or twice a week during the spring, thus possibly causing more hydrolysis than under typical field conditions.

Longevity, translocation, and adsorption of active ingredients vary with environmental conditions. The results of this research indicated that fipronil had limited leaching based on the concentration of active ingredient recovered through time in leachate samples (despite frequent watering), which is consistent with the octanol water coefficient of log 4.0 and water solubility of 1.9-2.3 mg/liter

(Anonymous 1996). There were significant differences ($p < 0.05$) between the concentrations of fipronil in the soil profile through time, which indicated slight movement of the active ingredient through the soil, but the product was still available in amounts detrimental to subterranean termites 12 months after treatment (Table 1 no plant, Table 2). There were also significant differences ($p < 0.05$) between concentrations of active ingredient in test units containing plants through time (Table 1), but this was not an indication that the active ingredient was mobile, due to the actual concentrations recovered. Based on the current data we believe it is unlikely that large amounts of fipronil move out of the target zone as documented by previous studies (Bobe et al. 1997, Chatterjee and Gupta 2010, Peterson 2010).

Fipronil is used to control a myriad of pests in urban and agricultural landscapes (Lin et. al 2008, Mize et. al 2008). Benefits of fipronil include 1) low mammalian toxicity (Hainzl et al. 1998), 2) slow-action, 3) non-repellence to termites, 4) binding well to soil, and 5) limited leaching (Su et al. 1997, Remmen and Su 2005, Rust and Saran 2006). All of these factors allow long-term suppression of termite populations (Saran and Rust 2007).

Acknowledgment

This research was supported by internal funds from the Center for Urban and Structural Entomology, Department of Entomology, Texas A&M University, College Station, TX, and from external funds provided by BASF Corporation.

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