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Stability of Imidacloprid (Premise® 75) in a Tank-Mixed Aqueous Solution When Stored in Shade or Sunlight

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Abstract Polyethylene tanks are commonly used by pest management professionals to mix and apply termiticides. These termiticides are susceptible to rapid photolysis and the ability of application tanks to filter sunlight has been questioned. We investigated the stability of imidacloprid (Premise® 75) in aqueous solutions stored in polyethylene tanks under shade or sunlight. Chemical analysis of aqueous solutions sampled at 0, 24, 48, 72, 168 and 336 h revealed that imidacloprid was relatively stable. Our results indicate that polyethylene tanks are adequate to protect imidacloprid from photo degradation.

Keywords Termiticide degradation · Imidacloprid · Polyethylene tanks · Photolysis

Nonrepellent liquid termiticides (e.g., Premise®, Termidor®, Phantom®) have become the products of choice for subterranean termite management (Potter 2007). These termiticides are commonly used as pre- and post-construction treatments for the preventive and remedial control of subterranean termites. Imidacloprid (Premise® 75) is formulated as pre-measured water soluble packets for convenience and to avoid calibration errors. The soluble packets dissolve in water during normal agitation resulting in the desired imidacloprid concentration. Because packets of Premise® are pre-measured, applicators are limited to tank volume increments of 94.63 L resulting in situations where excess termiticide is mixed causing increased costs to pest management professionals.

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Many commercial pest management professionals use truck-mounted tanks to mix and apply termiticides. Tanks vary in size and color but are commonly composed of polyethylene. Tank placement also varies depending on vehicle type and preference of the operating company. Tanks may be mounted inside modified vans or on truck beds. Tanks mounted on trucks are generally not protected from sunlight where as tanks mounted inside vans may have some protection from sunlight.

A common question is, how long will termiticides remain stable in aqueous solution in polyethylene tanks? In such a closed system, the two factors that are of the most importance are hydrolysis and photolysis. Imidacloprid has an aqueous hydrolysis half-life of >30 days (25°C at pH 7) and aqueous photolysis half-life of <1 h (24°C at pH 7) (Fossen 2006).

The kinetics and mechanism of imidacloprid hydrolysis was investigated by Zheng and Liu (1999). They found that imidacloprid was slowly hydrolyzed and was stable up to 3 months in acidic and neutral water. Hydrolysis was more rapid in solutions adjusted to pH 9 (20% loss in 3 months) and temperature also significantly increased imidacloprid hydrolysis under alkaline conditions (Zheng and Liu 1999). However, Sarkar et al. (1999) reported no significant differences in aqueous hydrolysis at pH 4, 7 and 9. In addition, Krohn and Hellpointner (2002) reported that imidacloprid was stable in water between pH 4 and 9 when protected from light under sterile conditions.

Wamhoff and Schneider (1999) investigated the photolysis of imidacloprid and imidacloprid in the formulated product Confidor®. They reported that irradiated imidacloprid in free and formulated aqueous suspensions had a half-life of 43 and 126 min, respectively. These results indicate that formulated imidacloprid may be protected to some degree when compared to non-formulated. However, photolysis still occurred rapidly under UV exposure. We expect imidacloprid to rapidly degrade if exposed to sunlight, even for relatively short periods of time.

Our research objectives were: (1) determine concentration-dependant degradation of imidacloprid (Premise® 75) in tank mixed solutions; (2) determine degradation trends of imidacloprid in tanks stored in shade or sunlight; and (3) determine losses of imidacloprid due to adsorption on tank surfaces.

Materials and Methods

Premise® 75 was obtained from Bayer Environmental Science (Montvale, NJ), batch number 4-98-0181. The active ingredient imidacloprid, 1-[(6-Chloro-3-pryidinyl) methyl]-*N*-nitro-2-imidazolinimine, is contained in formulated water soluble packets. Two packets of Premise® 75 were added to 94.64 L tap water and agitated to create a tank mix of 0.1% imidacloprid in a 132.5 L cylindrical polyethylene leg-tank (Snyder Ind. Lincoln, NE). Dilutions were made of the tank mix stock solution to create 0.05% and 0.075% concentrations.

To simulate conditions used by pest management professionals we used individual polyethylene tanks in this study. Subsamples of each stock tank mix were randomly assigned and transferred to 3.785 L Hudson® Quick 'n' Easy polyethylene deck sprayers (Hastings, MN). Initial volumes of individual tanks were 3.785 L of imidacloprid tank mixes (0.05%, 0.075%, and 0.1%). A total of eight individual 3.785 L tanks were prepared for each concentration tested. To address the issue of imidacloprid adsorption to tank surfaces we also analyzed the degradation of imidacloprid in glass jars. Similar subsamples of each Premise® 75 tank mix concentrations were randomly assigned and transferred to 0.95 L Ball® mason jars (Alltrista Consumer Products Company, Muncie, IN). Tanks and glass jars were randomly assigned to either sunlight or shaded conditions. Glass jars assigned to sunlight conditions were placed inside a 132.5 L cylindrical polyethylene leg-tank and subjected to the same sunlight conditions as the 3.785 L tanks. The experimental setup was a $2 \times 3 \times 2$ factorial with four replications.

Sun and shade tank locations were at the University of Nebraska-Agricultural Research and Development Center (ARDC) near Mead, NE. The sun location was on a field plot >75 m from trees and buildings. Individual tanks were placed on a 1.83 m by 3.66 m metal trailer (ground clearance of 30.5 cm) with flat metal mesh bottom for the duration of the experiment. The shade location was in a metal storage building (4.572 m wide by 12.192 m long by 4.27 high) with no windows approximately 100 m from sun plot location. Individual tanks were placed on a 1.22 m by 2.44 m piece of 1.91 cm plywood lying flat on the concrete floor.

All tanks and glass jars were agitated for 120 s prior to sampling. Samples of the imidacloprid tank mixes were placed in 120 mL amber bottles (The Glass Group, Inc. Millville, NJ). Bottles were then transported back to the laboratory. The sampling interval for this study was 0, 24, 48, 72, 168, and 336 h.

Extraction of imidacloprid from tank samples began with removal of 75 mL of aqueous solution and subsequently combined with 25 mL acetonitrile (ACN) in a 120 mL amber bottle. Sampler bottles were shaken for 10 min on a Wrist Action® shaker (Burrell Corp. Pittsburg, PA). After shaking, a 10 mL sample was removed and weighed. The 10 mL sample was further diluted to 100 mL with 50:50 ACN:H_2O. Samples of this dilution were centrifuged in an Eppendorf centrifuge 5415C (Eppendorf Int., Hamburg, Germany) at 1.0×10^4 rpm for 5 min. The liquid was then removed and filtered with an Arcodisc® 0.45 m filter disc (Pall Corp. East Hills, NY) into a 1.8 mL amber sample injection vial (VWR International). The HPLC used for imidacloprid analysis was a 9050 variable wavelength UV–VIS detector with a 9100 autosampler and 9012 solvent delivery system (Varian Inc. Walnut Creek, CA). The mobile phase was 70:30 H20:ACN. The detector was set to 270 nm and conditions were flow rate of 1 mL per min., 10 μL injection volume, with a total runtime of 20 min. The attached column was a Phenomenex Luna 5u C18 (2) 100A (250 × 4.6 mm) (Torrence, CA). Technical grade imidacloprid, 99% pure, lot #322-16A was obtained from Chem Service (West Chester, PA) and used for the standard curve. Imidacloprid (0.0510 g) was diluted with 50 mL ACN to make the stock solution (1.0098 mg per mL). Serial dilutions of stock solution (0.30, 0.20, 0.16, 0.10, 0.06, 0.03, 0.003 mg per mL) were run by HPLC using the method described above.

Tank solution concentrations were computed from the standard curve and the percent concentration of the tank mixture was calculated based on the following equation:

$$\%\text{AI} = \left[\frac{\text{mg}}{\text{L}}\right] * \left(\frac{1000\text{mL}}{1\text{L}}\right) * \left(\frac{V\text{s}}{W\text{s}}\right) * \left(\frac{V\text{t}}{V\text{tmused}}\right) * (100)$$

where

Concentration = mg/L found using the standard curve
Vs = Sample volume that has been diluted (liters)
Ws = Weight of the sample volume (milligrams)
Vt = Total volume of diluted imidacloprid solution (liters)
Vtmused = Volume of tank mixed used in the dilution (liters)
Conversion factor = 0.1% AI = 1,000 ppm

Concentration (ppm) of imidacloprid tank mixes were analyzed by analysis of variance using the PROC MIXED program (SAS 2001) ($\alpha = 0.05$). Differences were determined using Fisher's LSD procedure ($p \leq 0.05$).

Results and Discussion

No differences were detected in the amount of recovered imidacloprid from 0.1% solutions in tanks held in sunlight versus shade conditions and polyethylene versus glass surfaces at 0 h ($F = 3.33$; df = 3, 12; $p = 0.0562$), 24 h ($F = 0.11$, df = 3, 12; $p = 0.9555$), and 48 h ($F = 2.54$, df = 3, 12; $p = 0.1057$) sampling intervals (Fig. 1). Differences were detected at the sampling intervals 72 h ($F = 4.92$; df = 3, 12; $p = 0.0187$), 168 h ($F = 7.44$; df = 3, 12; $p = 0.0045$), and 336 h ($F = 3.52$; df = 3, 12; $p = 0.0488$).

In tanks with a starting concentration of 0.075%, differences between tanks exposed to sun and shade and between tank surface type were found at 0 h ($F = 15.56$; df = 3, 12; $p = 0.0002$) (Fig. 2). Within the 0 h sampling interval the polyethylene tank type was significantly lower than the concentration detected within the glass jars. No differences were observed among the treatments at 24 h ($F = 2.13$; df = 3, 12; $p = 0.1498$), 48 h ($F = 0.53$; df = 3, 12; $p = 0.6677$), 72 h ($F = 1.39$; df = 3, 12; $p = 0.2935$), 168 h ($F = 0.76$; df = 3, 12; $p = 0.5382$), and 336 h ($F = 0.88$; df = 3, 12; $p = 0.4795$).

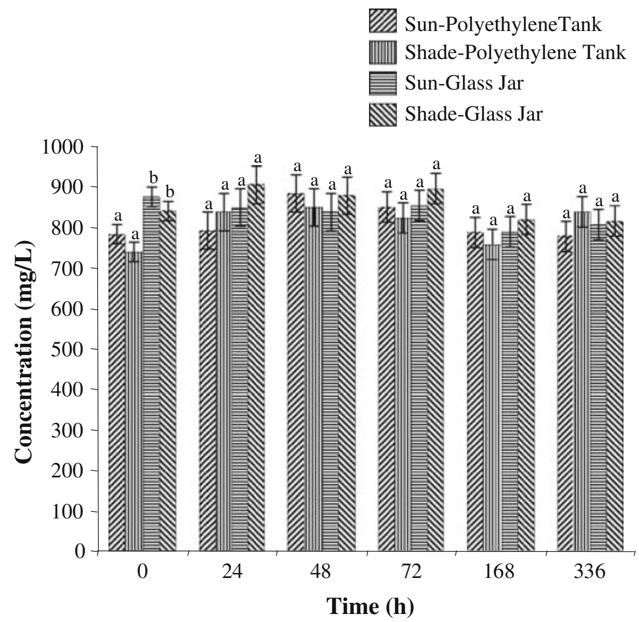

Fig. 2 Degradation of 0.075% imidacloprid in polyethylene and glass tanks exposed to sun or shade conditions. Letters indicate significant differences within specific sampling intervals ($p < 0.05$). Bars indicate standard error of the mean (SEM)

Data for the 0.05% imidacloprid starting concentration showed differences at 0 h ($F = 14.88$; df = 3, 12; $p = 0.0002$), 168 h ($F = 4.76$; df = 3, 12; $p = 0.0207$), and 336 h ($F = 10.01$; df = 3, 12; $p = 0.0014$). No differences occurred at 24 h ($F = 2.88$; df = 3, 12;

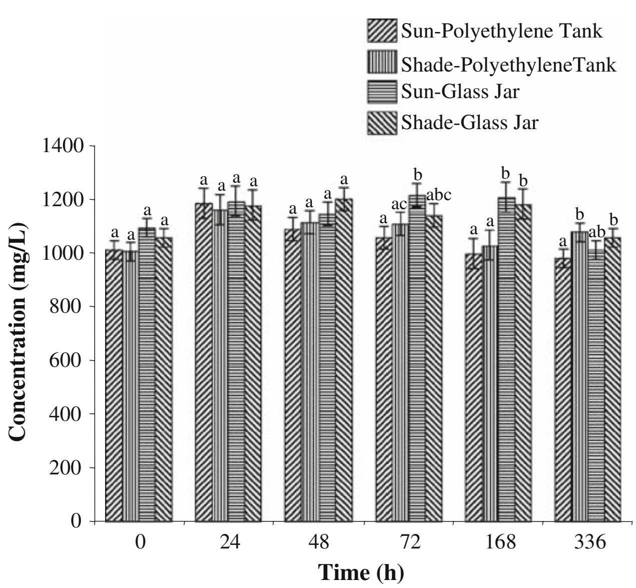

Fig. 1 Degradation of 0.10% imidacloprid in polyethylene and glass tanks exposed to sun or shade conditions. Letters indicate significant differences within specific sampling intervals ($p < 0.05$). Bars indicate standard error of the mean (SEM)

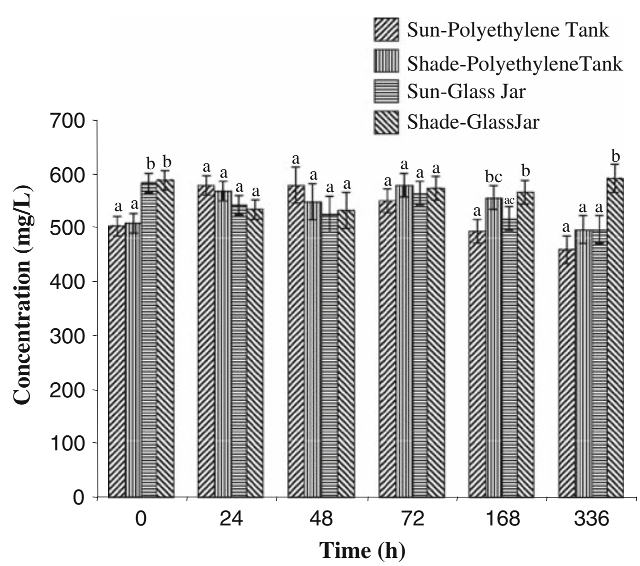

Fig. 3 Degradation of 0.05% imidacloprid in polyethylene and glass tanks exposed to sun or shade conditions. Letters indicate significant differences within specific sampling intervals ($p < 0.05$). Bars indicate standard error of the mean (SEM)

$p = 0.0803$), 48 h ($F = 1.02$; df = 3, 12; $p = 0.4164$), and 72 h ($F = 0.64$; df = 3, 12; $p = 0.6020$) (Fig. 3).

Differences between sampling intervals at all concentrations tested were inconsistent resulting in no definitive degradation trends. Statistical analysis indicated that the rate of degradation was similar among all concentrations tested. No significant differences were detected among light treatments and tank type over all sampling intervals ($F = 1.28$; df = 33, 220; $p = 0.1516$). Time analysis indicated little or no degradation of imidacloprid occurred during the 336 h of testing when exposed to sun versus shade conditions (Figs. 1–3). Additionally, recovered amounts of imidacloprid from polyethylene tanks were generally the same as those recovered from glass jars indicating that with adequate agitation, imidacloprid will not be significantly lost due to adsorption to the tank surface.

One unexplained result was the apparent increase in concentrations from 0 to 24 h. Our observed initial increase in concentration was possibly a result of imidacloprid settling during the short period of time between mixing and transfer to individual test tanks. As a result, we may have underestimated the initial concentration of imidacloprid. We made every attempt to reduce the likelihood of this happening; however it is possible that some settling still occurred.

The results of this study indicate that polyethylene tanks, commonly used by many pest management professionals, are adequate to filter sunlight. Temperature did not appear to cause significant degradation of imidacloprid. Temperatures varied between a nightly low of 13.15–24.76°C to a daily high of 25.65–34.67°C (HPRCC 2005) during this study. This temperature range is typical of that observed in Nebraska during peak remedial and preventative termite applications.

Imidacloprid has a very low Henry's constant of 6.5×10^{-11} atm m^3 $mole^{-1}$ (20°C) (Fossen 2006) essentially making it less volatile than water. As a result, formulated imidacloprid in water could potentially become more concentrated over time. This phenomenon may counter some of the degradation that occurs due to hydrolysis and photolysis as a tank mix ages. However, in a closed tank with no ventilation the air will become saturated with water (100% RH) and may limit further moisture loss and thus limit increasing concentrations (mg imidacloprid per L of water). Conversely, many application tanks are equipped with pressure valves that will release air when under high pressure and allow moisture to escape, especially during hot conditions such as inside of a vehicle or exposed to sunlight.

We recommend that pesticide applicators only mix the desired amount of termiticide required for application. Occasionally, the amount of termiticide required to complete a job may be over estimated leaving unused chemical remaining in the tank. Additionally, when using Premise® 75 applicators are required to mix termiticide in increments of 94.63 L. This may frequently result in more mixed product than is required. Other situations may occur where termiticide is pre-mixed and the subsequent application may be delayed due to inclement weather, etc.

Our results indicate that imidacloprid tank mixes may be used for up to 2 weeks after initial mixing. However, imidacloprid wettable powder will precipitate and may settle to the bottom of tanks and in the crevices as observed in this study. When using previously mixed Premise® 75 termiticide, adequate agitation prior to application is required. This will ensure that settled particulates are properly resuspended. Failure to do so may result in improper termiticide concentrations in the soil and possible control failures.

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