



Evaluation of leaching potential of three systemic neonicotinoid insecticides in vineyard soil

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ABSTRACT

Dinotefuran (DNT), imidacloprid (IMD), and thiamethoxam (THM) are commonly used neonicotinoid insecticides in a variety of agriculture operations. Although these insecticides help growers control pest infestation, the residual environmental occurrence of insecticides may cause unintended adverse ecological consequences to non-target species. In this study, the leaching behavior of DNT, IMD, and THM was investigated in soils collected from an active AgriLife Research Extension Center (AREC) vineyard. A series of column experiments were conducted to evaluate the leaching potential of insecticides under two experimental scenarios: a) individual pulse mode, and b) mixed pulse mode. In both scenarios, the breakthrough pattern of the insecticides in the mostly acidic to neutral vineyard soil clearly demonstrates medium to high leachability. Of the three insecticides studied for leaching, DNT has exhibited high leaching potential and exited the column with fewer pore volumes, whereas IMD was retained for longer, indicating lower leachability. Relative differences in leaching behavior of neonicotinoids could be attributed to their solubility with the leaching pattern $IMD < THM < DNT$ showing strong correlation with increasing aqueous solubility $610 \text{ mg/L} < 4100 \text{ mg/L} < 39,830 \text{ mg/L}$. Triplicate column study experiments were conducted to evaluate the consistency of the breakthrough pattern of these insecticides. The repeatability of the breakthrough curves shows that both DNT and IMD are reproducible between runs, whereas, THM shows some inconsistency. Leaching behavior of neonicotinoid insecticides based on the leachability indices such as groundwater ubiquity score, relative leaching potential, and partitioning between different environmental matrices through a fugacity-based equilibrium criterion model clearly indicates that DNT may pose a greater threat to aquatic resources compared to IMD and THM.

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1. Introduction

Long-term management of pest populations in agricultural operations such as vineyards, citrus orchards, and vegetable farms is a major cause of concern due to potential economic impact to growers. For many years, nicotine based insecticides (nicotinoids) have been used for insect control. The synthetic nicotinoids, hereafter called as neonicotinoids have the similar

mode of action as nicotinoids, but they differ in terms of potency, persistence, efficiency and selectivity (Jeschke and Nauen, 2008; Tomizawa and Casida, 2005). In 1994, imidacloprid (IMD) belonging to the chloronicotinyl class became the first generation of commercially available neonicotinoids followed by thiamethoxam (THM) of thianicotinyl class (second generation) in 2001, dinotefuran (DNT) of furanicotinyl class (third generation) in 2005, and finally in 2012, sulfoxaflor of sulfoximine chemical class became the newest member of the neonicotinoids family of insecticides (Cutler et al., 2013; Maienfisch et al., 2001; Wakita et al., 2003). Neonicotinoids have been extensively used

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in vector management, primarily because they exhibit high insecticidal activity at very low application rates (Jeschke and Nauen, 2008). The systemic insecticides such as DNT, IMD, and THM are among the most widely used neonicotinoids for controlling soil insects, termites, sucking insects such as glassy-winged sharpshooters, and therefore as protection against Pierces' disease (Byrne and Toscano, 2004; Cox et al., 1998; Liu et al., 2006). Although the use of neonicotinoids has greatly reduced the incidence of vector outbreak in vineyards, lawns and other agriculture applications, their occurrence in the environment may pose a greater threat to human health and ecology.

In the post-application scenario, the insecticides are subjected to various abiotic (photo-degradation, hydrolysis, chemical degradation, sorption, plant uptake, volatilization, wind erosion, surface runoff, leaching toward groundwater) and biotic (microbial degradation) fate mechanisms. A literature review of the occurrence, fate, and persistence of neonicotinoid insecticides indicates that there is little information currently available regarding the environmental fate of DNT and THM in a postapplication scenario. The occurrence, fate and movement of a first generation neonicotinoid IMD have been extensively studied; however, to date, there are no studies which demonstrate the movement of DNT in the subsurface environment. The movement of DNT and THM in post-application scenarios is not well understood, but reasonably expected to be a strong function of both the chemical properties of DNT and THM and physico-chemical soil properties.

Persistence and transformation studies conducted by Karmarkar et al. (2006) over a 30-day time period demonstrated that sandy clay loam has the highest leaching potential (81.6%) for THM compared to loamy sand (55.7%), silty clay loam (78.8%), and sandy loam soils (69.5%). Leaching studies on THM demonstrated that 66–79% of THM could leach with the water equivalent of 65 cm rainfall, indicating THM has a potential to leach and affect groundwater under heavy rainfall conditions (Gupta et al., 2008). The sorption behavior of THM on three Indian soils, sandy loam, clay and silty clay with varying physico-chemical properties demonstrated that THM had medium leaching potential (Banerjee et al., 2008). The authors of this study attributed THM's moderate leaching to the soil organic matter content. Unlike THM, no scientific literature is currently available on the leachability of DNT in soil.

To date, little research has been conducted regarding the leaching behavior of neonicotinoid insecticides at field sites. The objective of this research study is to provide insight into the leachability of three neonicotinoid insecticides through soil based on column leaching experiments, empirical models such as fugacity-based equilibrium criterion (EQC) model level III, Gustafson groundwater ubiquity score and relative leaching potential of these compounds in a vineyard soil. The information obtained through this research would help better understand the potential threat to groundwater resources. This is the first study conducted to evaluate the leaching potential of the first, second, and third generations of commonly used insecticides in soil.

2. Materials and methods

2.1. Chemicals

Analytical grade DNT (CAS # 165252-70-0; Assay 99.0%), IMD (CAS # 138261-41-3; Assay 99.9%), and THM (CAS #

153719-23-4; Assay 99.7%) were sourced from Sigma Aldrich (Allenton, PA, USA). The molecular structure and the absorbance spectrum of all three insecticides are shown in Fig. 1. High Performance Liquid Chromatography (HPLC) grade acetonitrile (CAS# 75-05-8; Assay 99.8%) came from Fisher Scientific (Pittsburgh, PA, USA). American Chemical Society-grade calcium chloride dihydrate (CAS# 10035-04-8; Assay 74–78%) was from Spectrum Chemical Manufacturing Corporation. For analytical separation, a reverse phase Phenomenex Kinetex 2.6 μm C18 (50 \times 2.1 mm ID) column was used for HPLC analysis. Millipore Millex® Sterile Syringe Filters (0.45 μm) from Fisher Scientific (Pittsburgh, PA) were used. All the solutions including 20 mg/L stock solutions of DNT, IMD and THM were prepared in nano-pure water (18.2 M Ω cm @ 25 °C) and stored in a refrigerator at 4 °C before use.

2.2. Soil sample collection

Soil samples were collected from the Texas A&M AgriLife Research and Extension Center (AREC) active vineyard located in Stephenville. The vineyard is located in Erath County in North Central Texas, USA. The soil in the vineyard is mapped as a Windthorst Series (Fine, mixed, active thermic Udic Paleustalfs) (Soil Survey Staff, 2012; Stahnke et al., 1980). Four aggregated soil samples (RW-1, RW-2, RW-3 and RW-4) were collected to represent the 5 acres of soils underlying the vineyard. The designation RW-1, RW-2 and RW-3 is used for the soil samples collected from the red grape vineyard; whereas RW-4, is used for the soil samples collected from the white grape vineyard. Each of the four samples is an equally weighted aggregate of five 30 cm deep hand dug excavations (Soil Survey Staff, 2009). Five excavations were used to make each of the aggregate samples and each of the excavations was separated from the others by 3 m. The soils were lightly crushed and air dried and characterized for texture by the pipette method, cation exchange capacity by ammonium acetate at pH 7, pH by 1:2 (weight of soil/weight of 0.01 M CaCl_2), and organic carbon by wet oxidation (Soil Survey Staff, 2009) (Table 1).

2.3. Column study experimental setup

To conduct column leaching experiments, a glass column with an internal diameter (measured at largest diameter) of 50 mm, and effective length (distance between ace-threads) of 300 mm (12 in.) was used (Ace Glass, Inc., Vineland, NJ). Both ends of the column were fitted with a bushing male (ace threaded) adapter at the top and a female NPT thread drilled into the center of the top of the bushing. Both of the adapters made air tight with an O-ring. The top connection facilitates Swagelok fittings and allows for the joining of plastic and metal tubing.

Soil samples collected from the vineyards were packed in the column with compacted lifts of 1 cm depth. A dry packing technique was used to compact the soil in which small lifts of soil (approximately 1 cm in height) were added followed by 50 firm blows from a rubber-tipped plunger. These lifts were repeated until 600 g of soil had been packed in the column creating a soil column height of approximately 20 cm. The lower end of the soil column consisted of an Ace Glass fitting with a 250 μm removable mesh packing support as well as 1 g

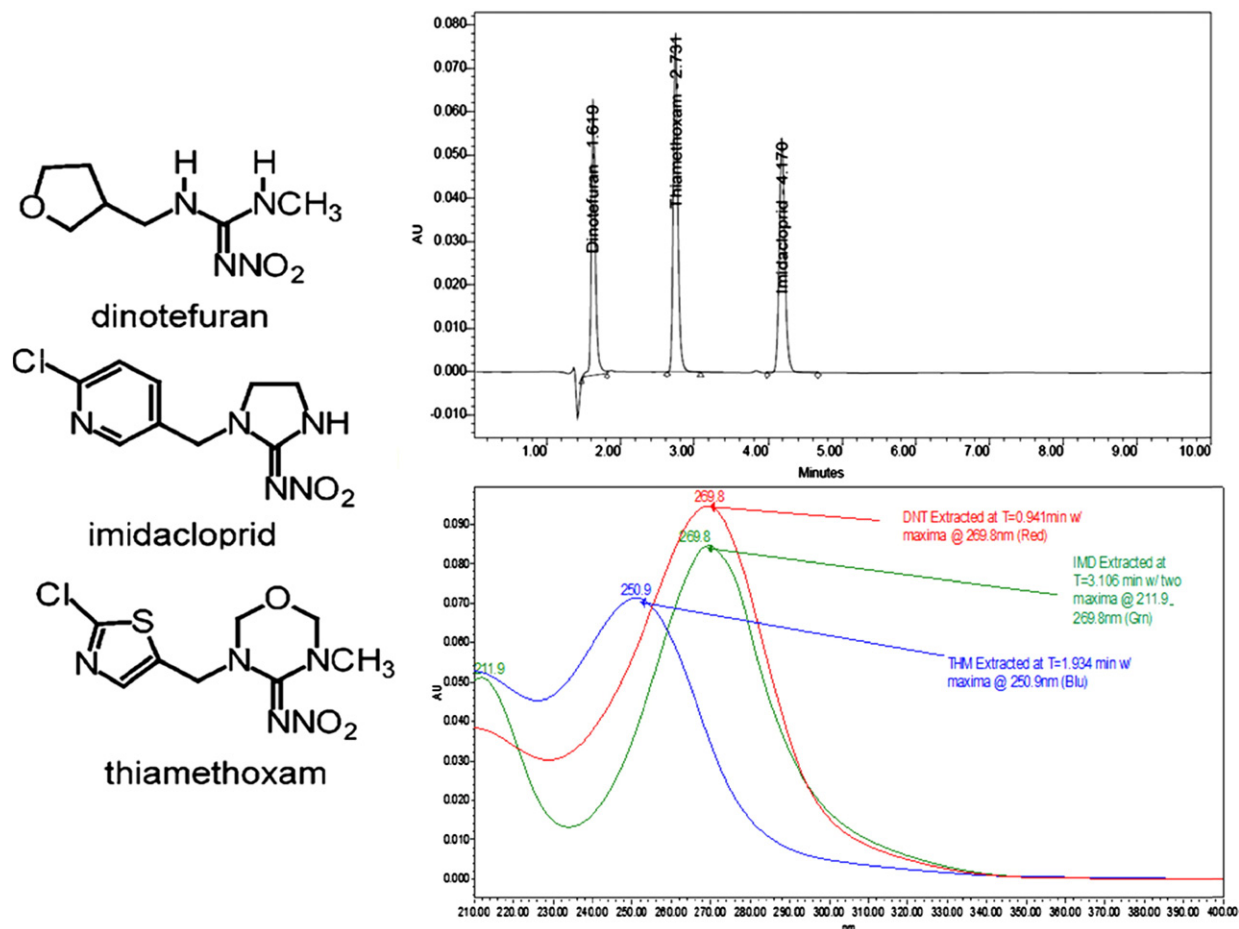


Fig. 1. Molecular structure, chromatogram and spectrum of DNT, IMD, and THM.

of glass wool to ensure the soil particles would not flow out of the column with the filtrate. Two grams of glass wool was placed on top of the soil to disperse the incoming flow and thus reduce channeling and preferential flow paths.

The column was saturated using 0.01 M CaCl₂ feed solution. In order to ensure a fully saturated column, pre-wetting was done by the bottom-up flow method using a Watson-Marlow 302 multiple channel peristaltic pump with 0.3 mm internal diameter tubing as well as a rheostat set to 60% to reduce the flow. This resulted in a flow-rate of around 4 mL/min. After saturation, the flow was reversed. A 1 mL pulse of 20 mg/L solution of insecticide was applied at the top of the column.

Table 1

Physical and chemical properties of soil collected from AREC vineyard located in Stephenville, Texas.

| Properties | Soil sampling locations | | | |
|------------------------------------|-------------------------|------|------|------|
| | RW-1 | RW-2 | RW-3 | RW-4 |
| pH | 6.4 | 5.7 | 6.1 | 6.8 |
| % organic carbon | 0.9 | 0.6 | 0.7 | 1.2 |
| Cation exchange capacity (cmol/Kg) | 14.0 | 13.2 | 11.3 | 15.3 |
| % sand | 57.7 | 67.4 | 56.8 | 57.7 |
| % silt | 9.4 | 11.3 | 15.2 | 22.2 |
| % clay | 32.9 | 21.2 | 28.0 | 20.1 |

Note: The soil texture for the AREC soil was identified as sandy clay loam.

Following the pulse application, the column was continuously flushed using 0.01 M CaCl₂ solution. At least one pore volume of solution was leached prior to collecting the sample for insecticide analysis. This was done to maximize the cost-efficiency of the experiment. The leaching of one pore volume resulted in minimizing the number of test tubes and the syringe filter utilized to process the samples collected in the fraction collector. Approximately one pore volume of water was flushed prior to the output tubing being connected to the fractionate collector to collect samples. The fractionate collector was programmed to pump 1 min of filtrate into each tube. Prior to analytical determination of insecticides, the collected fractionate was filtered through a syringe filter. The column residence time for DNT, THM and IMD was found to be 73, 85 and 200 min respectively.

2.4. Analytical approach

For analytical determination of insecticide concentrations, filtered samples were analyzed isocratically using a Waters Breeze HPLC system. This HPLC system is equipped with a Phenomenex-Kinetex 2.6 μm, C-18 column, 717⁺ autosampler, binary pump, and 2487 UV absorbance detector. The insecticides' separation was carried out under isocratic mode at a flow rate of 1 mL/min with a mobile phase of acetonitrile-water

(15:85, v/v). The retention time for DNT, THM and IMD was observed to be 1.6, 2.7 and 4.2 min respectively (Fig. 1.).

3. Results and discussion

3.1. Soil characterization

Soil was characterized (Table 1) using the commercially available services of the Cornell Nutrient Analysis Laboratory. There was a slight variation in soil properties across the samples. Particle size analysis provides important insight into soil physical continuity, and to a lesser extent chemical behavior (Soil Survey Staff, 2009; USDA and NRCS, 1998). The relative abundance of sand, silt, and clay provides insight into the boundaries of expected saturated conductivity. Large variability in textures, especially the clay fraction, across the study area would have warranted an expectation of variability of interaction of the insecticides with the mineral phases.

Samples RW-1 and RW-3 had greater clay content (32.9 and 28.0% respectively) than samples RW-2 (21.2%) and RW-4 (20.1%) though all are still within the sandy clay loam textural class. The soil reaction classes (pH) were reasonably similar running from moderately acid (pH 5.6–6.0) to neutral (6.6–7.3) (Soil Survey Division Staff, 1993). The percent organic carbon content varied from 0.63 to 1.9% and no relationship seems to exist between clay content and organic matter. The cation exchange capacity (CEC) ranged from 11.32 to 15.31 cmol/Kg soil. Clay content and CEC were not directly related. This is likely due to CEC contributions from the organic matter being uneven due to the difference between native soil reactivity and the characterization method where the index cation solution was buffered to pH 7. Soils with lower initial reactivity are expected to lose exchange capacity in the more alkaline buffered solution that exchanges the index cation. Soil organic matter can have great exchange capacity and there is no evidence of substantive differences in the humified organic matter between the sites because they are under similar management. Therefore, we attribute some of the reported CEC variability between the sites, to losses of measured exchange capacity due to pH dependent charge associated with the organic matter.

3.2. Effect of selected soil properties

All three neonicotinoids DNT, IMD and THM are polar compounds and exhibit weak sorption to soil mineral phases. In the column leaching experiment, low sorption of DNT, IMD and THM in vineyard soil could be attributed to the presence of low organic carbon content. Typically the soil mineral surfaces are predominantly polar in nature with exposed combination of hydroxy- and oxy-moieties to their exterior. These polar surfaces have high affinity for water molecules to form hydrogen bond (Schwarzenbach et al., 2003). Polar neonicotinoids in order to strongly sorb to the inorganic soil mineral surfaces require displacement of tightly bound water molecules which is an energy intensive process. Considering relatively high solubility of neonicotinoids (610 mg/L for IMD, 4100 mg/L for THM and 39,830 mg/L for DNT), it is expected that there will be a weak sorption between soil mineral surfaces and neonicotinoids. On the other hand, partitioning into the hydrophobic organic surfaces will be less energy intensive process and as such

sorption and leaching potential are dependent on organic matter present in soil. Based on the K_{oc} values (coefficient of binding to carbon) for IMD 440 L/Kg, THM 245 L/Kg and DNT 22 L/Kg, it can be seen that both DNT and THM have low binding affinity to organic carbon compared to IMD (Shetlar, 2008). The AREC soils investigated for leaching potential have low organic carbon and as such pose greater risk of leaching of neonicotinoids. It has been reported that leaching will be lower in soils with high organic matter content (Cox et al, 1997; Selim et al., 2010). Furthermore, neonicotinoids have high half-life in soil (over 1000 days) and as such continued application of neonicotinoid might result in accumulating concentrations in soils (Goulson, 2013; USDA, 2009) which under heavy rainfall event might potentially leach into the groundwater. It is generally accepted that sorption of many pesticides is closely related to the amount of soil organic matter than any other single property (Fenoll et al., 2010). Particularly IMD exhibits strong sorption to soil organic material compared to the presence of clay minerals (Broznic et al., 2012; Liu et al., 2002).

Typically, partitioning between insecticide and organic carbon restricts the leaching of insecticides; however, recent studies have offered conflicting views about the role of organic carbon. Research on IMD sorption by Flores-Céspedes et al. (2002) reported that dissolved organic carbon reduces IMD sorption by competing with the IMD molecules for sorption sites on the soil mineral surface. Facilitated leaching by dissolved organic carbon is expected, since the dissolved organic carbon besides competing for adsorption sites, can also potentially increase the solubility of the insecticides in the aqueous media thereby increasing the leaching of these compounds. While the soil organic carbon may increase the sorption of IMD as indicated by Liu et al. (2002), it is generally accepted that sorption increases with the increase in soil organic carbon content with subsequent increase in the hydrophobicity of the compound (Doucette, 2003). The competitive sorption could facilitate leaching of IMD thereby potentially increasing groundwater contamination.

Recent studies on sorption of these insecticides in the sandy clay loam soils suggest very low sorption because of high percentage of sand and silt that minimizes complexation and partitioning onto the solid phase (Kurwadkar et al., 2013). Research on soils similar to the AREC soils demonstrated that sorption–desorption of IMD is sensitive to the percent organic carbon with desorption being lower at low concentration (Cox et al., 1997; Broznic et al., 2012). Although the contribution of clay mineral surfaces to sorption cannot be absolutely overlooked especially when the soil has low organic carbon content, the possibility of weak interaction between these insecticides with the mineral surfaces could also be the reason for low sorption (Fortin et al., 1997).

Banerjee et al. (2008) studied sorption–desorption of THM in sandy loam clay and silty clay. Desorption of THM increased as sandy-loam < clay < silty-clay, which is exactly in the opposite order to that of the sorption process, indicating weak retention of THM in these soil types. Weak sorption of THM in sandy loam was also reported by Gupta et al. (2008) for both the analytical grade as well as commercial formulations of THM, indicating high leaching potential of THM. Perusal of the extensive literature indicates that, as of today, there are no known studies on the sorption–desorption of DNT except studies by Kurwadkar et al. (2013) that reported low sorption

of DNT owing to its high solubility and low octanol–water partitioning coefficient.

3.3. Leaching behavior of neonicotinoids

The breakthrough pattern (Fig. 2) in these moderately acidic to neutral soils demonstrated that DNT had the highest leaching potential compared to IMD and THM. In both, individual and mixed mode column study experiments, very slow leaching of IMD required more pore volumes for breakthrough to occur, compared to DNT and THM (Fig. 2). This behavior of neonicotinoids correlates well with their log–octanol water partitioning coefficient. A similar observation was reported in terms of relative percent mass leached out of the column, with IMD exhibiting the lowest recovery (69.92%) compared to DNT (79.12%) and THM (81.67%). While these differences in leaching potential of neonicotinoids could be attributed to their solubility in water, it is surprising that THM showed an overall larger percentage of mass leaching although at a slower rate. For example, in both individual pulse and mixed pulse mode scenarios, highly soluble DNT was observed to leach quickly and completely exit the soil column after four pore volumes, compared to THM and IMD which required nearly double the pore volumes (Fig. 2).

Both DNT and THM are highly water soluble, with solubility varying from 4100 mg/L for THM and 39,830 mg/L for DNT respectively (PPDB, 2012). Because of their higher solubility, both DNT and THM exhibit low propensity to sorb to the soil material thereby increasing leaching potential. The column leaching experimental data shows kinetic behavior. This is

thought to be due to interaction with soil material owing to its weak sorption. Two factors further added to the kinetic sorption behavior of the insecticides, one being the insecticides not being at sorption equilibrium over the duration of the experiments (<24 h). Studies by Kurwadkar et al. (2013) clearly demonstrated that at least 24 h of equilibration time was required for sorption of these neonicotinoids to occur. Typically for polar organic compounds, at partial equilibrium, rate-limited diffusion on/out of the soil affects sorption kinetics, thereby facilitating leaching of these compounds mostly through advection (Hu and Brusseau, 1996). This is particularly important because DNT, IMD and THM are all polar compounds and can be easily solvated by continuously flowing water molecules leading to weak sorption–desorption of these compounds from soil surfaces. Sorption in column leaching experiments cannot be directly compared with the batch sorption experiments due to the different experimental conditions such as aqueous phase equilibrium concentration, and solid to solution ratio. Furthermore, the accessibility of the sorption sites in the column leaching experiments may be restricted compared to the batch sorption experiments. This is particularly true for the case of densely packed soil columns (Bi et al., 2009). The cumulative effect of partial equilibrium conditions, high solubility of neonicotinoids coupled with low soil organic carbon content has created favorable conditions for sorption kinetics. The net result of these conditions is that the major portion of the insecticides remained in the aqueous phase and leached out of the column with leaching behavior typically following their solubility, i.e. DNT leach faster compared to THM and IMD.

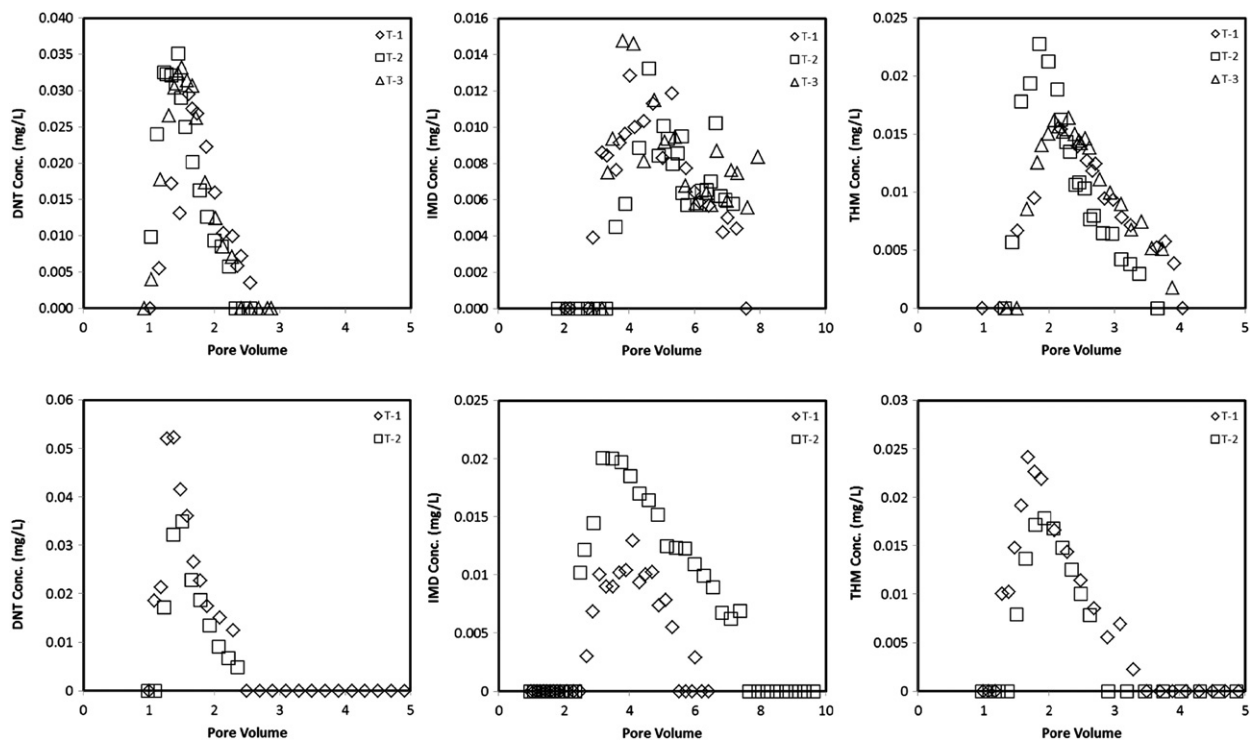


Fig. 2. Soil column leaching pattern of DNT, IMD, and THM under individual pulse mode scenario (top) and mixed mode (bottom). The legends show the triplicate and duplicate runs for the same compound where T-1, T-2, and T-3 indicate the test runs 1, 2, and 3 respectively.

When the similar experiments were repeated with a pulse of all three neonicotinoids, similar relative behavior was observed (Fig. 2). Triplicate runs of the column leaching experiments showed consistent breakthrough patterns. Paired *t*-test was used to evaluate the differences between the pair of trial runs (between T-1 and T-2; T-2 and T-3, and T-1 and T-3). The results of the paired *t*-test clearly demonstrate that at a significance level of 0.10, the trial runs were indistinguishable for DNT and IMD (Table 2). Slight variation in the reproducibility for the breakthrough pattern of THM was observed.

3.4. Leaching indicator: groundwater ubiquity score

Results of the column study experiment demonstrated that DNT has the highest mobility compared to IMD and THM. In general, a preliminary assessment on the mobility, or the leaching potential, of insecticides can be gauged from some of the chemical properties, notably: solubility, log-octanol water partitioning coefficient, etc. Combining the chemical properties of insecticides with soil properties, particularly the percent organic carbon, can offer a better understanding of the leaching potential of those insecticides. One such empirical model proposed by Gustafson (1988) relates the chemical properties of the compound and the soil properties to evaluate the leaching potential of the compound. This model is based on the persistence of insecticides in a subsurface environment (half-life DT_{50} or $t_{1/2}$, time (in days) required for 50% dissipation of initial concentration) and fraction of organic carbon normalized sorption coefficient (K_{OC}). The relationship between these two parameters is referred to as the groundwater ubiquity score (GUS) index.

$$\text{GUS index} = \text{Log}(DT_{50}) * [4 - \text{Log}(K_{OC})].$$

Higher values of the GUS index indicate the insecticide will have higher mobility thereby posing a greater threat to groundwater resources. In general, $\text{GUS} > 2.8 =$ High leachability (leacher); $1.8 < \text{GUS} < 2.8 =$ Marginal leaching potential and $\text{GUS} < 1.8 =$ Low leachability (non-leacher) (Gustafson, 1988).

From this empirical model, it can be clearly seen that, a given insecticide, with a relatively short half-life (DT_{50}) and a large K_{OC} value, will have a lower GUS index, suggesting lower leaching potential. The GUS index calculated for DNT, IMD, and THM (Table 3) indicates that both DNT and THM can be categorized as leachers whereas IMD could be categorized as

having marginal leaching potential. Similar observation was reported by Sarkar et al. (2001) in their studies on persistence and stability of IMD. The authors reported that IMD dissipation follows first order decay with DT_{50} values ranging from 28.7 to 47.8 days. On the other hand persistence studies by Kalpana et al. (2002) reported that residues of IMD were detected in the surface layer (0–10 cm) and also in a subsurface layer (20–30 cm) in two different locations nearly 2.75 years after application. These studies suggest greater persistence of IMD in the environment and subsequent greater leaching potential over longer duration. Based on the GUS index and long retention times in the column study experiments, all three neonicotinoids exhibited leachability. Since the GUS index depends on the persistence which itself is a function of soil properties, a generalization about the GUS index cannot be made because of the inherent variability in the soil material. As such, the GUS index could be tailored for a given soil conditions as shown in the variations in GUS index calculated for all three insecticides (Table 3) in different soil types.

A research study on IMD's GUS index for different soil types in the West Bengal region of India showed that the half-life of IMD and the GUS is both dependent on the type of soil investigated (Sarkar et al., 2001). The authors determined that the half-life of IMD ranged from 28.7 to 47.8 days for different soil types. Banerjee et al. (2008) reported a THM GUS index for sandy loam, clay, and silty-clay soils and observed that in these soil types, THM could be considered to have medium leaching potential. A similar observation was also reported by Fossen (2006) stating that the inability of IMD to adhere to soil particles makes it an ideal candidate to leach out of the active root zone.

The effects of prevailing environmental conditions such as antecedent moisture conditions can also affect the leaching potential. For example, Gupta et al. (2008) stated that under normal field capacity moisture level, THM exhibited high potential for leaching, whereas under natural field condition with inadequate moisture condition, they ruled out the possibility of THM contaminating groundwater. At present, there is no information available in the literature regarding the GUS index for DNT. Table 3 shows the calculated GUS index for DNT based on the K_{OC} and DT_{50} values derived from the literature. As evident from Table 3, a higher GUS index for DNT demonstrates greater leaching potential.

3.5. Leaching indicator: relative leaching potential of neonicotinoids

A variation of the GUS is the relative leaching potential (RLP) index proposed by Hornsby et al. (1991) based on the reduction in mass as the insecticides move through the soil and therefore indicates the leaching potential. The RLP index is essentially a ratio of K_{OC} and DT_{50} and is expressed as:

$$\text{RLP index} = \frac{K_{OC}}{DT_{50}} * 10.$$

The lower the RLP index the greater the leaching potential. This index directly relates persistence and the interaction of insecticides with the soil material as does the GUS index.

Table 2
Statistical reproducibility of column breakthrough between three runs.

| Insecticides | Reproducibility between runs | t-statistic | t-critical | Results |
|--------------|------------------------------|-------------|------------|---------|
| DNT | T-1 and T-2 | 1.605 | 2.110 | P |
| | T-1 and T-3 | 1.855 | 2.110 | P |
| | T-2 and T-3 | 0.241 | 2.110 | P |
| THM | T-1 and T-2 | 6.237 | 2.120 | F |
| | T-1 and T-3 | 6.161 | 2.120 | F |
| | T-2 and T-3 | 0.295 | 2.086 | P |
| IMD | T-1 and T-2 | 0.948 | 2.074 | P |
| | T-1 and T-3 | 2.071 | 2.074 | P |
| | T-2 and T-3 | 1.663 | 2.074 | P |

Note: T-1, T-2, and T-3 indicate the test runs 1, 2, and 3 respectively. P – Pass, F – Fail.

Table 3
Leaching indices of DNT, IMD and THM for various soil textures.

| Neonicotinoids | Soil type | K _{OC} | DT ₅₀ (days) | GUS index | RLP | Leachability | Reference |
|----------------|---------------|-----------------|-------------------------|-----------|-------------|---------------|-----------------------------|
| DNT | Silt loam | 22.00 | 45.40 | 4.40 | 4.85 | High | NYSDEC (2006) |
| DNT | Sandy loam | 45.00 | 173.00 | 5.25 | 2.60 | High | NYSDEC (2006) |
| DNT | Clay loam | 42.00 | 64.30 | 4.30 | 6.53 | High | NYSDEC (2006) |
| DNT | Five US soils | 25.40 | 19–65 | 3.23–4.70 | 3.91–13.37 | High | NYSDEC (2006) |
| DNT | N/A | 26.00 | 82.00 | 4.95 | 3.17 | High | PPDB (Typical) |
| DNT | N/A | 26.00 | 75.00 | 4.85 | 3.47 | High | PPDB (Field) |
| DNT | Various | 6–45 | 81.50 | 4.49–6.16 | 0.74–5.52 | High | USEPA (2004) |
| DNT | Loam | 31.40 | 138.40 | 5.36 | 2.27 | High | USDA (2009) |
| IMD | Various soils | 155–1120 | 365.00 | 2.44–4.64 | 4.25–30.68 | Marginal-High | NYSDEC (1996) |
| IMD | Various soils | 132–310 | 26.5–229 | 2.15–4.44 | 5.76–116.98 | Marginal-High | Fossen (2006) |
| IMD | N/A | 260.00 | 184.00 | 3.59 | 14.13 | High | Miranda et al. (2011) |
| IMD | N/A | 260.00 | 191.00 | 3.62 | 13.61 | High | PPDB ^a (Typical) |
| IMD | N/A | 260.00 | 187.00 | 3.60 | 13.90 | High | PPDB ^a (Lab) |
| IMD | N/A | 260.00 | 174.00 | 3.55 | 14.94 | High | PPDB ^a (Field) |
| THM | Sandy loam | 43–77 | 385–408 | 5.46–6.18 | 1.05–2.00 | High | NYSDEC (2002) |
| THM | N/A | 56.20 | 50.00 | 3.82 | 11.24 | High | PPDB (Typical) |
| THM | N/A | 56.20 | 121.00 | 4.69 | 4.64 | High | PPDB (Lab) |
| THM | N/A | 56.20 | 39.00 | 3.58 | 14.41 | High | PPDB (Field) |
| THM | N/A | 70.00 | 51.00 | 3.68 | 13.73 | High | Miranda et al. (2011) |

^a K_{OC} values are actually Freundlich adsorption coefficients (K_{FC}).

3.6. Equilibrium partitioning between environmental compartments

Besides leaching potential of neonicotinoid insecticides their overall environmental partitioning behavior is also investigated using the USEPA recommended equilibrium criterion (EQC) Level III model. The EQC model version 2.02 was downloaded from the Center for Environmental Modeling and Chemistry website and analyzed for the partitioning behavior of DNT, THM and IMD. This model is based on the fugacity approach (Mackay, 1991) which is the tendency of the compound to partition into different environmental matrices such as air, water, soil, and sediment. For distributions in different media concentrations, the physical/chemical properties and half-lives used in the model were derived from openly available database: Pesticide Properties Data Base (PPDB) developed by the Agriculture and Environment Research Unit of the University of Hertfordshire, UK, and the US Department of Agriculture (USDA, 2009). The partitioning coefficients used in the database were calculated using the K_{OC} values from the PPDB database and the organic carbon content of the AREC soil ($K_d = K_{OC} * f_{OC}$). The remaining values of the partitioning coefficients were obtained from PPDB and USDA databases. The bio-concentration factors were calculated using the USEPA's EPI Suite™ version 4.11. As per EPA recommendations, EQC Level III model analyses were conducted using the default environmental parameters.

Partitioning of these insecticides in the air medium is not considered because all three insecticides have very low vapor pressure, indicating that they are relatively non-volatile and also with low Henry's law constant they are least likely to volatilize from water (Table 4). McKay's classification relating vapor pressure and solubility indicates that both THM and IMD are categorized as type II compound whereas DNT is categorized as type I compound, and as such EQC Level III model analysis were performed accordingly. The EQC model clearly provides most realistic results for environmental distribution of chemicals across different environmental compartments by taking into account the overall chemical make-up of the insecticides and their stability in the defined environment.

The equilibrium partitioning of these insecticides clearly shows that the lowest amount of DNT (47.3% and 0.0946%) being retained in soil and sediment compared to IMD (89.9% and 0.0244%) and THM (72.9% and 0.0471%) (Table 4). Lower retention in soil and sediments is an indication of higher leachability. Based on the EQC Level III model analysis it can be inferred that all three neonicotinoid have leaching potential although their leachability rate varies. The results are consistent with USEPA's observation. According to the USEPA, "Dinotefuran may potentially be present in drinking water, due to its high water solubility, high mobility in soils, and potential persistence in the environment" (USEPA, 2004).

4. Summary and environmental implications

Neonicotinoid insecticides: DNT, IMD, and THM are commonly used in agriculture operations such as vineyards and orchards. Although these insecticides help growers control pest infestations, the application of these insecticides has environmental implications. The results of column experiments suggest that neonicotinoids may be readily available in pore water for plant uptake but may leach to groundwater. Compared to THM and IMD, DNT has consistently shown a higher GUS score and RLP index and lower retention time in the column study, indicating a very high leaching potential. Fugacity-based equilibrium partitioning modeling demonstrated that in the AREC soil, DNT is highly leachable compared to the other two neonicotinoids. A similar observation was reported by the USEPA (USEPA Fact Sheet, 2004).

Based on the results, the higher leaching potential of DNT may pose a greater threat to aquatic resources than IMD and THM. The column experiments demonstrated that all three insecticides have the potential to leach and impact the groundwater, although at varying rates. More specifically, a trend was established regarding the relationship between the solubility of the insecticide and its breakthrough characteristics. More investigations are necessary to better characterize the physico-chemical characteristics of soils that impact root zone efficacy and residency of these neonicotinoids. More

Table 4

Partitioning of insecticides using fugacity based equilibrium criterion level III model.

| Physico-chemical properties | DNT | IMD | THM | References |
|---|---------|---------|---------|-------------------|
| Molar mass (g/mol) | 202.21 | 255.66 | 291.71 | PPDB |
| Henry's Law Constant (Pa m ³ /mol) | 8.7E–09 | 1.7E–10 | 4.7E–10 | PPDB |
| Solubility (g/m ³) | 39,830 | 610 | 4100 | PPDB |
| Vapor pressure (Pa) | 1.7E–06 | 4.0E–10 | 6.6E–09 | PPDB |
| logK _{ow} | –0.55 | 0.57 | –0.13 | PPDB |
| Melting point (°C) | 107.5 | 144.0 | 139.1 | PPDB |
| Half-life (Hr) DT ₅₀ -water | 1939.2 | 720.00 | 734.40 | PPDB |
| Half-life (Hr) DT ₅₀ -soil | 1968 | 4584 | 1200 | PPDB |
| Half-life (Hr) DT ₅₀ -sediment | 2604 | 3096 | 960 | USDA (2009), PPDB |
| K _d (L/Kg) water–soil | 0.2236 | 2.236 | 0.6020 | PPDB ^a |
| K _d (L/Kg) water–sediment | 0.38 | 0.45 | 0.28 | USDA (2009), PPDB |
| BCF (L/Kg) | 0.9439 | 1.063 | 0.9536 | EPI Suite™ v4.11 |
| Percent distribution–water | 52.6 | 10.1 | 27.0 | EQC Level III |
| Percent distribution–soil | 47.3 | 89.9 | 72.9 | EQC Level III |
| Percent distribution–sediment | 0.0946 | 0.0244 | 0.0471 | EQC Level III |

^a Only K_{OC} values were used from PPDB, f_{OC} values were from AREC soil.

refined characterization of the soil (metal oxide content, surface area, un-buffered CEC) might help guide the use of neonicotinoids based on soil conditions.

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