Imidacloprid Fate and Transport in Florida Flatwoods Soils during Control of the Asian Citrus Psyllid

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INTRODUCTION

- **Imidacloprid** (***IMD***, Fig.1) is a systemic insecticide applied to Florida citrus trees as a soil-drench to control the **Asian Citrus Psyllid (*ACP*)** *Diaphorina citri* (Kuwayama), primary vector of the citrus greening disease (CG) (Fig.2). IMD has a high aqueous solubility and low partition coefficient (K_{OC}) values ([1]).
- We have studied IMD environmental fate in Florida Flatwoods soils after soil-drench applications to control ACP.
- The **objectives** of this study were to characterize IMD sorption and degradation in citrus production areas in Florida Flatwoods soils, to monitor IMD leaching from the root zone, to develop a practical citrus leaf tissue extraction procedure and analytical method, to estimate plant uptake, and to correlate ACP control with tissue concentrations.

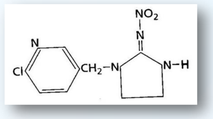

Fig.1. Imidacloprid Molecule.

Fig.2. Citrus Greening Symptoms and ACP ([2]).

HYPOTHESES

- IMD has a high leaching potential in Florida Flatwoods soils (Immokalee Fine Sand, *IFS*) after soil-drench applications due to its low sorption coefficients (K_{OC}).
- IMD is moderately persistent in IFS soils because of its high half-life ($t_{1/2}$) measured in the laboratory.
- IMD leaching out of the root zone will negatively affect the control of the Asian Citrus Psyllid (ACP).
- ACP populations (immatures and adults) will show an inverse relationship with IMD concentrations in citrus leaf tissue.

MATERIALS AND METHODS

1. **Sorption Isotherms**: soil samples from 5 depths (0-15, 15-30, 30-45, 45-60, 60-75 cm) from IFS (sandy, siliceous, hyperthermic Arenic Haplaquods) were equilibrated for 24 h with 4 IMD levels (2, 4, 6, and 8 µg g^{-1} in 0.01 M $CaCl_2$) and K_D values were calculated.
2. **Degradation Study**: Soil samples from 5 depths (Table 1) were spiked with 10 µg IMD g^{-1}. The samples were kept at field capacity (θ_v=0.1) and at room temperature in the dark. IMD concentrations in soil samples were extracted periodically during 17 months.
3. **Leaching Study**: IMD (and Br^- as tracer) were soil-drenched (Fig.3) to young Hamlin orange trees at the University of Florida Southwest Florida Research and Education Center, Immokalee. Soil samples were taken from the root zone (**Planted Area, *PA***. Fig.3), and from nearby soil with no citrus roots (**Non-Planted Area, *NPA***). Both areas were under the same micro-sprinkler irrigation system.
4. **Systemic Pest Control**: ACP adult and nymph populations were monitored during 8 weeks after IMD application using the *tap sample* technique ([3]), and taking leaf tissue samples.
5. **IMD in Citrus Tissue**: We have developed a fast and simple extraction protocol using Methanol (MeOH) and cell disruption using Bullet Blender (Next Advance Inc.). The extracts were filtered with syringes before HPLC MS/MS analysis.

HPLC ANALYTHICAL METHODS

1. **IMD in *soils*** (during degradation and leaching experiments) were extracted with MeOH:Water (80:20), with a 1:2 soil:solution ratio ([4]). We used an Agillent HPLC with UV detection (270 nm), MeOH:Water (40:60) as mobile phase, 1.0 mL min^{-1} flow, and Supelco LC-18 Column. LOD and LOQ (limits of detection & quantitation) were in **ppm** level (µg g^{-1}).
2. **IMD** in ***citrus tissue*** was extracted using 0.25 g of dry mass and 10 mL of MeOH. The extract was diluted 1:1 with HPLC grade water and filtered before HPLC MS/MS analysis ([5]). LOD and LOQ were in ***ppb*** level (ng g^{-1}).

Fig.3. Imidacloprid (and Br^-) Soil-Drench Application to Young Hamlin Orange Trees Root Zone (PA).

RESULTS AND DISCUSSION

- **Sorption Isotherms and Degradation:** Table1 summarizes IMD sorption data indicating **low K_D values** especially for the E horizon.
- The Ap and Bh horizons had higher (and similar) K_D values than the E horizon due to higher organic carbon content (OC, Table 1).
- The data followed **zero-order degradation** rate (k) at all depths (Table 1). Consequently IMD average half-lives ($t_{1/2}$) varied between 0.86 and 2.28 years.
- The highest and the lowest $t_{1/2}$ were measured in the E horizon (30-45 cm) and the Bh horizon (60-75 cm), respectively.

Table 1. IMD Sorption Coefficients (K_D, K_{OC}) and Half-Lives ($t_{1/2}$) at Different Depths in IFS. 95% Confidence Interval Shown.

Depth (cm)	K_D (mL g^{-1})	K_{OC}	OC (g g^{-1})	*k* (µg g^{-1} day^{-1})	$t_{1/2}$ (years)
0-15 (Ap)	1.66 ± 0.09 a	208 ± 11	0.008	0.011 ± 0.002	1.24 ± 0.23
15-30 (E1)	0.31 ± 0.02 b	163 ± 8	0.002	0.008 ± 0.001	1.71 ± 0.22
30-45 (E1)	0.23 ± 0.01 c	230 ± 14	0.001	0.006 ± 0.001	2.28 ± 0.39
45-60 (E2)	0.08 ± 0.002 d	13.3 ± 0.4	0.006	0.014 ± 0.002	0.98 ± 0.14
60-75 (Bh)	1.59 ± 0.06 a	63 ± 2	0.025	0.016 ± 0.002	0.86 ± 0.11

- **IMD Leaching:** The leaching profiles in Fig.4 show IMD relative concentrations at different depths as a function of time (days after application).
- Note that at most sampling dates ***concentrations were higher for NPA than PA***. This is related the citrus *roots uptake*.
- Also, the Br^- tracer was completely leached out from the soil profile (*data not shown*) about 8 days after application.

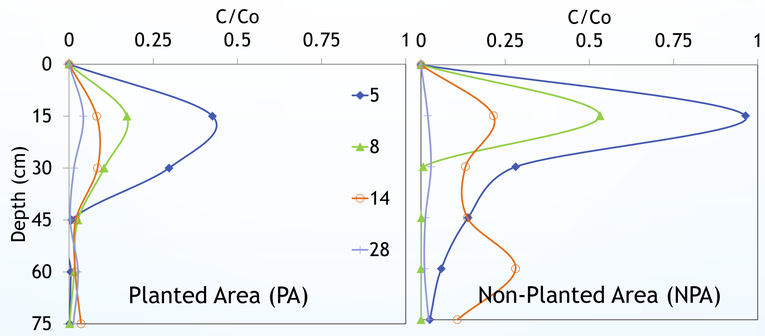

Fig.4. IMD Relative Concentrations (C/C_o) with Depth at Days 5, 8, 14, and 28 After Application for PA and NPA. Summer 2011.

- **ACP Systemic Control:** IMD controlled ACP (adults and immatures) for several weeks. Fig. 5 shows data for Spring 2012, on the same trees where the leaching study was conducted.
- The systemic action on the ACP began about 2 weeks after the soil-drench application, but persisted for up to 7 weeks (Fig.5).

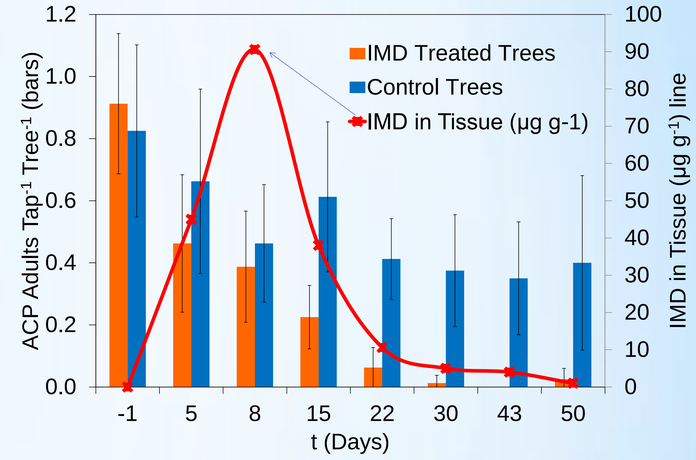

Fig.5. IMD Systemic Control on the ACP (Adults Tap^{-1} $Tree^{-1}$) and Leaf Tissue Concentrations (µg g^{-1}) as a function of time.

- **IMD in Citrus Tissue:** The methods developed for IMD determination in citrus tissue have shown better results using HPLC-MS/MS analysis compared to HPLC-UV.
- Data in citrus tissue show close agreement with IMD concentrations in soils and the systemic control of ACP.
- The peak of IMD tissue concentration (Fig.5) was about 1 week after the application, one week before the ACP adults counts declined to very low values (2-3 weeks after application).

CONCLUSIONS AND RECOMMENDATIONS

- IMD low K_D and long $t_{1/2}$ values indicated that it has a high potential for **leaching** below the root zone, but persistent in Immokalee Fine Sand.
- IMD was mobile in the soil profile but slower than the Br tracer which is not adsorbed (Br leached out about 1 week after application). **IMD leached out** of the root zone about 4 to 7 weeks after application.
- IMD showed **effective systemic control** of the ACP two weeks after application and persisted for 7 weeks even though IMD had leached out of the root zone.
- IMD in citrus tissue data are in close agreement with the ACP control and the IMD soil leaching data.
- IMD efficacy to **control ACP could be improved** by further retarding its movement in the citrus root zone through soil amendments, by close monitoring of application rates, supplemental irrigation and rainfall events.

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