Imidacloprid Miscible Displacement in Soil Columns of Immokalee Fine Sand during Saturated Flow

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INTRODUCTION

- **Imidacloprid** (***IMD***) is a systemic insecticide applied to Florida citrus trees as a soil-drench to control the **Asian Citrus Psyllid** (***ACP***) *Diaphorina citri* (Kuwayama), the primary vector of the citrus greening disease. IMD has a high aqueous solubility and low partition coefficient (K_{OC}) ([1]).
- We studied IMD environmental fate in Florida Flatwoods soils after soil-drench applications to control ACP. Previous work on IMD miscible displacement have shown sorption nonequilibrium during the transport process in soils described by multi-reaction models ([2]).
- The **objectives** of these column studies were to characterize IMD miscible displacement under saturated flow conditions in SW Florida Flatwoods Soils (Immokalee Fine Sand horizons, A, E, and Bh), to analyze IMD breakthrough curves (BTCs), and to obtain solute transport parameters to model its fate using the Convective-Dispersive (CD-Model) and the Two-Site Nonequilibrium model (TSNE) ([3]).

HYPOTHESES

1) IMD will have higher retardation factors (R) in horizons of **Immokalee Fine Sand** (**IFS**) with higher organic carbon content.
2) IMD will show piston displacement in E horizon due to coarse texture and low organic matter content of IFS.
3) IMD will show sorption nonequilibrium during transport in IFS.

MATERIALS AND METHODS

- **Soil Series and Horizons**: The study was conducted in soil samples from 3 diagnostic horizons: A (surface horizon), E (albic horizon), Bh (spodic horizon). The soil is representative of IFS series (sandy, siliceous, hyperthermic, Arenic Haplaquods).
- **Soil packing**: We packed each horizon (A, E, and Bh, separately in a 7.5 cm in diameter and 15 cm long Fig.1).
- **Saturated flow conditions**: We used a pump to maintained a constant pore water velocity (Table 1). Florida rain was used to saturate the soil columns.
- **Fraction collection**: Every 2 min. samples of 10 mL were collected (Fig.2) and kept in the refrigerator until analysis.

Fig.1. Soil Column Showing Wetting front During Bh Horizon Saturation. Photo: J. Leiva

- **Pulse and Tracers:** IMD solution of 70 μg mL^{-1} concentration was applied to the column simultaneously with the fertilizer mixture containing Cl^- and NO_3^-, which were used as tracers for water movement.
- **HPLC Analysis**: IMD solution samples were analyzed by HPLC with UV detection (270 nm), MeOH:Water (40:60) as mobile phase, 1.0 mL min^{-1} flow rate, and Supelco LC-18 Column ([4]).

Fig.2. Experimental setup: column and fraction collector. Photo: J. Leiva

Table 1. Soil Colum Properties.

Column	ρ_b	OC	v	θ	Sand	Clay
A	1.47	1.0	32	0.43	98	1.0
E	1.72	0.6	39	0.35	97	0.1
Bh	1.64	2.5	35	0.37	89	7.0

ρ_b = bulk density (g cm^{-3})
OC = organic carbon (%)
v = pore water velocity (cm h^{-1})
θ = water content
Sand and Clay = %

RESULTS

- **A Horizon:** IMD showed retardation and sorption kinetics. Fig.3 shows how the tracer was eluted after 6 pore volumes (CD-model), whereas IMD showed long tailing and was still present in the column after 16 pore volumes (TSNE-model). The Peclet number was optimized from the tracer breakthrough curve (BTC), and for IMD the optimized parameters were R, β, and ω (Table 2).

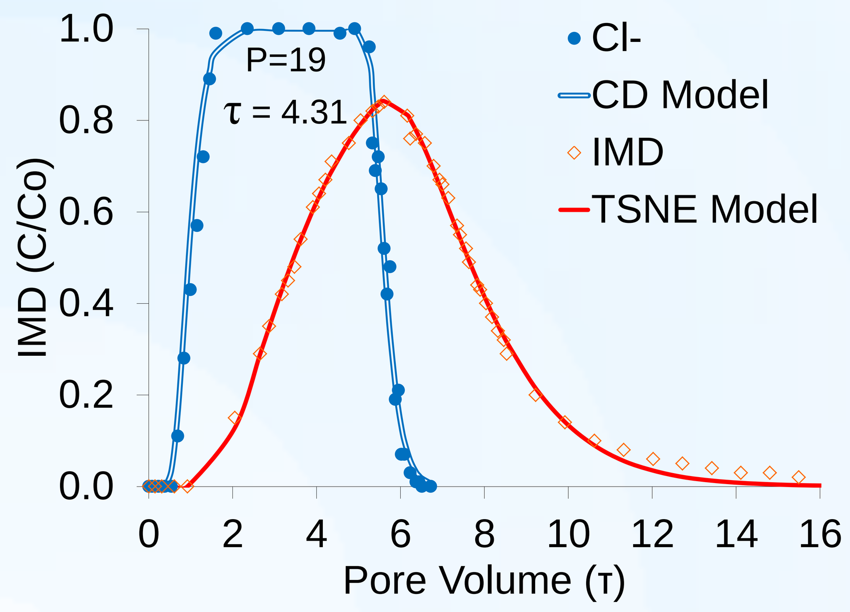

Fig.3. IMD breakthrough curve (diamonds) in A horizon column. Cl tracer (circles). Straight lines show fitted models.

- **E Horizon:** The BTC for IMD showed almost no sorption and no kinetics during transport in the E horizon (Fig.4).

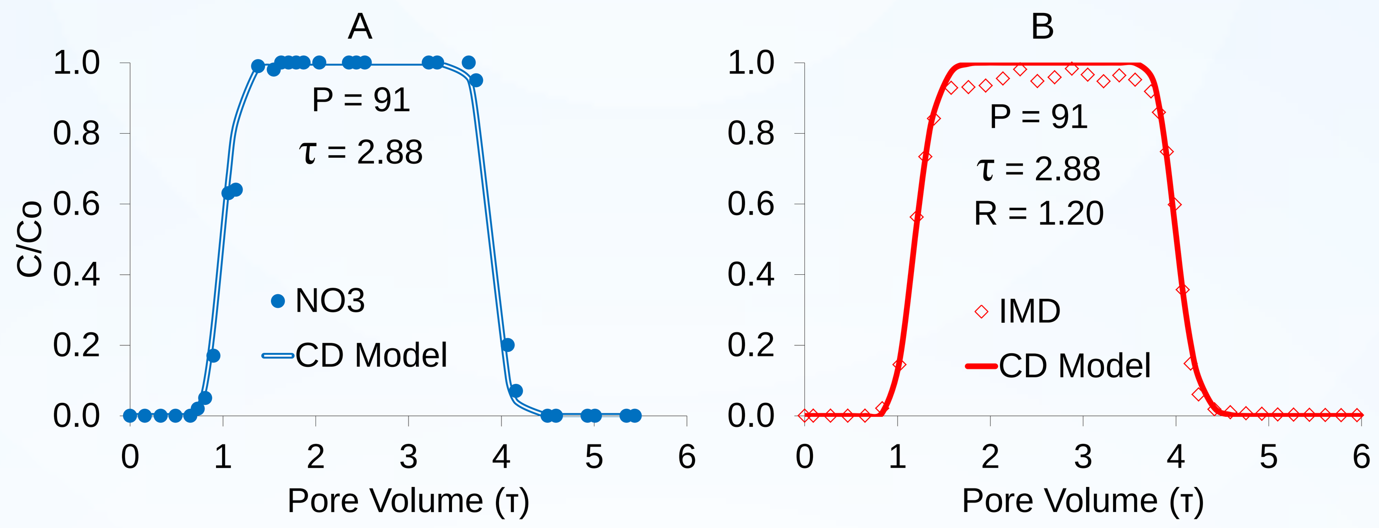

Fig.4. Breakthrough curves in **E horizon** column and fitted CD models. A) BTC for NO_3^- tracer (circles) and B) BTC for IMD.

- The BTC for IMD mirrored the NO_3^- tracer movement and were both simulated with the CD-model, that resembled piston displacement (Fig.4).
- **Bh Horizon:** The BTC for the tracer (CD-model) and IMD (TSNE-model) in the Bh horizon (Fig.5) were very similar to the A horizon (Table 2).
- Based on the BTCs data, IMD transport was described by the CD Model in the E horizon, and TSNE model in the A, and Bh horizons. However, all tracer's BTCs were described by the CD Model.

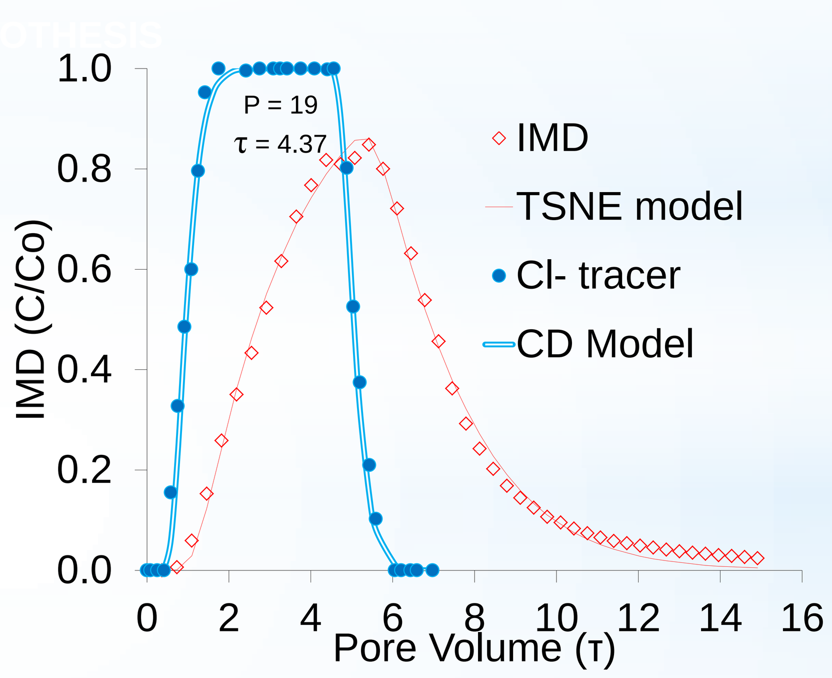

Fig.5. IMD breakthrough curve (diamonds) in **Bh** horizon column. NO_3^- tracer (circles). Straight lines show fitted models.

- **Model Parameters (CD Model and TSNE Model):** Table 2 summarizes the solute transport parameters used to fit the BTCs. Note that the BTCs data were used to optimize parameters R, β, and ω for IMD. Parameters τ and P were not optimized for IMD.

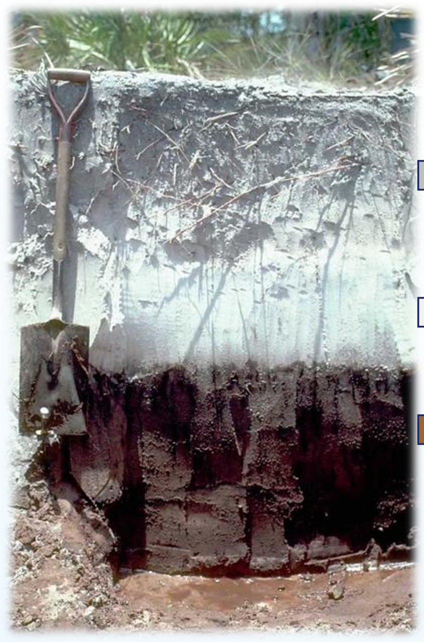

Fig.6. Profile for Immokalee Fine Sand Series. Soil Taxonomy: sandy, siliceous, hyperthermic, Arenic Haplaquods. Photo: USDA-NRCS.

Table 2. Dimensionless Parameters for the CD and TSNE Models in the A, E, and Bh columns.

	τ	P	R	β	ω
A	4.31	19 ± 5	3.83 ± 0.07	0.68 ± 0.07	1.87 ± 0.96
E	2.88	91 ± 30	1.20 ± 0.02	NA	NA
Bh	4.37	19 ± 4	3.20 ± 0.08	0.49 ± 0.20	1.40 ± 0.46

- *τ = pulse (pore volumes)*
- *P = Peclet number [vL/D]*
- *R = Retardation Factor* $[1+\rho_b K_D/\theta]$
- *β = Fraction of instantaneous retardation* $[1+F(\rho_b K_D/\theta)]/R$
- *ω = Ratio of convective residence time to sorption reaction time [k2(1-β)RL/v]*
- *NA : Not Applicable*

DISCUSSION

- **IMD Sorption:** In our studies on sorption we have concluded that IMD is a pesticide with moderate mobility in IFS, but with high leaching potential when it reaches the E horizon (Fig.6).
- Also, IMD retardation factor in the E horizon was much less than in the A and Bh horizons. However, the kinetic parameters were similar between A and Bh horizons (Table 2).
- **Peclet Number:** The E horizon was characterized by high Peclet number (91) indicating minimal dispersion which is due to highly homogeneous sandy soil with low organic matter and clay content (Table 1).
- The exception was the A and Bh horizon that have higher clay and organic matter content that increased dispersion in the porous media, and therefore yielded lower Peclet numbers (Table 2).
- **Sorption Nonequilibrium**: The BTCs for the tracers indicated no presence of physical nonequilibrium (no immobile water) in all three horizons and were described by the CD-model.
- However, the BTCs for IMD in the A and Bh horizons clearly showed presence of intra-sorbent diffusion (TSNE-model). IMD showed a rapid partitioning in instantaneous sites and a long tail, typical of intra-sorbent diffusion nonequilibrium, where an important fraction of the sites (in organic matter) in the soils were rate limited.

CONCLUSIONS

- All hypothesis were accepted based on our findings for IMD miscible displacement in saturated flow column with Immokalee Fine Sand samples.
- Our findings confirm that IMD is a moderately sorbed chemical in IFS, but retardation factors (R were higher in the A and Bh horizons due to higher organic matter contents than the E horizon.
- In practice, the pesticide can be considered as non-adsorbed while passing through the E horizon. This is due to the very low organic matter content found in the E horizon.
- We have found evidence of nonequilibrium in IMD transport in IFS, especially in the A and Bh horizons. We believe the TSNE model can successfully simulate IMD transport phenomena, not only in laboratory conditions, but also for fate and transport modeling in the field.
- In general, after IMD is soil drenched to IFS soil during integrated pest management programs for citrus production in SW Florida, it is important to remember that IMD will be lost through leaching once it passes the A horizon (citrus root zone).

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