Pesticides Sorption Kinetics, Equilibria, and Column Transport Using Fertilizer Mixtures in Soils from Florida and Nigeria

Jorge A. Leiva[1], Nasiru M. Danmowa[1], Peter Nkedi-Kizza[1], Kelly T. Morgan[2], James Jawitz[1], and P. Christopher Wilson[1]

University of Florida, Soil and Water Sciences Department, ([1]) Gainesville, FL; ([2]) Immokalee, FL

ABSTRACT

• **Pesticides soil sorption kinetics (SK) and equilibria (SE)** are measured in *single-pesticide* mixtures with supporting electrolytes such as $CaCl_2$, or KCl ([1]-[2]). Since soil solutions are *complex mixtures* in the field, our **objective** was to compare SK-SE data obtained from both single and complex mixtures of pesticides and nutrients.

• **Soils used (n=3):** Candler sand and Immokalee fine sand (Florida), and Tulluwa upland soil (Semiarid Nigeria). **Chemicals (n=4):** Atrazine (ATR), Imidacloprid (IM), Imidacloprid urea (IM-urea), and Pentafluorobenzoic acid (PFBA, as tracer). (i) **Mix#1:** all 4 chemicals in fertilizer mixture (0.01M NH_4NO_3, KH_2PO_4, and KCl); and, (ii) **Mix#2:** single-pesticide mixtures prepared in 0.01M KCl.

• **SE data** from Mix#1 and Mix#2 were similar across soils. SE was reached before 24 hours and followed the Freundlich isotherm model. **SK data** in Mix#1 were described by **one-site nonequilibrium (OSNE)** or **two-site nonequilibrium (TSNE)** models. The results suggest that these chemicals did not interact in solution and/or did not compete for the same "sorption sites" on soil surfaces.

• **Breakthrough curves** (BTCs) were also analyzed in soil columns at constant saturated water-flow. Tracer's BTCs were described by the convective-dispersive (CD) model. The pesticides' BTCs showed sorption nonequilibrium features described by the OSNE or TSNE, confirming results from SK experiments. Tulluwa soil showed the **lowest sorption,** followed by Candler and Immokalee, a trend explained by the soil organic carbon content. IM-urea was less sorbed than IM across soils.

• **SK and SE data** obtained from either mixture could be used to determine sorption coefficients (K_f or K_D) when pesticides and nutrients exist in the soil solution simultaneously. **Sorption and transport parameters** from CD, OSNE, and TSNE models were not statistically different between batch SK-SE data and BTC optimized parameters, but, the 95% confidence intervals were *smaller* for the BTCs derived parameters.

HYPOTHESIS

Ho: Background electrolyte does not affect sorption kinetics (SK) nor sorption equilibria (SE) of ionizable organic pesticides when the ambient pH is much greater than pKa in three acidic mineral soils from Florida and Nigeria.

Atrazine pKa=1.60, log Kow=2.61, weak base.

Imidacloprid pKa=1.56, log Kow=0.57, weak base.

Imidacloprid-urea pKa=n.d., log Kow=n.d., weak base?.

PFBA pKa=1.60, log Kow=2.06, weak acid.

Fig.1. Molecular structures of Atrazine (ATR), Imidacloprid (IM), Imidacloprid urea (IM-urea), and Pentafluorobenzoic acid (PFBA).

MATERIALS AND METHODS

1. **Soils used:** Immokalee fine sand and Candler sand (Florida), Tulluwa upland (Semiarid Nigeria). Table 1.

2. **Organic Analytes** (Fig.1): ATR; IM, IM-urea, and PFBA.

3. **Supporting electrolytes: Mix#1** = 0.01M NH_4NO_3, KH_2PO_4, and KCl (fertilizer mixture); **Mix#2** = 0.01M KCl.

4. **Sorption Kinetics (SK), Fig.3**: Triplicated 4 g of soil were equilibrated for 2, 4, 6, 8, 12, and 24 hours in 20 mL of Mix#1. C_o was serially diluted with 0.01M KCl to ½C_o and ¼C_o.

5. **Sorption Equilibria (SE), Table 3**: 4 g of soil were equilibrated for 24 hrs. in 20 mL of Mix#2, to compare sorption coefficients obtained in Mix#1.

6. **Breakthrough Curves (BTCs), Fig.4**: Columns (L=15 cm, i.d. 2.54 cm) were packed (see Table 1), and saturation was conducted overnight at steady water-flow rate of 0.5 mL min^{-1} (Fig.2). Eluents were sampled with a fraction collector every 10 to 20 min.

Fig.2. Soil Column or BTCs experimental set-up.

(Soil Column, Fraction Collector, Pump)

7. **Analytical Method** (modified from [3]): SK and SE solutions, and column eluents were analyzed in an Agilent Infinity-1260 HPLC-UV. Mobile phase was 25 mM H_3PO_4 (Na) buffer (pH=4), and acetonitrile (80:20). The flow rate was 0.9 mL min^{-1}. Injection volume was 20 µL in a Supelco C-18 column. LOD and LOQ were at the ppm level (µg mL^{-1}). The method allowed multi-residue determination with gradient elution, and sections with different wavelengths (220 nm & 270 nm).

Table 1. Selected chemical and physical for soils and packed columns, using samples from subtropical Florida (Immokalee, Candler) and semiarid Nigeria (Tulluwa).

	Property	Immokalee	Candler	Tulluwa
Soil	pH H_2O (1:2.5)	4.4	5.5	5.4
	CEC (cmol_c kg^{-1})	7.63	4.50	0.17
	Organic C (%)	0.8	0.7	0.2
	Sand-Silt-Clay (%)	94-5-1	97-1-2	92-6-2
Column	Bulk density ρ_B (g cm^{-3})	1.50	1.63	1.64
	Pore water velocity v (cm hr^{-1})	12.8	15.1	16.2
	Porosity θ (cm[3] cm^{-3})	0.43	0.38	0.37

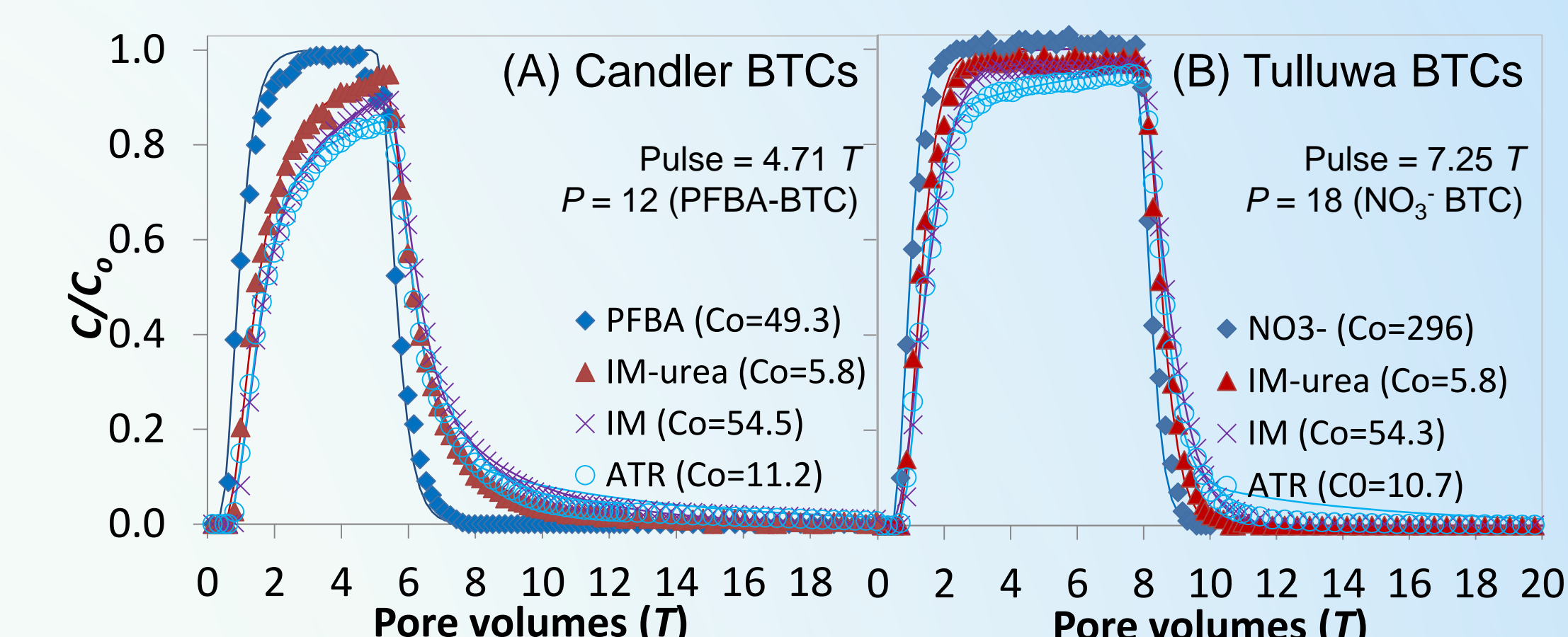8. **Transport Models** (optimized with Stanmod [4]): CD model, OSNE and TSNE models, dimensionless form ([5]) (Table 2).

CD:
$$R\left(\frac{\partial C}{\partial T}\right) = \frac{1}{P}\left(\frac{\partial^2 C}{\partial X^2}\right) - \frac{\partial C}{\partial X}$$

TSNE:
$$\beta R\left(\frac{\partial C_1}{\partial T}\right) = \frac{1}{P}\left(\frac{\partial^2 C_1}{\partial X^2}\right) - \frac{\partial C_1}{\partial X} - \omega(C_1 - C_2)$$
$$(1-\beta)R\left(\frac{\partial C_2}{\partial T}\right) = \omega(C_1 - C_2)$$

OSNE:
$$\left(\frac{\partial C}{\partial T}\right) = \frac{1}{P}\left(\frac{\partial^2 C}{\partial X^2}\right) - \frac{\partial C}{\partial X} - \omega(C - S^*)$$
$$(R-1)\left(\frac{\partial S^*}{\partial T}\right) = \omega(C - S^*)$$

Table 2. Dimensionless expressions for transport model parameters.

Parameter	CD	TSNE	OSNE
P & $[R]$	– –	vL/D & $[1 + \rho_B K_D/\theta]$	– –
β	-	$\dfrac{\theta + f\rho_B K_D}{\theta + \rho_B K_D}$	$1/R$
ω	-	$\dfrac{\alpha(1-\beta)RL}{v}$	$\dfrac{\alpha(R-1)L}{v}$
C_1 or C	C/C_o	C/C_o	C/C_o
C_2 or S^*		$\dfrac{S_k}{(1-f)K_D C_o}$	$\dfrac{S_k}{K_D C_o}$

P= Peclet number
R = Retardation factor
f = Fraction of type-1 sites
β= Instantaneous retardation fraction
ω = Mass transfer time by total time
K_D = Linearized partition coefficient (from K_f, Fig. 4)
S_k = Soil-sorbed concentration

RESULTS AND DISCUSSION

SK Data

• The analytes reached equilibrium concentration (C_t) before 24 hours of shaking, regardless of soil (Fig.3), and the best model describing SK was the two-site kinetic model. Nonetheless, IM showed one-site kinetic mass transfer in Tulluwa showing the importance of soil class (or type) in kinetic sorption processes ([6]).

Fig.3. Sorption kinetics (C_t) as a function of equilibration time for IM, IM-urea and ATR in Mix#1 at 2, 4, 6, 8, 12, and 24 hrs in Immokalee fine sand.

TSNE kinetic mass transfer parameters (Fitted model lines) ± 95% conf. intervals.

Analyte	α (hr^{-1})	f	K_D (mL g^{-1})
ATR	0.08 ± 0.06	0.49 ± 0.08	2.82 ± 0.44
IM	0.11 ± 0.09	0.53 ± 0.10	2.35 ± 0.32
IM-urea	0.08 ± 0.06	0.36 ± 0.09	1.71 ± 0.34

SE Data

• Sorption coefficients followed the Freundlich model ($S_e=K_f C_e^N$) with N exponents between 0.58 to 0.91, and r^2 >0.95 (except ATR in Tulluwa, with a linear K_D, Table 3). K_f **and** N **values** were essentially the **same** between Mix#1 and Mix#2. Tulluwa showed the lowest K_f values, followed by Candler and Immokalee, a trend explained by the soil organic C content (Table 1). IM-urea (a metabolite of IM) was less sorbed than IM across all soils (Table 3).

Table 3. Freundlich sorption coefficients (K_f, mL g^{-1}) and exponent (N) for IM, IM-urea and ATR in Mix#1 and Mix#2 after **24 hours** in three soils (Immokalee, Candler, Tulluwa). ± 95% confidence intervals.

Soil	Analyte	Mix#1 K_f	Mix#1 N	Mix#2 K_f	Mix#2 N
Immokalee	ATR	3.97±0.30 a	0.80±0.05	4.27±0.44 a	0.78±0.06
	IM	5.97±1.01 a	0.74±0.05	5.17±1.03 a	0.76±0.06
	IM-urea	2.94±0.16 a	0.60±0.05	3.50±0.69 a	0.79±0.16
Candler	ATR	0.78±0.20 a	0.79±0.13	1.05±0.56 a	0.75±0.25
	IM	2.10±0.33 a	0.58±0.04	2.01±0.48 a	0.60±0.07
	IM-urea	0.38±0.15 a	0.78±0.27	1.18±0.29 b	0.58±0.17
Tulluwa	ATR	0.20±0.06 a	1.11±0.13*	0.22±0.04 a	1.04±0.09*
	IM	0.30±0.05 a	0.88±0.05	0.27±0.05 a	0.91±0.05
	IM-urea	Not sorbed	Not sorbed	Not sorbed	Not sorbed

Fig.4. Observed (symbols) and fitted (lines) BTCs for PFBA (or NO_3^-), IM, IM-urea, and ATR in Candler (A) and Tulluwa (B) soils. *Co*: Mix#1 (µg mL^{-1}).

(A) Candler BTCs — Pulse = 4.71 T, P = 12 (PFBA-BTC); PFBA (Co=49.3), IM-urea (Co=5.8), IM (Co=54.5), ATR (Co=11.2)

(B) Tulluwa BTCs — Pulse = 7.25 T, P = 18 (NO_3^- BTC); NO_3^- (Co=296), IM-urea (Co=5.8), IM (Co=54.3), ATR (C0=10.7)

Table 4. ATR, IM, IM-urea sorption and transport parameters in fertilizer Mix#1 (±95% confidence intervals) for three soils (Immokalee, Candler, Tulluwa), obtained from SK, SE, and BTC data.
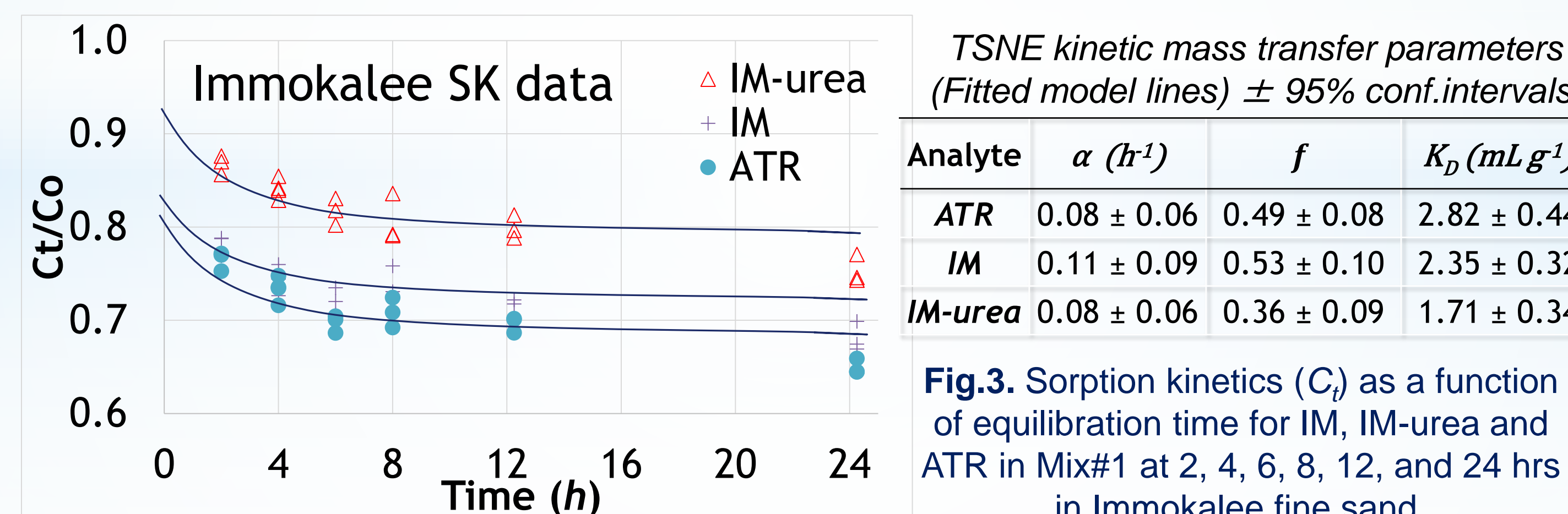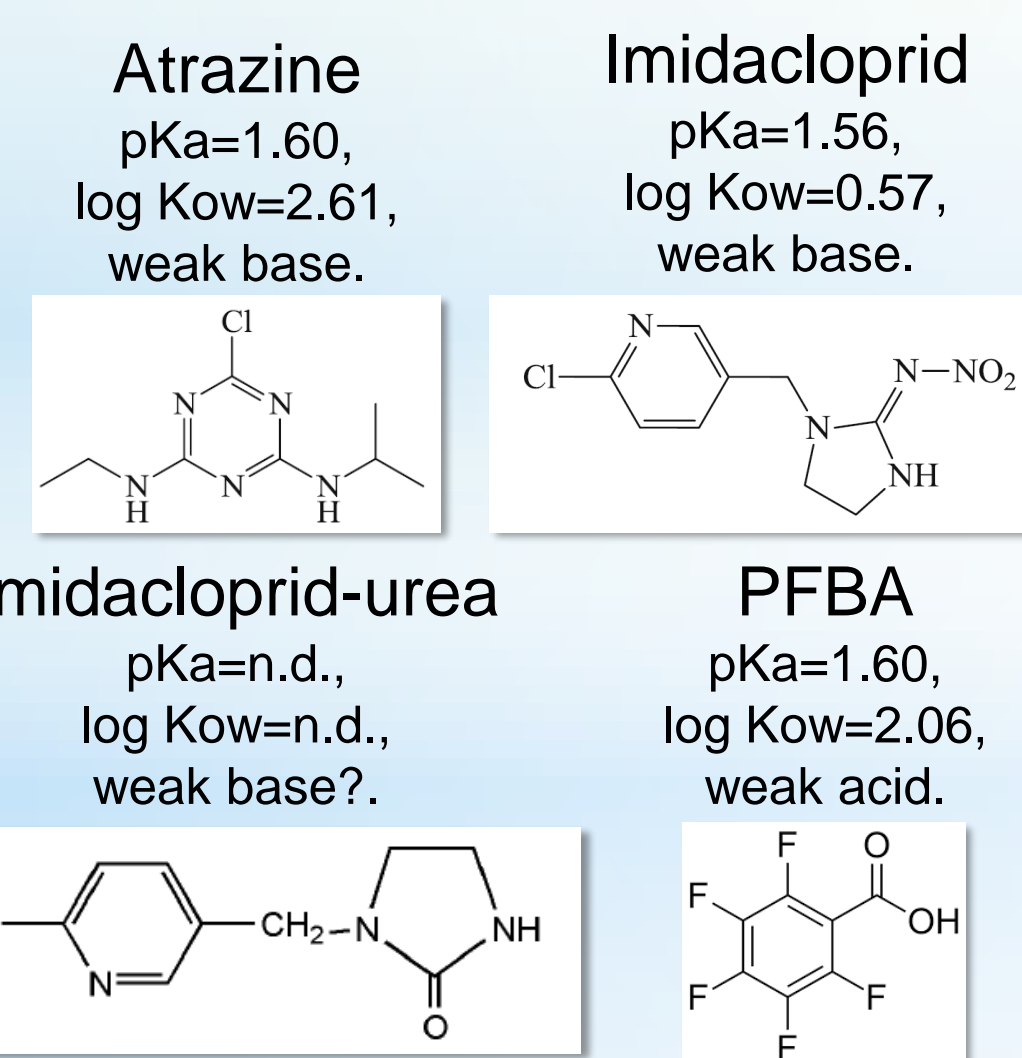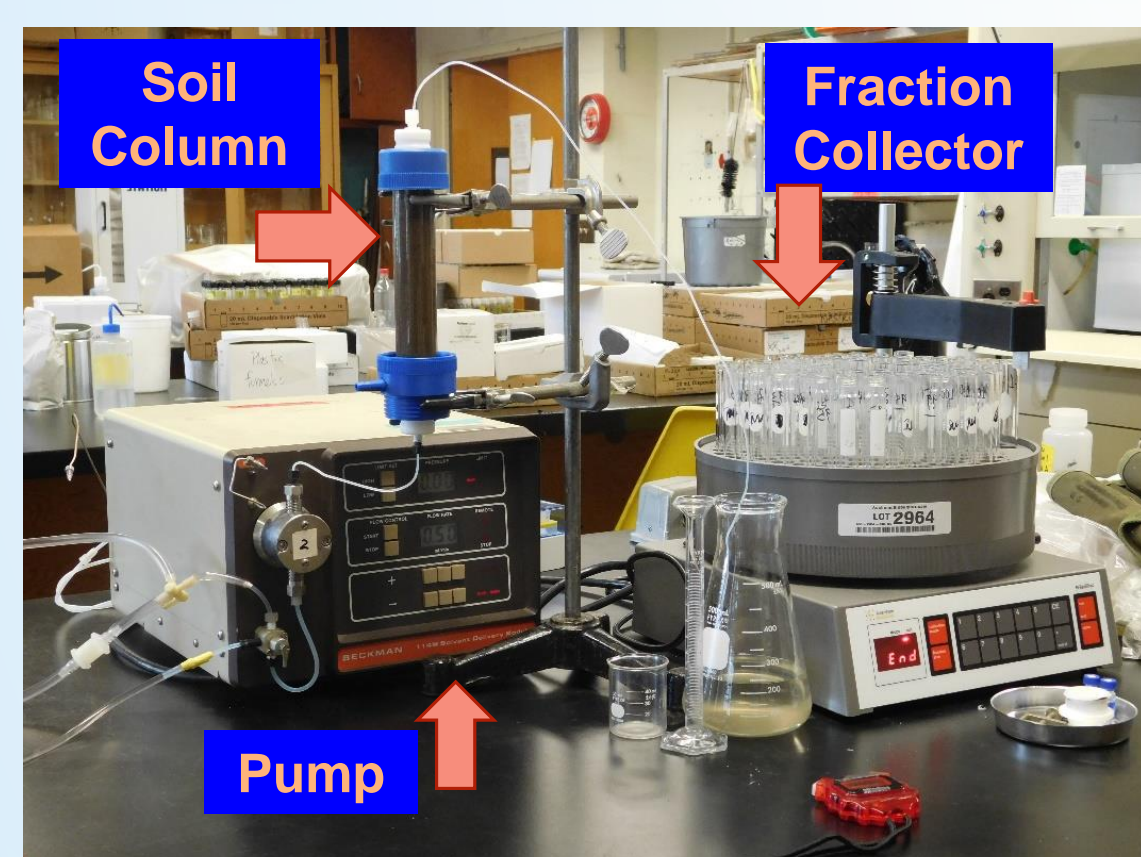
Analyte	Parameter	Immokalee	Candler	Tulluwa
ATR	$R_{(BTC)}$	8.73 ± 0.34	3.16 ± 0.19	2.20 ± 0.17
	$R_{(SE) lin.}$*	11.2 ± 1.50	3.06 ± 1.13	2.11 ± 0.69
	$\omega_{(BTC)}$	1.27 ± 0.07	0.31 ± 0.03	0.15 ± 0.02
	$\omega_{(SK)}$	0.47 ± 0.35	0.51 ± 0.28	n.s.
	$\beta_{(BTC)}$	0.44 ± 0.01	0.52 ± 0.03	0.65 ± 0.04
	$\beta_{(SK)}$	0.54 ± 0.16	n.s.	n.s.
IM	$R_{(BTC)}$	8.80 ± 0.54	2.56 ± 0.05	1.61 ± 0.02
	$R_{(SE) lin.}$	9.96 ± 3.06	2.77 ± 0.59	1.82 ± 0.30
	$\omega_{(BTC)}$	1.08 ± 0.07	0.39 ± 0.03	0.27 ± 0.05 OSNE
	$\omega_{(SK)}$	0.66 ± 0.12	1.16 ± 0.31	n.s.
	$\beta_{(BTC)}$	0.42 ± 0.02	0.65 ± 0.01	n.a.
	$\beta_{(SK)}$	0.58 ± 0.20	n.s.	n.s.
IM-urea	$R_{(BTC)}$	5.96 ± 0.95	1.99 ± 0.04	1.36 ± 0.02
	$R_{(SE) lin.}$	7.00 ± 0.74	2.12 ± 1.03	n.a.
	$\omega_{(BTC)}$	0.60 ± 0.09	0.33 ± 0.05	n.a.
	$\omega_{(SK)}$	0.31 ± 0.22	0.61 ± 0.34	n.s.
	$\beta_{(BTC)}$	0.48 ± 0.07	0.73 ± 0.01	n.a.
	$\beta_{(SK)}$	0.45 ± 0.22	n.s.	n.s.

n.a. = not applicable.
n.s. = nonlinear regression not significant.
* K_D was linearized with the Rao model ($K_D=K_f C_{max}^{N-1}$)

BTCs data

• The tracers' (PFBA and NO_3^-) transport was described by the CD model, with no evidence of regions of mobile-immobile water. Immokalee showed a larger Peclet # (P=58) than Tulluwa and Candler, indicating convective-dominated transport in the former, and evidence of larger hydrodynamic dispersion (D, cm[2] h^{-1}) in the latter.

• IM, IM-urea, and ATR showed chemical nonequilibrium transport described mostly by the TSNE transport model, and by the OSNE describing IM transport in Tulluwa.

• Sorption and/or transport parameters obtained from column BTCs and SK-SE data were not statistically different (Table 4). However, the 95% confidence intervals for the optimized parameters from the BTCs were several times smaller compared to SE or SK results.

CONCLUSIONS

• SE parameters obtained using complex-mixtures could be used to estimate sorption and transport processes when hydrophobic pesticides and nutrients exist in the soil solution simultaneously. The background electrolyte did not affect the SE data for our set of ionizable organic pesticides in acidic soils from Florida and Nigeria that had solution with >> 2 pH units above the pKa values of the probe organic compounds.

• SK data was described by the one-site and two-site kinetic mass transfer models, confirmed by the column transport BTCs.

• Environmental fate and transport parameters (*retardation factors, sorption, and mass transfer coefficients*) derived from BTCs data showed smaller confidence internals than SK-SE data, in general.

REFERENCES

(1) Wauchope *et al.* 2002. Pest Manag. Sci. 58:419-445. -- (2) Katagi, T. 2013. Rev. Environ. Contam. Toxicol. 221:1-105. -- (3) Liu *et al.* 2002. *J. Agric. Food Chem.* 50:6823-6827. -- (4) van Genuchten *et al.* 2012. Transactions of the Asabe 55:1353-1366. -- (5) Skaggs *et al.* 2002. p. 1353-1380. *In* Methods of Soil Analysis: Part4 Physical Methods. SSSA, Madison, WI. -- (6) Leiva *et al.* 2015. J. Agric. Food Chem. 63:4915-4921.