Sorption and Transport of Phosphorus and Nitrogen in Soils from Florida and Nigeria in a Mixture of Fertilizers and Pesticides

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INTRODUCTION

Sorption kinetics and equilibria (SKE) parameters of solutes in soils can be used to understand the fate and transport of solutes in the environment. Most of the sorption parameters are determined for a single solute in soils. However for most agricultural operations in the field a mixture of nutrients and pesticides are applied to crops essentially at the same time. This research was therefore designed to study the effect of a mixture of fertilizer nutrients and pesticides on sorption kinetics (SK) and sorption equilibrium (SE) parameters of P in soils from sub-tropical Florida and tropical Nigeria.

Objectives

- To study the effect of mixtures of organic pesticides and fertilizers (commonly used for citrus and sorghum production) on the sorption of P in soils.
- Use sorption parameters in solute transport models to predict P transport in soils.

MATERIALS AND METHODS

- Surface soil samples (0-30 cm) were collected from Florida (Candler sand and Immokalee fine sand soil series) and from Semi-arid Northern Nigeria (Tulluwa upland soil).
- Two supporting electrolyte mixtures were prepared for P sorption. Mixture 1 (Mix#1) was composed of fertilizers (NH_4NO_3 + KH_2PO_4 + KCl, at 0.01M ionic strength), pesticides (Atrazine, Imidacloprid, Imidacloprid-urea) and a tracer pentafluorobenzoic acid(PFBA). Mixture 2 (Mix#2) was 0.01 M KCl.

Batch kinetics and equilibria experiments

- Batch kinetics and equilibria studies were conducted for each of the three soils at 2, 4, 6, 8, 12 and 24 hours using Mix#1
- P Sorption isotherms were determined for each soil, using Mix#1 and Mix#2 after shaking the samples for 24 hours.

Miscible displacement studies

- Soil column were 15 cm long and 2.5 cm in diameter.
- Mix#2 was used to saturate the columns and Mix#1 was applied as a pulse that was eluted with Mix#2 (0.01M KCl).
- A pump was used to apply 0.5 mL/min, and the effluent collected every 10 mins.

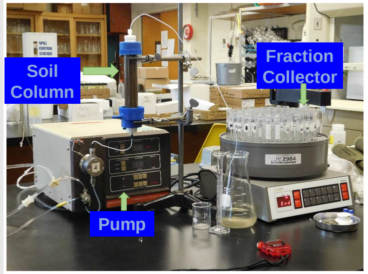

Fig.1. Soil Column experimental set-up.

Table 1. Selected properties for soils used in this study.

Property	Immokalee fine sand	Candler sand	Tulluwa upland
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
Bulk density ρ_B ($g\ cm^{-3}$)	1.50	1.63	1.64
Sand/Silt/Clay (%)	94/5/1	97/1/2	92/6/2
Pore water *v* ($cm\ hr^{-1}$)	12.8	15.1	16.2
Porosity ϑ ($cm^3\ cm^{-3}$)	0.43	0.38	0.37
Oxalate Al (mg/kg)	282	813	142
Oxalate Fe **(mg/kg)**	236	91	302
% (NO_3) recovered from BTC	100	100	100
% P recovered from BTC	66	69	67
% Atrazine recovered from BTC	100	100	100
% Imidacloprid recovered from BTC	100	100	100

Analytical methods

- Nitrate was analyzed by the automated colorimetric method EPA 353.2 (EPA, 1993).
- Phosphorus in solution was analyzed using a modified method of the molybdenum blue method (Murphy and Riley, 1962).

Transport Models (Parameters optimized with STANMOD)

CD model (van Genuchten, 1980), OSNE and TSNE models with sink term (Toride et al., 1995).

CD model

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

TSNE model

$$\begin{cases}\beta R\left(\frac{\partial C_1}{\partial T}\right)=\frac{1}{P}\left(\frac{\partial^2 C_1}{\partial X^2}\right)-\frac{\partial C_1}{\partial X}-\omega(C_1-C_2)\\(1-\beta)R\left(\frac{\partial C_2}{\partial T}\right)=\omega(C_1-C_2)-\mu_2 C_2\end{cases}$$

OSNE model

$$\begin{cases}\left(\frac{\partial C}{\partial T}\right)=\frac{1}{P}\left(\frac{\partial^2 C}{\partial X^2}\right)-\frac{\partial C}{\partial X}-\omega(C-S^*)\\(R-1)\left(\frac{\partial S^*}{\partial T}\right)=\omega(C-S^*)-\mu_2 C\end{cases}$$

Table 2. Dimensionless and Dimensional Parameters

P, R	$---\ vL/D\ ,\ [1+\rho_B K_D/\theta]\ ---$		
β	-	$\frac{\theta+f\rho_B K_D}{\theta+\rho_B K_D}$	$1/R$
ω	-	$\frac{\alpha(1-\beta)RL}{v}$	$\frac{\alpha(R-1)L}{v}$
C_1 or C	C/C_o	C/C_o	C/C_o
C_2 or S^*	-	$\frac{s_k}{(1-f)K_D C_o}$	$\frac{s_k}{K_D C_o}$
μ_2		$\frac{L(1-f)\rho_B K_D \mu_{s,k}}{\theta v}$	$\frac{L(R-1)\mu_s}{v}$

P= Peclet number; R= Retardation factor
β= Instantaneous retardation fraction
ω= Mass transfer time by total time
K_D= Sorption coefficient,
μ_2 = Dimensionless first order decay coefficient for phase 2.
θ = water content; ρ_B = bulk density,
C = solution concentration
(s, k = sorbed, kinetic).

RESULTS AND DISCUSSION3

Sorption Kinetics Data

- P sorption reached equilibrium in 12 hours for all soils (Figs. 3, 4 and 5).

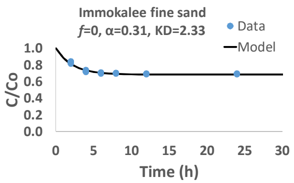

Fig.3. Relative concentration of P as a function of time

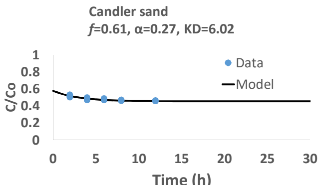

Fig.5. Relative concentration of P as a function of time.

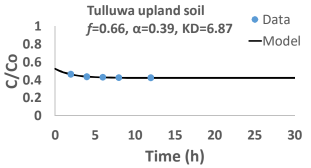

Fig.4. Relative concentration of P as a function of time.

Sorption equilibrium Data

- Sorption isotherm measures in Mix#1 and Mix#2 followed the Freundlich model ($S=K_fC^N$) in the three soils.
- Sorption equilibrium parameters were similar in each soil for both Mix#1 and Mix#2 (Table 3).
- Immokalee fine sand had the lowest sorption coefficient value (Table 3).

Table3: P Sorption isotherm ($S=K_fC^N$) parameters with 95%CI in Mix#1 and Mix#2.

Soil series name	K_f – Mix#1	K_f – Mix#2	N- Mix#1	N- Mix#2
Immokalee	**3.70 (4.56-2.99)**	**4.02 (4.98-3.24)**	**0.82± 0.09**	**0.83±0.10**
Candler	**21.89 (24.01-19.96)**	**19.98 (21.72-18.38)**	**0.66±0.06**	**0.52±0.05**
Tulluwa	**20.60 (27.64-15.36)**	**16.31 (17.63-15.09)**	**0.60± 0.18**	**0.81±0.05**

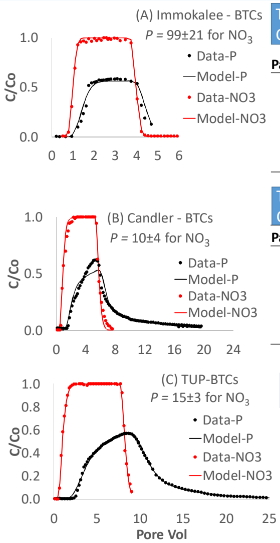

Fig.6: P and NO_3 Breakthrough Curves for Immokalee fine sand (A), Candler sand (B), and Tulluwa Upland (C).

Table4: P Transport parameters with 95% CI for Immokalee fine sand.

Parameter	Value	Optimized	Upper	Lower
P	99	No	NA	NA
R	1.57	Yes	1.68	1.45
$\beta=1/R$	0.65	No	-	-
ω	8.38	Yes	16.63	0.13
μ_2	0.62	Yes	0.68	0.57

Table5: P Transport parameters with 95% CI for Candler sand.

Parameter	Value	Optimized	Upper	Lower
P	10	No	NA	NA
R	13.6	Yes	22.3	4.82
β	0.19	Yes	0.31	0.07
ω	0.77	Yes	0.86	0.69
μ_2	0.09	Yes	0.19	0.01

Table6: P Transport parameters with 95% CI for Tulluwa Upland soil.

Parameter	Value	Optimized	Upper	Lower
P	15	No	NA	NA
R	11.36	Yes	12.51	10.2
β	0.36	Yes	0.39	0.33
ω	0.83	Yes	0.88	0.78
μ_2	0.87	Yes	0.94	0.8

BTCs data.

- NO_3^- transport data were described by the CD model, with no evidence of regions of mobile-immobile water in the soil columns (Fig. 6A, 6B, and 6C). The Peclet number obtained was used to simulate P transport.
- Immokalee fine sand had the largest Peclet number compared to Candler sand and Tulluwa upland (Figs. 6A, 6B, and 6C).
- P sorption was in the order Candler ≥ Tulluwa >> Immokalee.
- The recovered P (based on the areas under the BTCs) was consistently lower than the applied pulse length (about 66% of applied pulse) in all soils. Solute transport models (TSNE and OSNE), that incorporate a sink term (**μ_2**) in the sorbed fraction, were therefore used to describe P transport in all soils (Tables 4, 5, and 6).
- P transport in Immokalee fine sand was described by the OSNE, while TSNE described P transport in both Candler sand and Tulluwa Upland. Because of the irreversibly adsorbed P, the sorption parameters determined in batch studies could not be used to predict P transport. Therefore the parameters (β, ω, μ2 and R) were optimized in the TSNE and OSNE.

CONCLUSIONS

P sorption equilibrium parameters (Kf and N) obtained using a complex-mixture of fertilizers and pesticides were essentially equal to parameters obtained using 0.01M KCl. Therefore the supporting electrolyte did not affect the SE data for the soils from Florida and Nigeria used in the study. However, the batch sorption data could not be used to predict P transport in these soils due to irreversible sorption of P.

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