Langmuir Parameters and Soil Phosphorus Saturation Ratio

B. Dari, V.D. Nair, R.D. Rhue, and R. Mylavarapu
Soil and Water Science Department, University of Florida, Gainesville , FL 32611

UF IFAS UNIVERSITY of FLORIDA

Introduction

- Determination of Langmuir isotherms and subsequent calculation of the phosphorus (P) bonding strength (k), and the equilibrium P concentration (EPC_0) of a soil is a tedious and time-consuming process .
- Higher k-value indicates stronger bonding energy of P with Fe, Al oxides (i.e., low solution P).
- The P retention capacity of a non-calcareous soil depends on the Fe and Al content of the soil.
- The P saturation ratio (PSR) of a soil is the molar ratio of P to (Fe+Al).
- Based on a threshold PSR value (i.e., the PSR above which P release is high; Nair et al., 2004), the soil P storage capacity (SPSC) of a soil can be calculated (Nair and Harris, 2004).
- The SPSC, unlike the PSR, takes into account the Fe and Al responsible for the remaining soil P storage (see Eq. 1 under calculations).
- SPSC can be calculated from P, Fe and Al in an oxalate solution (Ox) or a soil test solution such as Mehlich 1 (M1) (Eq. 1 and Eq. 2) http://edis.ifas.ufl.edu/pdffiles/SS/SS54100.pdf

Hypothesis

- The Langmuir k will be high before the threshold PSR and will tend to zero once the threshold is reached.
- The k value will increase with increase in positive SPSC.
- EPC_0 will be related to the PSR (and SPSC) as determined in an oxalate (Ox) solution or a soil test solution like Mehlich 1 (M1).

Objectives

- To obtain a relationship between: i) EPC_0 and soil PSR, and ii) Langmuir k and soil PSR for Bh horizon of Spodosols dominated by Fe and Al.
  Note: A and E horizons of Spodosols have no P sorbing capacity and generation of isotherms are not possible (Nair et al., 1998).
- To verify that the above k/PSR relationships are applicable to surface horizons of soils (A horizons of Ultisols taken as an example) where the Fe and Al content are lower.
- Relate EPC_0 and Langmuir k to SPSC.

Materials and Methods

Sampling locations: i) Lake Okeechobee Basin, Florida (Spodosols – sandy A and E horizons with no P retention capacity with an underlying spodic (Bh) horizon dominated by Fe and Al
ii) Suwannee River Basin, Florida (Ultisols –sandy marine sediment, A horizon)
Numbers of soil samples collected : 54 (Spodosols) and 10(Ultisols).
Soil Extractions & Chemical Analyses:

- ✓ Soil pH
- ✓ Total elemental analysis using ICP
- ✓ Mehlich-1 extractable P, Fe, Al, Ca and Mg
- ✓ Oxalate extractable P, Fe and Al
- ✓ Water Soluble Phosphorus (WSP)
- ✓ Total Phosphorus (TP)
- ✓ Phosphorus Isotherm determination

References

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Calculations

- $SPSC_{Ox} = (0.05 - \text{Soil } PSR_{Ox})^* [(Fe/56) + (Al/27)] * 31$ (mg kg^{-1})…Eq. 1
- $SPSC_{M1} = (0.08 - \text{Soil } PSR_{M1})^* [(Fe/56) + (Al/27)] * 31 * 1.3$ (mg kg^{-1}) …….Eq. 2

  [0.05 = Threshold PSR_{Ox} for Bh horizon and 0.08 = Threshold PSR_{M1} for Bh horizon of Spodosols; 95% confidence interval from 0 to 0.1 (Chakraborty et al., 2011) using SAS 9.2 software].
- Adsorption parameters (k and EPC_0) were calculated using Langmuir equation:

$$C/S = 1/k\ S_{max} + C/\ S_{max}$$

Where, S = S'+S_0, the total amount of P sorbed, mg kg^{-1}
S' = P sorbed by the solid phase, mg kg^{-1}
S_0 = Originally sorbed P on the solid phase, mg kg^{-1}
C = Concentration of P after 24 h equilibration, mg L^{-1}
S_{max} = P sorption maximum, mg kg^{-1}
k = A constant related to bonding energy, L mg^{-1} P

Linearized form of equation:

$$S' = k'C - S_0$$

EPC_0 is the value of C when S' = 0

Results and Discussion

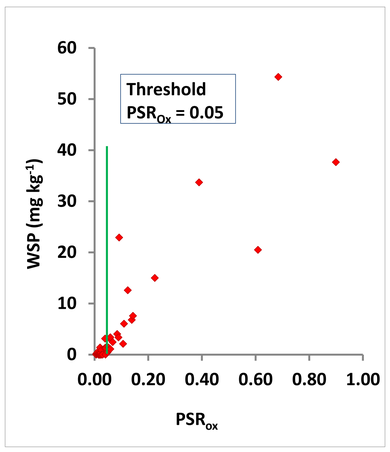

Fig. 1: Relationship between Water Soluble P (WSP) and P Saturation Ratio (PSR) for the spodic horizon calculated using P, Fe and Al in an oxalate extract (PSR_{ox}). Note: WSP increases rapidly after the threshold PSR of 0.05 (Charaborty et al, 2011).

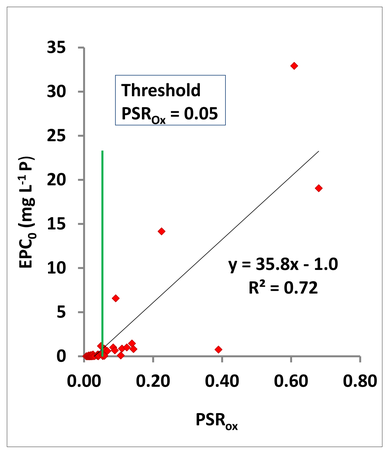

Fig. 2: Relationship between Equilibrium P Concentration (EPC_0) and P Saturation Ratio (PSR) calculated for the spodic horizon using P, Fe and Al in oxalate extract (PSR_{ox}). Note that EPC_0 shows an increase after the change point of 0.05.

- WSP and EPC_0 minimal below the threshold PSR_{Ox} (Figs. 1 and 2)
- WSP increases with PSR_{Ox} above the threshold PSR_{Ox} (Fig. 1)
- EPC_0 increases linearly (R^2 =0.72) with PSR (calculated in either oxalate or a soil test solution like Mehlich 1; only PSR_{Ox} shown here) (Fig. 2)

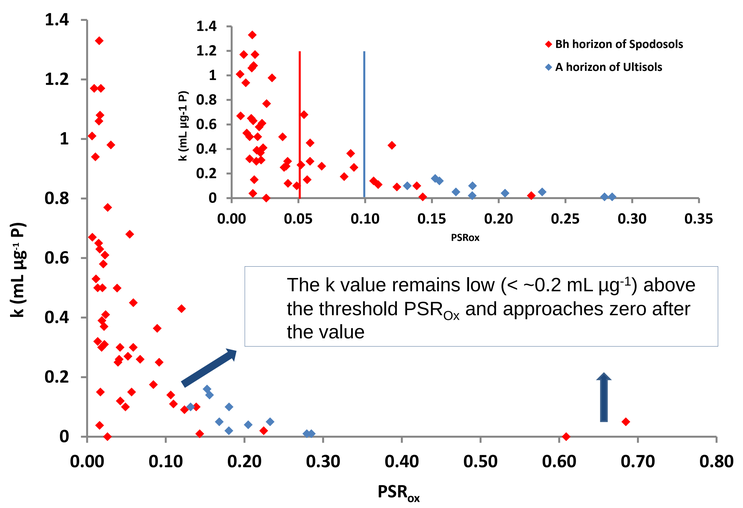

Fig. 3: Relationship between P Saturation Ratio (PSR) calculated from the Bh horizon of Spodosols and A horizon of Ultisols using P, Fe and Al in an oxalate extract (PSR_{Ox}) and the P bonding strength (k) obtained from Langmuir isotherms.
Threshold PSROx = 0.05 for Bh horizons in the graph and indicated with a read line
Threshold PSROx = 0.10 for A horizons and indicated with a blue line

- The PSR/k relationship suggests that the strength of P bonding is high below the threshold PSR (Fig. 3) for both surface horizon of Ultisols and Bh horizon of Spodosols.

- Not able to obtain any specific value of k for PSR below the threshold (Fig. 3)
- Note: The threshold PSR for A horizons of Ultisols, Spodosols, Entisols and Alfisols is 0.10 (CI = 0.05 – 0.15; Nair et al., 2010) and the relationships noted here is expected to be applicable to all Florida A horizon soils.

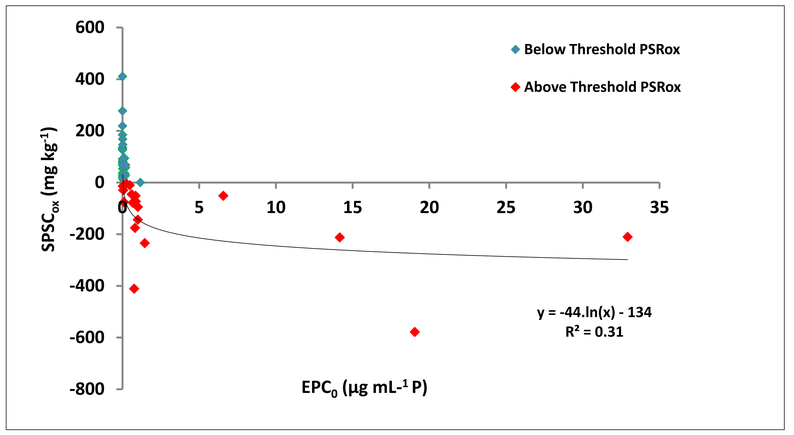

Fig. 4: Relationship between Soil P Storage Capacity ($SPSC_{Ox}$) calculated for the spodic horizon using P, Fe and Al in oxalate extract, and the equilibrium P concentration, EPC_0

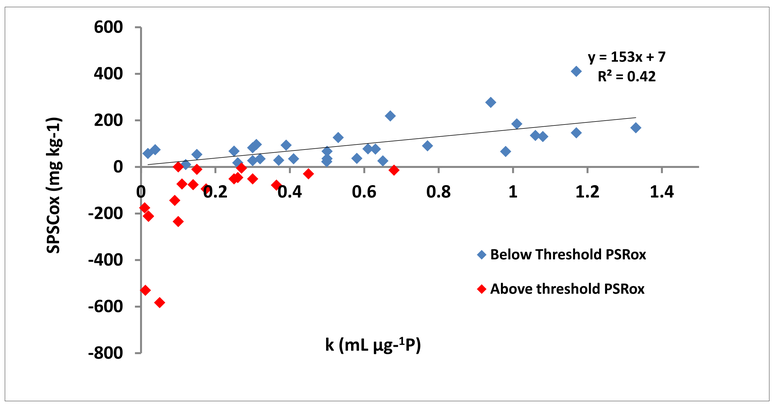

Fig. 5: Relationship between Soil P Storage Capacity ($SPSC_{Ox}$) calculated for the spodic horizon using P, Fe and Al in oxalate extract, and the Langmuir k

- EPC_0 is minimal below the threshold PSR; increases after the threshold value (Fig. 4)
- A SPSC/k relationship allows the strength of bonding (k) for soils below the threshold PSR (positive SPSC) to be estimated (Fig. 5).
- Relationship between EPC_0/PSR and EPC_0/SPSC above threshold value might be better explained by other soil factors like pH, Al, Fe and Ca content of soils.

Multiple Regression Analysis for EPC_0 (above the threshold PSR):

EPC_0 = 13.37 – 4.40 pH * + 0.52 WSP * - 0.0009 TP + 0.002 Ox-Al + 0.001 Ox-Fe - 0.001 Mg + 0.012 Ca * (R^2 = 0.98, P=0.0025*)

- Empirical equation to predict EPC_0 from available soil characteristics using JMP Pro 9.
- EPC_0 is positively related to WSP and M1-Ca but negatively related to pH.

Conclusions

- EPC_0 and P bonding strength (k) can be estimated from P, Fe and Al in an oxalate or soil test solution like Mehlich 1 easily obtained from a soil testing lab without constructing Langmuir equations.
- P bonding strength increases with increase in positive SPSC (i.e., below the threshold soil PSR); such a relationship cannot be obtained from a k/PSR relationship which just indicates that k is high.
- The k/PSR relationship is applicable to surface horizons of all Florida soils where the Fe and Al content are lower.
- Soils with different bonding energies (k) could potentially be used to rank the risk of P loss from land-use systems.
- A simple procedure for determining k would be valuable when such values are needed as input in models for predicting P release from soils on a site-specific basis.

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