

# DIVISION S-2—SOIL CHEMISTRY

## Phosphorus-Sorption Characteristics of Calcareous Soils and Limestone from the Southern Everglades and Adjacent Farmlands

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### ABSTRACT

The understanding of P sorption and desorption by soils is important for safeguarding water quality and for fertilizer management. Little is known about the P-sorption characteristics of the calcareous soils and limestone bedrocks in southern Florida. In this study, 19 samples of calcareous soil and subsurface limestone bedrock were collected from the southern Everglades wetland, pineland, and nearby farmland. At very low P concentrations, P sorption in these soils fit the linear isotherm. The equilibrium P concentration at zero-net P sorption (EPCo) of soils correlated positively with P saturation. Phosphorus-sorption data of soils at medium P concentrations fit the Freundlich and Langmuir equations up to a point at high P concentrations where the slope of the isotherm changed abruptly. In bedrock samples the sorption-isotherm-inflection point, which is caused by P precipitation, occurred at much lower solution P concentrations than in the case of soils (4–18 vs. 400–600 mg mL<sup>-1</sup>). Also bedrock samples had significantly lower Freundlich values,  $K_f$ , than soils. The sorption of P in soils occurred at relatively low solution P concentrations (as indicated by Freundlich value,  $K_f$ ), and appears to be caused by strong affinity of the noncarbonate clay, while the P sorption at relatively high solution concentrations (as indicated by Langmuir maximum sorption,  $S_{max}$ ) appears to be caused by the affinities of both the noncarbonate clay and carbonate clay. Phosphorus-sorption values ( $P_{sorption}$ ) estimated from the one-point isotherm were comparable with the  $S_{max}$  values calculated from the Langmuir isotherm. Phosphorus saturation and the P-retention capacities ( $S_{max}$  or  $P_{sorption}$ ) were correlated strongly to the percentage of P desorption.

THE CHEMISTRY OF P in Florida's acid and organic soils has been well documented (Flaig and Reddy, 1995; Reddy et al., 1995; Harris et al., 1996; Zhou et al., 1997; Li et al., 1999). The relative P sorption, a P-sorption index of the relative P-sorption capacity of sandy soils, has been developed using a one-point isotherm for Florida's acid soils (Harris et al., 1996). However, the P-sorption capacities and desorption potentials of calcareous soils in south Florida have not been reported. This is a serious gap in knowledge because P is considered to be a major factor responsible for ecological degradation of Everglades. Calcareous soils under both sawgrass (*Cladium jamaicense* Crantz) wetland and pineland occupy most of the area of the southern Everglades. Clearly an indepth understanding of P chemistry

in calcareous soils of the southern Everglades and of adjacent areas is needed urgently.

The relationships between P-sorption capacity, P availability and soil components in calcareous soils have been studied in other states and countries. Ryan et al. (1985) reported that P sorption in soils is related more to their Fe oxide than CaCO<sub>3</sub> content. Solis and Torrent (1989) found P-sorption capacity of soil to be highly correlated with Fe oxide and clay content, and that CaCO<sub>3</sub> plays a less important role in P sorption. However, Sharpley and Smith (1985) observed that concentrations of labile P in calcareous soils after fertilizer applications are negatively correlated to CaCO<sub>3</sub> content. Afif et al. (1993) also reported that the ratio of Olsen-P to applied P is negatively correlated to Fe oxides content at low P application rates and to CaCO<sub>3</sub> content at high P application rates. Most previous studies involved agricultural soils with active CaCO<sub>3</sub> content of <300 g kg<sup>-1</sup> (Holford and Mattingly, 1974, 1975a). Thus the P chemistry in nonagricultural soils or agricultural soils with CaCO<sub>3</sub> contents as high as 928 g kg<sup>-1</sup> has not been elucidated clearly. Calcareous soils often contain limestone fragments or lie directly upon limestone bedrock. Holford and Mattingly (1975b) measured the P-sorption capacity of ground limestone. Since the P-sorption capacity of carbonate depends strongly on its surface area (Amer et al., 1985), more research is needed to study the P-sorption characteristics of unground intact limestones.

The ability of soil to release sorbed P to the environment is dependent on both P-sorption capacity and amount of P sorbed. When the amount of sorbed P increases after P application to soils, soil-P desorption tends to increase, and this in turn, leads to increases in P loss through runoff or leaching. The concept of the degree of P saturation (DPS) has been introduced recently as an environmental index of soil P available to be released through runoff and leaching to surface and subsurface waters. This concept has been applied successfully to different soils in the Netherlands and to some soils in the USA (Breeuwsma and Silva, 1992; Sharpley, 1995). Phosphorus saturation is defined as:

$$DPS (\%) = \frac{\text{Extractable P } (\mu\text{g/g})}{\text{P-sorption Maximum } (\mu\text{g/g})} \times 100 \quad [1]$$

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Published in Soil Sci. Soc. Am. J. 65:1404–1412 (2001).

**Abbreviations:** EPCo, equilibrium phosphorus concentration at zero-net P sorption; DPS, degree of phosphorus saturation; PSI, phosphorus-saturation index; \*, \*\*, \*\*\*, Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

where extractable P is either oxalate-extractable P from noncalcareous soils (Breeuwsma and Silva, 1992), Mechlich-1 P (Sallade and Sims, 1997), or Mechlich-3 P extractable from acid and calcareous soils (Sharpley, 1995). The P-sorption maximum can be calculated from oxalate-extractable Al and Fe of noncalcareous soils (Breeuwsma and Silva, 1992; Pote et al., 1996), or determined from the Langmuir sorption maximum for acid and calcareous soils (Sharpley, 1995; Sallade and Shims, 1997). For estimating the P-sorption maximum in calcareous soils, the development of a simple, inexpensive measurement to replace the Langmuir-sorption isotherm, such as a single-point-isotherm method is needed.

The objectives of this study were (i) to determine P-sorption parameters of calcareous soils and limestone bedrocks from wetland, pineland, and farmland in southern Florida; (ii) to develop a single-point isotherm for estimating the P-sorption capacity; and (iii) to determine the relationships between P saturation, equilibrium-P concentration at EPC<sub>0</sub>, sorption capacity, desorption potential, and selected soil properties.

## MATERIALS AND METHODS

### Soil Properties

Samples of soils and limestone bedrock were collected from native pineland and wetland from the southern Everglades, and from adjacent vegetable fields and fruit groves (Table 1). The samples of Krome soil (loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents) were taken from farmland, and the samples of Biscayne soil (loamy, carbonatic, hyperthermic, shallow Typic Fluvaquents) were taken from wetland and vegetable fields, while the samples of Chekika soil (loamy skeletal, carbonatic, hyperthermic Lithic Udorthents) were taken only from vegetable fields. The very shallow, non-rock-plowed soil from pineland was classified as Rockdale in 1958 soil survey (USDA, 1958). Rock-plowed Rockdale soils were renamed as Krome soils in 1996 soil survey (USDA, 1996b). The soil samples were air dried, and ground to pass a 2-mm sieve.

The equivalent carbonate content was analyzed using a titrimetric method (USDA, 1996a). Organic C was determined using the method of Walkley and Black (1934). Soil particle size was determined using a pipette method after removal of carbonate and organic C using pH 5 NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, respectively, and then using Na<sub>2</sub>CO<sub>3</sub> as a dispersion agent. Soil particle-size distribution without removal of carbonate was measured also by means of the pipette method after removal of organic C using 5% NaClO<sub>3</sub> and 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution, and using Na<sub>2</sub>CO<sub>3</sub> as a dispersion agent. Extractable P in soils was determined colorimetrically (Olsen et al., 1954). Soil pH was measured after 2-h equilibration in deionized water at a soil/solution ratio of 1:2.5.

### Phosphorus Sorption and Desorption

A 3-g soil sample or a near 3-g piece of bedrock, was weighed into a 50-mL centrifuge tube. Thirty milliliters of 50 mM KCl solution containing 0, 0.1, 1, 5, 20, 50, 100, 200, 400, 600, 800, 1000, or 1250 mg P mL<sup>-1</sup> was added to each soil sample, respectively. Also 0, 0.04, 0.1, 1, 2, 5, 20, 50, 100, 200, or 400 µg P mL<sup>-1</sup> was added to each bedrock sample, respectively. Each tube with suspension was shaken for 24 h

**Table 1. Summary of soil characteristics data.**

| Sample no.                  | Soil name | Total clay | Noncarbonate clay† | g kg <sup>-1</sup> |                      |           | pH   |
|-----------------------------|-----------|------------|--------------------|--------------------|----------------------|-----------|------|
|                             |           |            |                    | Carbonate clay     | Carbonate equivalent | Organic C |      |
| <b>Pineland</b>             |           |            |                    |                    |                      |           |      |
| 3                           | Rockdale‡ | 464        | 447                | 16.5               | 61.4                 | 48.3      | 7.80 |
| 17                          | Rockdale  | 735        | 699                | 36.0               | 45.8                 | 46.7      | 7.50 |
| 20                          | Rockdale  | 725        | 715                | 10.4               | 34.1                 | 93.5      | 7.31 |
| <b>Wetland</b>              |           |            |                    |                    |                      |           |      |
| 16                          | Biscayne  | 619        | 494                | 215                | 317                  | 55.4      | 7.84 |
| 18                          | Biscayne  | 603        | 451                | 452                | 724                  | 85.5      | 7.81 |
| 21                          | Biscayne  | 273        | 58.7               | 214                | 743                  | 87.2      | 7.65 |
| <b>Vegetable field</b>      |           |            |                    |                    |                      |           |      |
| 2                           | Krome     | 275        | 107                | 168                | 652                  | 15.8      | 7.96 |
| 5                           | Biscayne  | 219        | 1.92               | 217                | 928                  | 19.8      | 8.18 |
| 6                           | Krome     | 278        | 164                | 114                | 621                  | 29.6      | 7.83 |
| 7                           | Krome     | 206        | 117                | 89.5               | 624                  | 16.6      | 7.99 |
| 8                           | Chekika   | 188        | 83.1               | 105                | 576                  | 26.1      | 7.98 |
| 9                           | Chekika   | 196        | 85.8               | 110                | 467                  | 24.9      | 7.83 |
| 22                          | Krome     | 378        | 134                | 244                | 806                  | 174       | 7.69 |
| 23                          | Krome     | 204        | 34.8               | 169                | 898                  | 15.0      | 7.73 |
| 24                          | Krome     | 235        | 90.4               | 144                | 838                  | 18.3      | 7.62 |
| <b>Tropical fruit grove</b> |           |            |                    |                    |                      |           |      |
| 1                           | Krome     | 392        | 321                | 70.5               | 256                  | 41.5      | 7.92 |
| 10                          | Krome     | 168        | 115                | 52.8               | 243                  | 14.5      | 7.81 |
| 11                          | Krome     | 236        | 147                | 88.9               | 423                  | 26.7      | 8.01 |
| 12                          | Krome     | 313        | 202                | 111                | 412                  | 27.3      | 7.90 |

† Noncarbonate clay is measured after removal of carbonate. Carbonate clay is calculated as the difference between total clay and noncarbonate clay.

‡ Classification from 1958 soil survey (USDA, 1958). The series was renamed as Krome for rock-plowed Rockdale in 1996 soil survey (USDA, 1996b).

at room temperature. After centrifugation at 1800 × g for 15 min, the supernatant was filtered through a 0.45-µm membrane. The P concentration in the filtered solution was determined colorimetrically using the modified EPA method 365.3 (USEPA, 1982) with a method detection limit of 0.001 µg P mL<sup>-1</sup>. The amount of P sorbed by soils and rocks was calculated from the difference in P concentration between the initial P solution and equilibrium P concentration in the solution.

After completion of the sorption study, 0.050 M KCl solution was added to each tube that contained soil with sorbed P to reach the total solution volume of 15 mL. The desorption was performed by shaking the suspension for 24 h. The same procedures (centrifugation, and filtration) used for P sorption, were also used for P desorption determination. The P concentration in solution was measured using colorimetric method (USEPA, 1982). The percent P desorption was calculated as follows:

Percent P desorbed =

$$\frac{\text{Amount P released to solution } (\mu\text{g})}{\text{Total adsorbed P } (\mu\text{g})} \times 100 \quad [2]$$

### Sorption Isotherms and Saturation Index

Sorption parameters were calculated using linear, Freundlich, and Langmuir isotherms as follows:

Linear isotherm:

$$S = KC - S_0 \quad [3]$$

where  $S$  is the amount of P sorbed by the solid phase (µg g<sup>-1</sup>),  $K$  is the P-sorption coefficient (slope),  $C$  is the P concentration in solution after a 24-h equilibration period, and  $S_0$  is a constant, namely the amount of originally adsorbed P. The equilibrium P concentration at EPC<sub>0</sub> is defined as the concen-

tration of P in a solution, where no net P sorption or desorption occurs, and is equal to the value of  $C$  when  $S$  is 0.

Freundlich isotherm:

$$S = K_f C^n \quad [4]$$

where  $K_f$  and  $n$  are empirical constants, with  $n < 1$ .

Langmuir isotherm:

$$\frac{C}{S} = \frac{1}{bS_{\max}} + \frac{C}{S_{\max}} \quad [5]$$

where  $S_{\max}$  is the sorption maximum, and  $b$  is a constant related to the bonding energy.

One-point isotherm and P saturation index (PSI):

The PSI was calculated as follows:

$$\text{PSI} = P_{\text{Olsen}}/P_{\text{sorption}} \quad [6]$$

where  $P_{\text{Olsen}}$  is Olsen P, and  $P_{\text{sorption}}$  is the soil P-sorption capacity from the one-point isotherm at the initial solution P concentration of  $400 \mu\text{g mL}^{-1}$  and determined as described in the procedures for P-sorption study.

## RESULTS AND DISCUSSION

### Soil Characteristics

Soils in southern Florida, except for those from pineland, are characterized by high pH,  $\text{CaCO}_3$ , and carbonate clay contents (Table 1). The native soils in the area had very shallow depths over bedrock. Rock-ploving, a practice introduced during the early 1950s, crushes the natural oolitic limestone bedrock into a growth medium, and increases the soil depth for crop production. Prob-

bly the use of the rock-plov was the primary factor responsible for creating both high carbonate content and high carbonate clay content of Krome and Chekika soils in vegetable fields (USDA, 1996b).

### Phosphorus Sorption

The P-sorption isotherm at very low concentrations (equilibrium-solution P concentration of  $0\text{--}1 \mu\text{g mL}^{-1}$ ) was found to fit the linear isotherm ( $R^2 = 0.956\text{--}0.999$ ) (Fig. 1). The higher equilibrium P concentration (EPCo) (Table 2) in farmed soils than in pineland and wetland suggests that farmed soils tend to act as sources of P at very low solution P concentrations, whereas pineland and wetland soils may act as sinks of P. More than 99% of the added P was adsorbed by pineland soils at initial P concentration of  $0.1$  to  $5 \mu\text{g mL}^{-1}$ . The slopes ( $K$ ) of nonfarmed soils were difficult to measure because the final equilibrium P concentrations were below the method detection limit.

Phosphorus-sorption isotherms at medium P concentrations (equilibrium-P concentrations of  $1\text{--}400 \mu\text{g P mL}^{-1}$ ) for all soils (Fig. 2) fit both the Freundlich and Langmuir isotherms well ( $R^2 = 0.960\text{--}0.998$  and  $0.914\text{--}0.988$  for Freundlich and Langmuir, respectively). Based on the  $R^2$  values the Freundlich isotherm is better in predicting the P sorption than the Langmuir isotherm. The soils of nonfarmed lands (wetland and pineland) had higher Freundlich  $K_f$  and Langmuir P-sorption maximum ( $S_{\max}$ ) values than soils of vegetable fields and tropical fruit groves (Table 2).

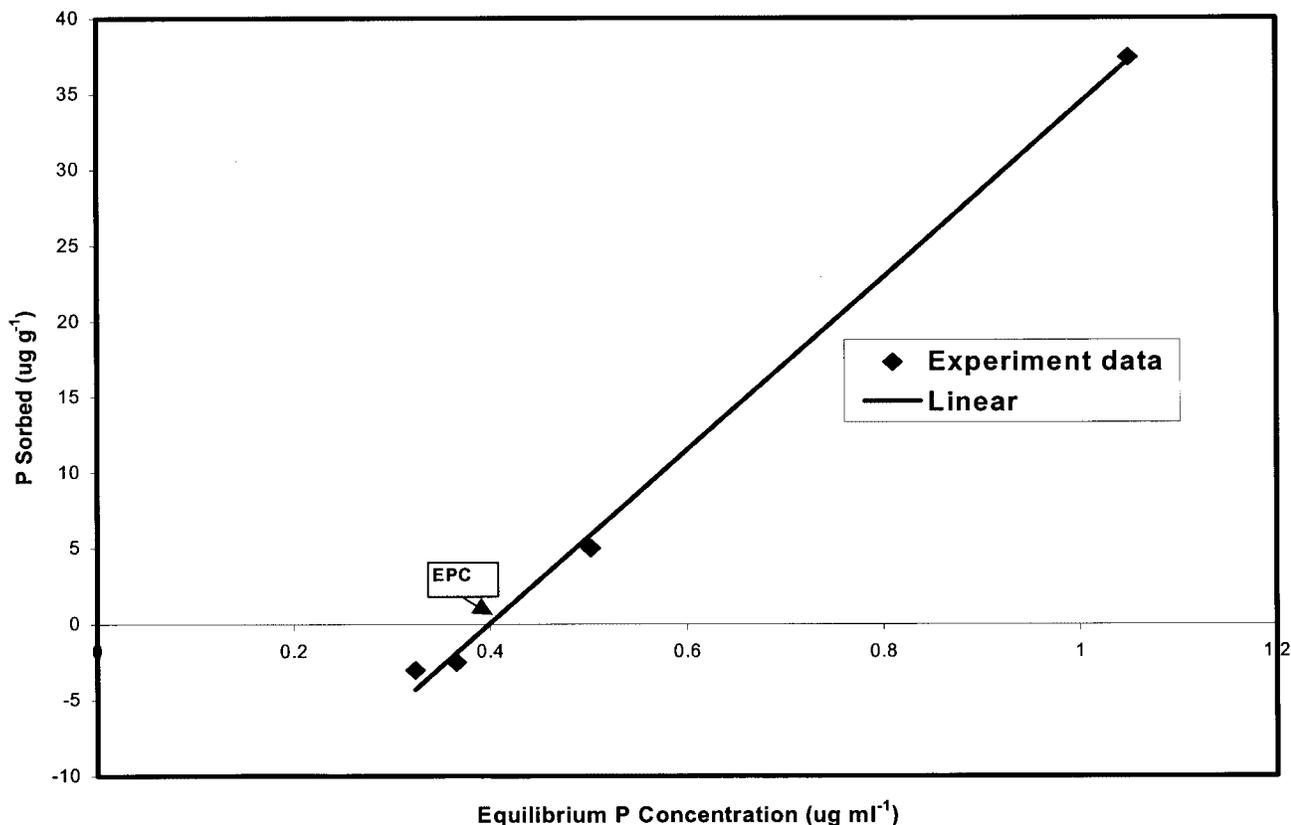


Fig. 1. Linear P-sorption isotherm of Chekika Soil 9.

The slope of the sorption isotherm changed dramatically when the equilibrium P concentration reached 400 to 600  $\mu\text{g P mL}^{-1}$  (Fig. 2), but in soils low in carbonate and high in noncarbonate clay (Table 1), this change in slope did not occur (Fig. 3). The abrupt change in slope of the sorption isotherms suggests that P precipitation at the carbonate surface began to dominate the process as concentrations increased beyond that of the point of inflection (Cole et al., 1953).

Phosphorus sorption onto limestone bedrocks at low P concentrations in solution is well described by the Freundlich isotherm (Fig. 4). As the P concentration in solution increased, the slope of the sorption isotherm changed abruptly (Fig. 5). This may be because of P precipitation on the carbonate surface. Freeman and Rowell (1981) reported that P precipitates on carbonate at a P concentration ( $10^{-4} M$ ) similar to that found in this study to be associated with the abrupt change. The P-sorption capacities ( $K_f$ ) of limestone bedrocks were found to be very much lower than those of soils (Tables 2 and 3). The low P sorption ability of the bedrocks is due to their small surface areas. The P-sorption capacity of carbonate depends strongly on its surface area (Amer et al., 1985), and sorbed P is associated only with a small part of the calcite surface area (Freeman and Rowell, 1981). The low Freundlich  $K_f$  values indicate that limestone bedrocks have low P retention capacities at low P concentrations ( $1 \mu\text{g P mL}^{-1}$ ). Even though limestone bedrock can retain large amounts of P by its precipitation at high P concentrations (Fig. 5), the potential risk of subsurface P movement cannot be excluded when the concentrations of P in surface soils are high.

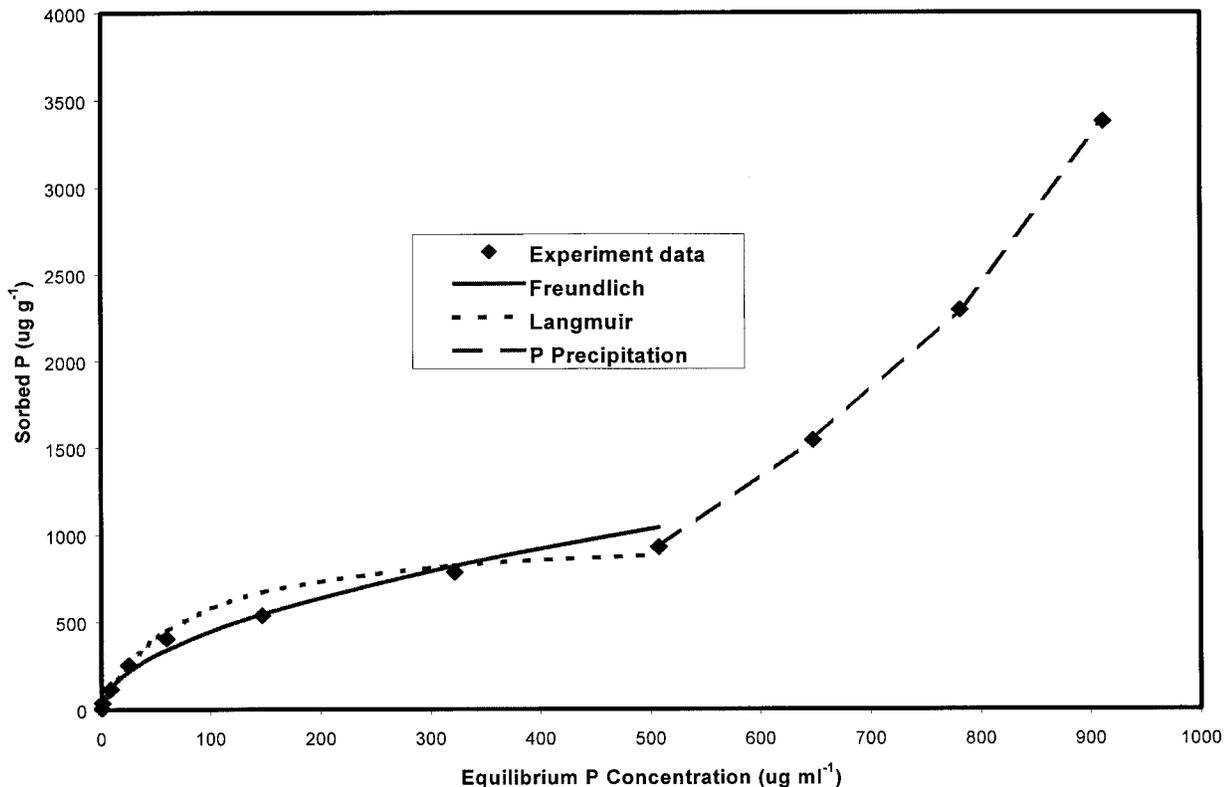
**Table 2. Linear, Freundlich, and Langmuir sorption parameters of soils.**

| Soil no.                    | Linear                    |  | Freundlich                  |       | Langmuir                                 |                              |
|-----------------------------|---------------------------|--|-----------------------------|-------|--|------------------------------|
|                             | $K$<br>$\text{ml g}^{-1}$ | $\text{EPCo}^\dagger$<br>$\mu\text{g ml}^{-1}$ | $K_f$<br>$\text{ml g}^{-1}$ | $n$   | $S_{\text{max}}$<br>$\mu\text{g g}^{-1}$ | $b$<br>$\mu\text{ml g}^{-1}$ |
| <b>Pineland</b>             |                           |  |                             |       |  |                              |
| 3                           | –‡                        | MDL  | 395                         | 0.375 | 4167                                     | 0.0245                       |
| 17                          | –                         | MDL  | 387                         | 0.384 | 4336                                     | 0.0277                       |
| 20                          | –                         | MDL  | 690                         | 0.327 | 5556                                     | 0.0281                       |
| <b>Wetland</b>              |                           |  |                             |       |  |                              |
| 16                          | –                         | 0.002  | 372                         | 0.365 | 3528                                     | 0.0290                       |
| 18                          | –                         | MDL  | 159                         | 0.428 | 2897                                     | 0.0098                       |
| 21                          | 331                       | 0.010  | 119                         | 0.503 | 3043                                     | 0.0015                       |
| <b>Vegetable field</b>      |                           |  |                             |       |  |                              |
| 2                           | 50.7                      | 0.28   | 58                          | 0.579 | 1664                                     | 0.0140                       |
| 5                           | 22.5                      | 0.37   | 25                          | 0.659 | 1327                                     | 0.0088                       |
| 6                           | 47.0                      | 1.01   | 34                          | 0.638 | 1544                                     | 0.0113                       |
| 7                           | 33.0                      | 0.87   | 32                          | 0.572 | 909                                      | 0.0148                       |
| 8                           | 69.4                      | 0.28   | 51                          | 0.470 | 941                                      | 0.0135                       |
| 9                           | 57.0                      | 0.40   | 40                          | 0.523 | 1011                                     | 0.0133                       |
| 22                          | 46.9                      | 0.70   | 25                          | 0.608 | 1244                                     | 0.0063                       |
| 23                          | 16.8                      | 1.70   | 12                          | 0.663 | 691                                      | 0.0087                       |
| 24                          | 46.1                      | 0.67   | 25                          | 0.635 | 1059                                     | 0.0106                       |
| <b>Tropical fruit grove</b> |                           |  |                             |       |  |                              |
| 1                           | 47.8                      | 0.67   | 40                          | 0.600 | 1887                                     | 0.0084                       |
| 10                          | 14.8                      | 1.69   | 25                          | 0.502 | 591                                      | 0.0095                       |
| 11                          | 76.3                      | 0.53   | 54                          | 0.585 | 1862                                     | 0.0113                       |
| 12                          | 49.5                      | 1.30   | 31                          | 0.629 | 1373                                     | 0.0109                       |

† Zero-net equilibrium Phosphorus concentration.  
‡ The equilibrium P concentrations were below the method detection limit (MDL), and therefore the K could not be calculated.

### One-Point-Sorption Isotherm and Phosphorus Saturation

The P-maximum-sorption capacity ( $S_{\text{max}}$ ) and DPS calculated from the Langmuir isotherm, and the P-sorp-



**Fig. 2. Freundlich and Langmuir P-sorption isotherms and P precipitation of Chekika Soil 9.**

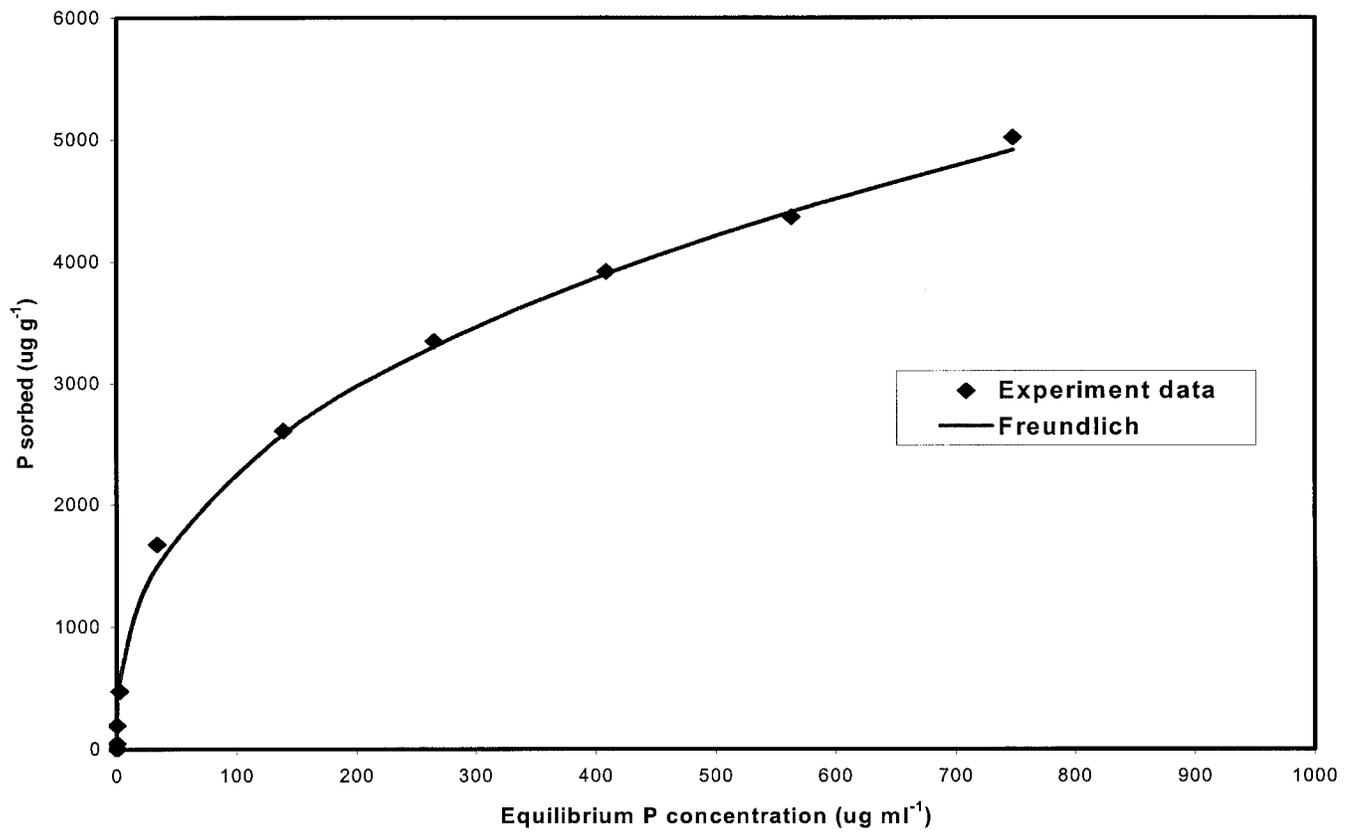


Fig. 3. P-sorption isotherm of pineland soil with low in carbonate and high in noncarbonate clay (Soil 17).

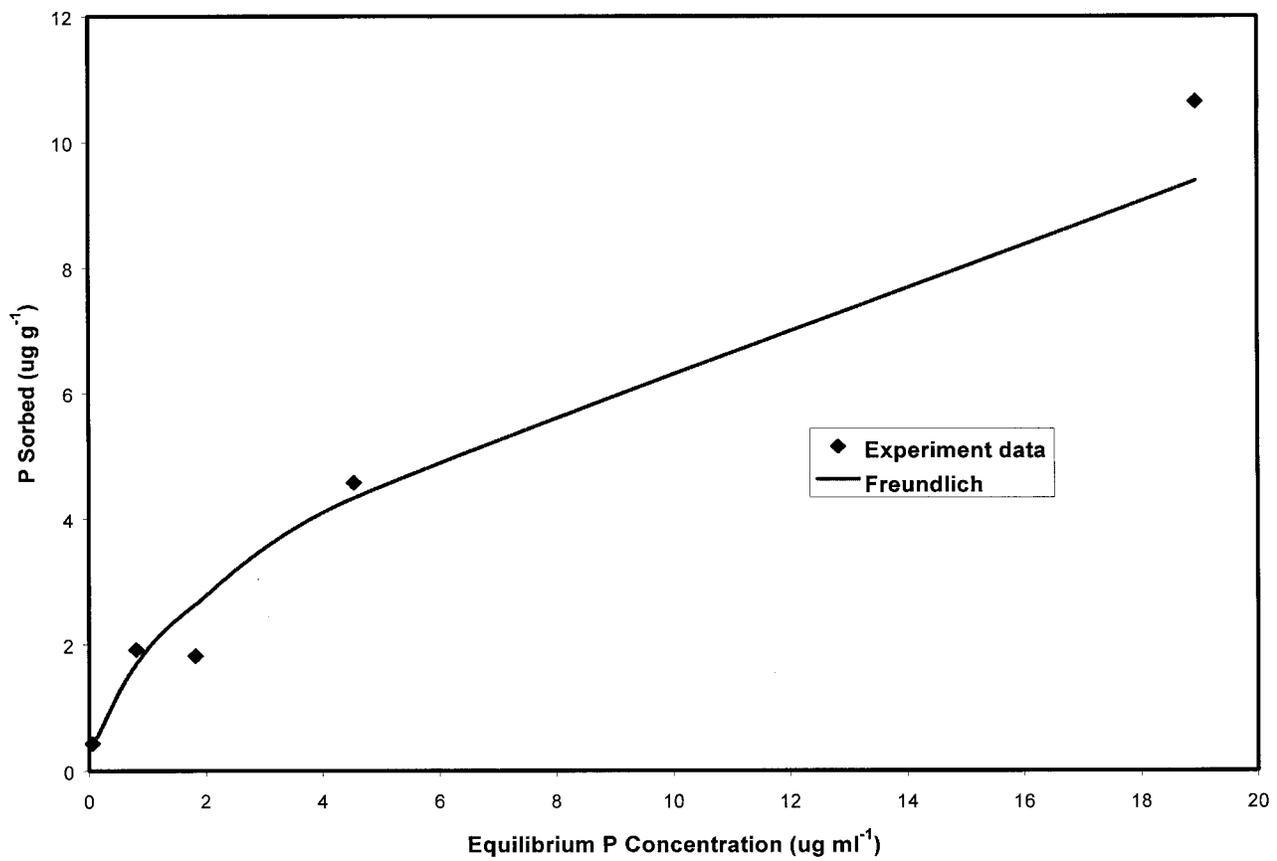


Fig. 4. Freundlich P-sorption isotherm of Limestone Bedrock 2.

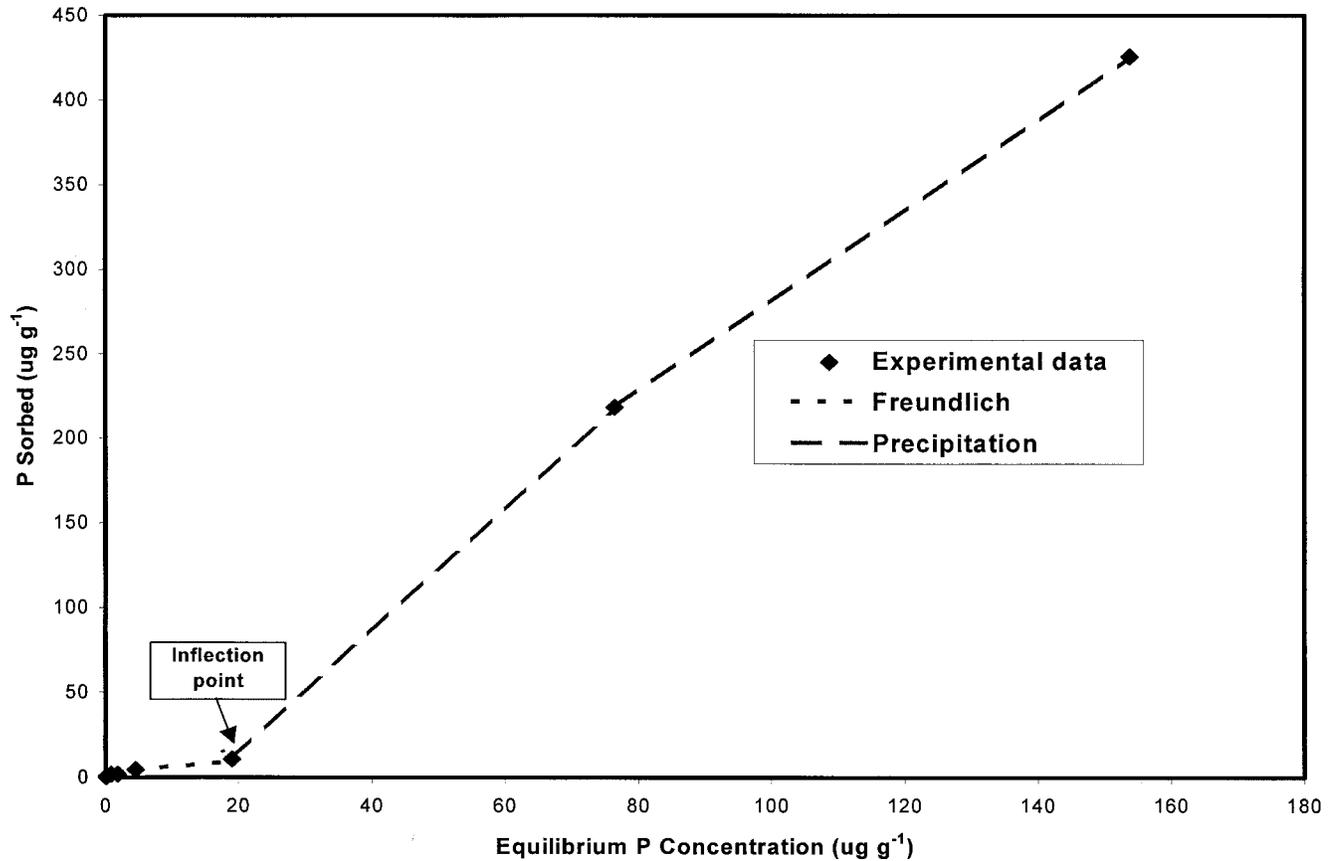


Fig. 5. P sorption and precipitation of Limestone Bedrock 2.

tion value ( $P_{sorption}$ ) and PSI obtained from the one-point isotherm are shown in Table 4. In acid soil, the maximum P-sorption capacity has been estimated from oxalate extractable Fe and Al (Breeuwsma and Silva, 1992). However, no simple method exists for estimating P retention capacities in calcareous soils, and determination of the maximum sorption from the Langmuir isotherm may be too complex for practical application. In calcareous soils, the slope of the P-sorption isotherm increased abruptly as the P concentration rose from 400 to 600  $\mu\text{g mL}^{-1}$  (Fig. 2). Therefore we should not use a solution containing a high initial P concentration to estimate the P-sorption capacity, since precipitation on the carbonate surface is likely the dominant process at high P concentrations. On the other hand if a much lower initial solution P concentration is used, the P sorption on soils may be too low to determine a sorbed-P value that is comparable with the sorbed-P maximum. Therefore, to estimate the P-sorption value, the one-point isotherm for calcareous soils was selected using an initial P concentration of 400  $\mu\text{g mL}^{-1}$  and a soil/solution ratio of 1:10. The Langmuir P maximum-sorption values and the

P-sorption values estimated from the one-point sorption isotherm proved to be strongly correlated (Fig. 6).

The degree of saturation has been used to estimate the potential concentration of P in runoff and leachate from soils. The Olsen-P method was selected to deter-

Table 4. Phosphorus-sorption capacity, P saturation and desorption of soils.

| Soil no.             | $S_{max}$<br>g g <sup>-1</sup> | $P_{sorption}$<br>g g <sup>-1</sup> | DPS†   | PSI‡   | P Desorption<br>% |
|----------------------|--------------------------------|-------------------------------------|--------|--------|-------------------|
| Wetland              |                                |                                     |        |        |                   |
| 16                   | 3528                           | 2575                                | 0.0002 | 0.0002 | 3.2               |
| 18                   | 2897                           | 1780                                | 0.0003 | 0.0005 | —                 |
| 21                   | 3043                           | 1818                                | 0.0027 | 0.0046 | 2.3               |
| Vegetable field      |                                |                                     |        |        |                   |
| 2                    | 1664                           | 1322                                | 0.0406 | 0.0511 | 10.9              |
| 5                    | 1327                           | 1176                                | 0.0399 | 0.0451 | 7.5               |
| 6                    | 1544                           | 1124                                | 0.0899 | 0.1234 | 9.6               |
| 7                    | 909                            | 787                                 | 0.1149 | 0.1327 | 12.0              |
| 8                    | 941                            | 716                                 | 0.0446 | 0.0586 | —                 |
| 9                    | 1011                           | 782                                 | 0.0473 | 0.0611 | —                 |
| 22                   | 1244                           | 770                                 | 0.1119 | 0.1809 | 16.4              |
| 23                   | 691                            | 546                                 | 0.2089 | 0.2642 | 25.8              |
| 24                   | 1059                           | 867                                 | 0.0941 | 0.1148 | 15.3              |
| Tropical fruit grove |                                |                                     |        |        |                   |
| 1                    | 1887                           | 1239                                | 0.0727 | 0.1108 | —                 |
| 10                   | 591                            | 477                                 | 0.1012 | 0.1253 | —                 |
| 11                   | 1862                           | 1309                                | 0.0462 | 0.0658 | 10.8              |
| 12                   | 1373                           | 1017                                | 0.0871 | 0.1175 | 14.5              |

† DPS is the degree of P saturation.  
‡ PSI is the P saturation index.

Table 3. Freundlich sorption parameters ( $K_f$  and  $n$ ) of limestone bedrocks.

| Bedrock no.                | R3    | R17   | R16   | R2    | R7    | R22   | R24   | R1    | R11   |
|----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $K_f$ , ml g <sup>-1</sup> | 3.72  | 3.27  | 3.16  | 2.34  | 1.91  | 5.09  | 7.99  | 0.84  | 4.44  |
| $n$                        | 0.587 | 0.538 | 0.533 | 0.627 | 0.542 | 0.435 | 0.685 | 0.712 | 0.639 |

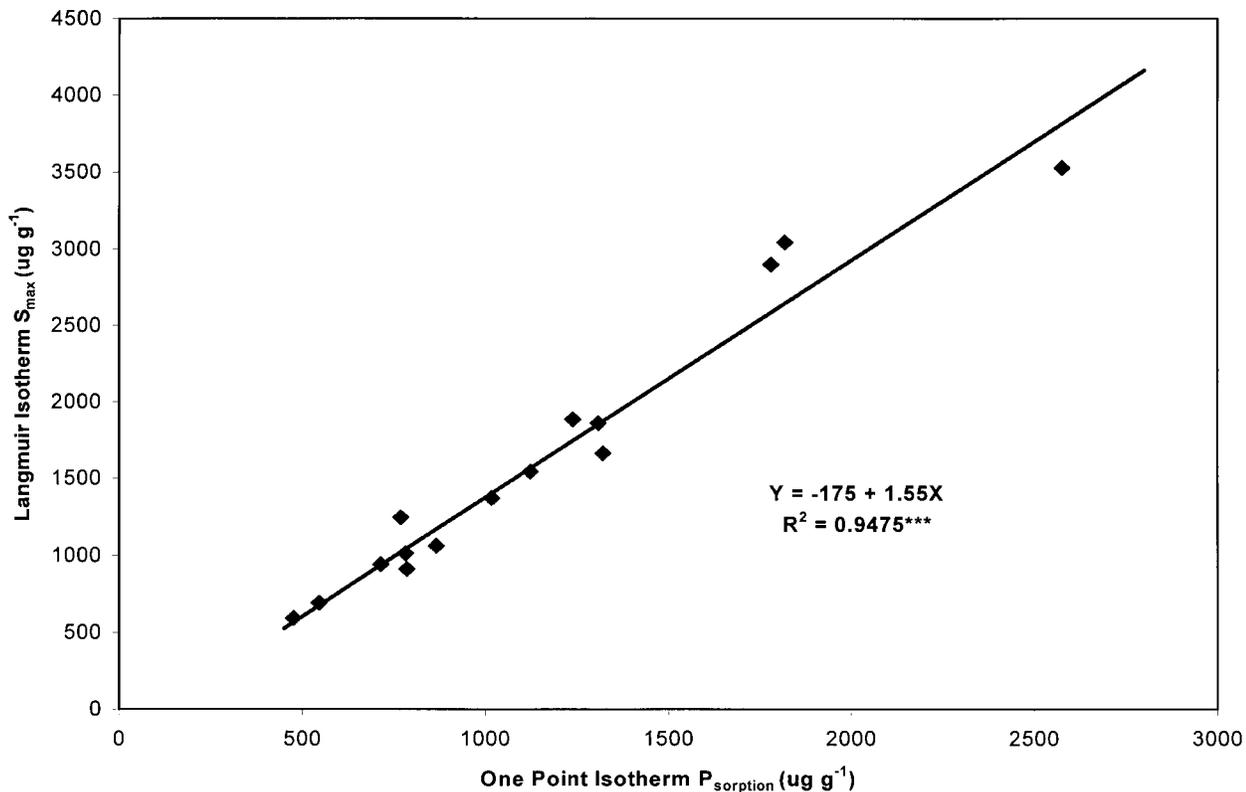


Fig. 6. Relationship in soils of P-sorption values of the Langmuir Isotherm  $S_{\text{max}}$  to those of the one-point isotherm ( $P_{\text{sorption}}$ ).

mine extractable P concentrations. This method is commonly used with calcareous soils. The DPS in this study was calculated from the Olsen P and the maximum P-sorption capacity ( $S_{\text{max}}$ ). The PSI was obtained from the Olsen P and the P-sorption values at  $400 \text{ mg P L}^{-1}$  initial concentration. The DPS from the Langmuir isotherm was found to be very highly correlated with the PSI from the one-point isotherm (Fig. 7).

#### The Relationship between Phosphorus Desorption and Phosphorus Saturation

Farmed soils had higher P desorption potentials than wetland soils (Table 4). The percentage of P desorption was correlated best with the PSI, and with the DPS, followed by EPCo and Olsen P ( $r = 0.940***$ ,  $0.939***$ ,  $0.857***$ , and  $0.827**$ , respectively,  $n = 11$ ). Sharpley (1995) reported that the DPS, which integrates the effects of soil properties with the soil test P content, provides better estimates of the potential for P runoff than does soil test P. Never the less, the complexity of P-saturation measurement may limit its application. However the complexity of saturation measurement can be simplified by using the one-point isotherm to replace the Langmuir isotherm. There is no significant difference in the correlation coefficients of the percent P desorption vs. P saturation that were calculated from the Langmuir isotherm and from the one-point isotherm. Moreover, the P-saturation value can be obtained much more easily from the one-point isotherm measurement than that from the Langmuir isotherm. Therefore, the

one-point isotherm provides a simple measurement for determining the P release potential of calcareous soils.

#### The Relationship between Soil Properties and Phosphorus Sorption

The Freundlich  $K_f$  and Langmuir sorption maximum ( $S_{\text{max}}$ ) parameters were found to correlate positively with total clay and noncarbonate clay content of soils, but not with the carbonate clay of soils (Table 5). This implies that the noncarbonate clays (such as Fe oxide, Al oxide, and Si clays) are the main principles of P sorption. On the contrary, total carbonate content appeared to have a negative influence on P sorption (Table 5). Indeed, an indirectly negative effect of total carbonate has been reported in other calcareous soils (Ryan et al., 1985). For the calcareous soils in southern Florida, we found a negative correlation between total carbonate and noncarbonate clay ( $r = -0.827***$ ). On the other hand, we found total carbonate to have a positive correlation with carbonate clay ( $r = 0.702***$ ). It appears that the noncarbonate clay in limestone rock was diluted by the sand-size lime rock fraction created when the lime rock was being broken and crushed to soil-size particles by the rock plowing. In this process, substrates with high total carbonate content were converted to soils with low noncarbonate clay content and high carbonate clay content. This has caused the simple regression between carbonate clay and P-sorption parameters ( $K_f$  and  $S_{\text{max}}$ ) to be meaningless for evaluating the role of carbonate clay in P sorption in the soils of southern

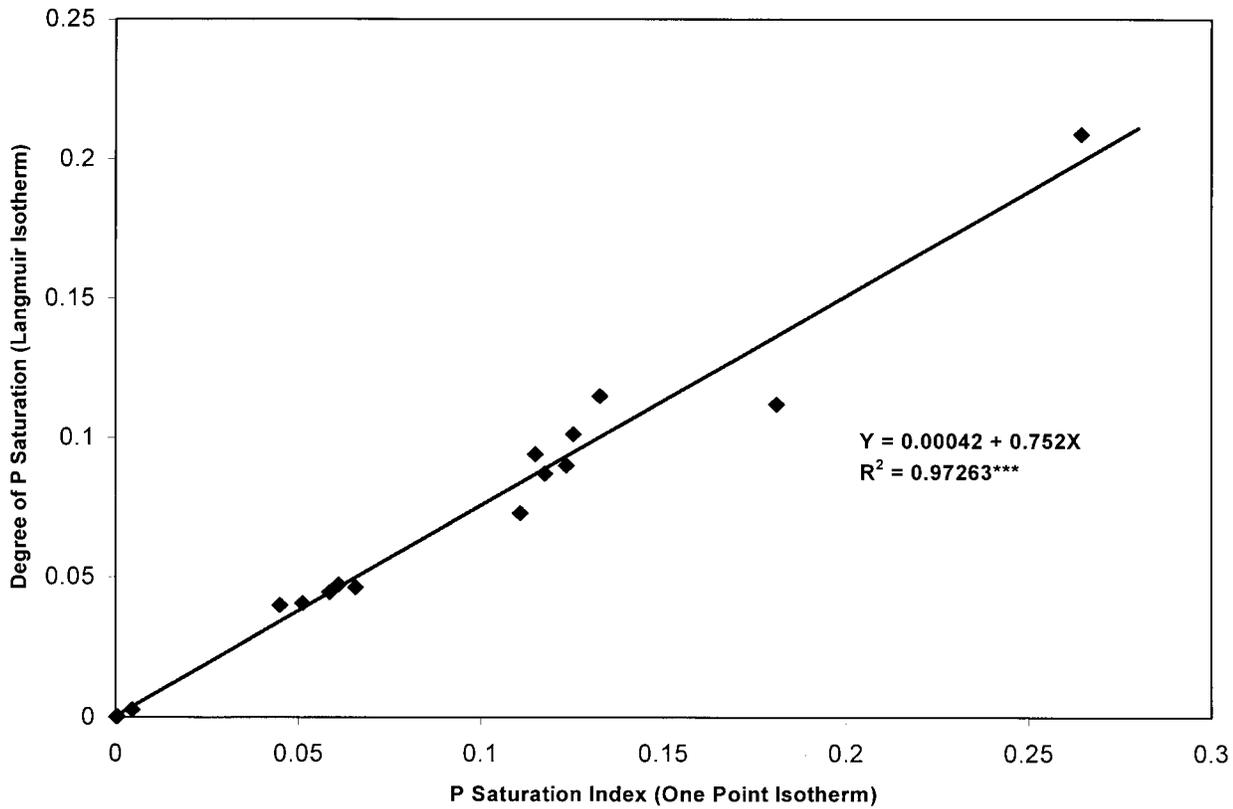


Fig. 7. Relationship between degree of P saturation (DPS;  $P_{Olsen}/S_{max}$ ) and P-saturation index (PSI;  $P_{Olsen}/P_{sorption}$ ).

Florida. Never the less, the use of ratios of soil properties or multiple regression may elucidate such obscured relationships. The ratio of carbonate clay to equivalent carbonate (i.e., the of carbonate clay as a proportion of total carbonate) was found to be correlated highly with the P-sorption parameters,  $K_f$  ( $r = 0.469^*$ ) and  $S_{max}$  ( $r = 0.589^{**}$ ), especially the  $S_{max}$  (Table 5). When P-sorption parameters were regressed with two properties (noncarbonate and carbonate clay), the regression coefficient ( $r$ ) for the maximum P sorption was found to be high, whereas the regression coefficient for the Freundlich  $K_f$  did not increase significantly (Table 5). The regression slope of noncarbonate clay is 3.4 and 1.6 times higher than that of carbonate clay for  $K_f$  and  $S_{max}$ , respectively. These values indicate that noncarbonate clay has the greater P-sorption capacity, even though carbonate clay also contributes to the P sorption especially at high P concentrations in solution ( $S_{max}$ ). Since marl soil contains much more carbonate clay than noncarbonate clay (Table 1), the carbonate clay probably is largely responsible for this soil's P-sorption capacity.

**CONCLUSIONS**

The P-sorption capacities of southern Florida calcareous soils are mainly the result of the strong affinity for P of the noncarbonate clay, especially at low concentrations of solution P. Carbonate clay also contributes to P sorption when it is dominant in the soil, and when large amounts of P are applied. Soils with high PSIs have

high EPCo and P desorption potentials. Phosphorus applied to agricultural land can desorb, and thereby be a source of P contamination in adjacent areas. Phosphorus sorption in nonagricultural land surrounding agricultural land can act as a sink for P to prevent further movement. A soil with a high level of P saturation also can be a source of P to subsurface limestone bedrock. Since limestone bedrock has a very limited capacity to remove P leached from the overlying soil, there is a potential risk for P movement in this porous subsurface rock.

Table 5. Summary of regression coefficients between soil properties and P sorption parameters ( $n = 19$ ).

| Regression equation                                  | <i>r</i> |
|--|----------|
| $K_f = -0.37 + 7.85 \text{ NC}^\dagger$              | 0.901*** |
| $K_f = -0.82 + 8.42 \text{ NC} + 2.48 \text{ CC}$    | 0.908*** |
| $K_f = -1.65 + 8.49 \text{ TC}$                      | 0.849*** |
| $K_f = 2.2 - 6.31 \text{ CC}$                        | 0.342    |
| $K_f = -24.8 + 550 \text{ CC/CE}$                    | 0.469*   |
| $K_f = 3.62 - 0.044 \text{ CE}$                      | 0.688**  |
| $S_{max} = 8.28 + 57.4 \text{ NC}$                   | 0.863*** |
| $S_{max} = 0.54 + 67.1 \text{ NC} + 57.4 \text{ CC}$ | 0.902*** |
| $S_{max} = -2.94 + 67.4 \text{ TC}$                  | 0.884*** |
| $S_{max} = 24.6 - 28.1 \text{ CC}$                   | 0.200    |
| $S_{max} = 549 + 5272 \text{ CC/CE}$                 | 0.589**  |
| $S_{max} = 36.8 - 0.31 \text{ CE}$                   | 0.634**  |

\* Significant at the 0.05 probability level.  
 \*\* Significant at the 0.01 probability level.  
 \*\*\* Significant at the 0.001 probability level.  
 † NC, noncarbonate clay (%)  
 ‡ CC, carbonate clay (%)  
 § TC, total clay (%)  
 ¶ CE, carbonate equivalent (%)

The P-desorption potential is strongly correlated with the P saturation of soils. Phosphorus sorption values estimated from the one-point isotherm are very similar to those calculated from the Langmuir sorption isotherm. The one-point isotherm provides a good first approximation of the DPS, and therefore of potential environmental contamination because of soil P in calcareous soils.

### ACKNOWLEDGMENTS

This research was supported in part by a grant from the Center of Natural Resources, University of Florida. We thank Dr. Waldemar Klassen for his support, and valuable review and comments on the manuscript.

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