Phosphorus Adsorption by Soils from Four Land Use Patterns

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This study was designed to survey the surface soils characteristics, which collected from *Chinese chestnut* woodland (S1), *Phyllostachys edulis* woodland (S2), paddy rice farmland (S3) and vegetable farmland (S4), to assess the phosphorus sorption isotherm and analyze the relationship between soil properties and sorption parameters. Results indicated that soils from paddy rice and vegetable fields were hydragric anthrosols and alluvial soils with a silt clay texture, while soils from *Chinese chestnut* and *Phyllostachys edulis* woodland were stony soils with a sandy texture. All the soils were generally acidic and pH ranged from 4.48 to 7.45. Fe-P and Ca-P contents in paddy rice and vegetable soils were higher than the contents of *Chinese chestnut* and *Phyllostachys edulis* soils. Crystalline iron oxides were the dominant forms of iron oxide in these soils. Sorption isotherm experiments showed that these soils exhibited a wide range of phosphorus sorption capacity values and the sequence of sorption capacity was S3 > S4 > S1 > S2. The Langmuir, Freundlich and Temkin models can be used to describe phosphorus sorption data, with R^2 ranging from 0.75 to 0.98. The parameters of Q_{max} (phosphorus sorption maximum), K and B (Freundlich and Temkin adsorption constant) ranged from 71.20 to 325.11 mg kg^{-1}, 36.51-121.15 mg kg^{-1} and 44.12 to 159.69 mg kg^{-1}, respectively. Q_{max}, F and B had a highly significant positive relationship with pH (NaF), Ca-P, clay, Al_t and Al_o. About 92-99 % of the maximum phosphorus sorption capacity of these soils could be estimated by the combination of some of these properties.

Key Words: Farmland, Woodland, Soils, Sorption, Sorption capacity.

INTRODUCTION

Upland and flat farmland used for economic and ecological forest and crop production is a traditional custom. However, in recent years, the upland, which slope more than 25° has been completely forbidden plant in China, as the serious soil and water erosion phenomena. Though in the southern part of China this problem is less serious than in the northern, its harmfulness is greater because the leanness soil specifically in mountain and hilly area.

Soil and water erosion always leads to a lot of nutrient losses and has a serious consequence for agriculture and water ecosystem. Phosphorus loss is a complex process, it has a close relationship with soil's sorption and desorption properties and also capacity.

Phosphate sorption isotherms indicating the potential of phosphorus transport from soils to ecosystems are good tools to identify the soil constituents and soil properties responsible for sorption of phosphorus and to compare phosphate sorption capacity of diverse soils[1], which is vital information for both crop production and environmental protection. The phosphorus sorption capacity of soils has been related to soil pH, mineralogy, organic anions, organic complexes of Fe and Al, extractable Fe and Al oxides, hydroxides and oxyhydroxides and other soil properties. Phosphorus sorption has been studied for diverse soils in many area and countries[2-8]. There are few reports on phosphorus sorption about different soil types based on the different land use patterns. The purposes of this research are to understand the phosphorus sorption characteristics of different soils collected from different land use patterns in Fushi watershed of Anji Town in Zhejiang, P.R. China and to analyze relationships between these characteristics and soil properties, which are an important contribution to developing approach for phosphorus fertilizer application. The objectives of the study were (1) to measure and analyze the characteristics of the soil samples; (2) to identify the sorption isotherm characteristics and calculate the relevant parameters; (3) to analyze the relationship between sediment characteristics and sorption parameters.

EXPERIMENTAL

Experiments were designed and conducted in Zhejiang University, China. Instruments were provided by college of

environmental and resource sciences. The experiment included samples collection, preparation and analysis, phosphate adsorption and Statistical analysis.

Soil samples and study area: Four soil samples were collected from subsurface (1-10 cm) of 4 sites representing three different soils and four kinds of land use patterns in Fushi watershed in Anji County (30° 38' N and 119° 40' E), Zhejiang province, China. This area experiences a typical subtropical marine-monsoon climate. The mean annual precipitation is 1344.1 mm and the mean annual temperature is 16.6 °C. Samples were collected from *Chinese chestnut* woodland, *Phyllostachys edulis* woodland, paddy rice farmland and vegetable farmland,respectively for S1,S2, S3 and S4. These four land use types were the mostly usage models and provided most of farmer's economic and food resources. This watershed area was low mountain and foothill areas, most parts were covered by *Phyllostachys edulis* and minority *Chinese chestnut*, only few flat land could plant vegetable and paddy. The soils in low mountain and foothill were leanness and easy to be eroded. Therefore more fertilize were used for high production, it led to more serious environment problems.

Samples analysis: Sediment pH was measured in distilled water (w/v ratio of 1: 2.5) and 1 M NaF (pH 8.2) (w/v ratio of 1: 50). Particle size distribution of sediment was determined by the hydrometer method[9]. Total nitrogen (TN) was measured by Kjeldahl apparatus (Kjelflex k-360) after digestion with sulphuric acid (H_2SO_4). Total phosphorus (TP) was determined using the molybdenum-blue complex method after total digestion with $HClO_4/H_2SO_4$ at 370 °C. Available phosphorus (Avail-P) was extracted with 0.5 mol/L $NaHCO_3$[10]. The organic matter (OM) was measured by the dichromate volumetric method. Cation exchange capacity (CEC) was measured by ammonium acetate exchanging method. Fe and Mn were all measured by flame atomic absorption spectroscopy (A-A6300) and Al was measured by xylenol-orange photometric (UV/VIS-2550) method. Total Fe, Al and Mn (Fe_t, Al_t and Mn_t) were measured after digested with 30 mL mixture of HF, HNO_3 and $HClO_4$ as 10:15:5. Crystalline and non crystalline forms of Fe, Al and Mn were extracted by the dithionite-citrate-bicarbonate solution (Fe_d, Al_d, Mn_d) and 0.2 M ammonium-oxalate solution at pH 3.0 (Fe_o, Al_o, Mn_o), respectively[11]. Inorganic phosphorus, which combined with aluminum phosphate (Al-P), iron phosphate (Fe-P) and calcium phosphate (Ca-P) were measured by molybdenum-blue method after extracted by 0.5 M ammonium fluoride solution at pH 8.2, 0.1 M sodium hydroxide solution and 0.5 M sulfuric acid, respectively.

Phosphate adsorption: For the phosphorus sorption study, 0.5 g soil samples were put in a series of 50 mL poly-ethylene centrifuge tubes with 25 mL 0.01 M $CaCl_2$ solution. $CaCl_2$ solution contained phosphorus at a series of concentrations. The phosphorus concentrations (C_o) were 0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 mg L^{-1} and prepared by analytical pure anhydrous potassium phosphate (K_2HPO_4), respectively. Two drops of toluene (0.1 % chloroform) were added to restrict microbial activity. Then, the tubes were screwed and shaken at 200 rpm on a rotary shaker at 25 °C for 24 h. After shaking, suspensions were centrifuged at 3500 rpm for 10 min. Then supernatants were filtered through a 0.45 μm filter membrane. Phosphorus equilibrium concentration (C_{eq}) of the supernatant was measured by the molybdate blue method using a UV/VIS (UV-2550) spectrophotometer. The amount of P adsorbed by the sediment was calculated by the difference between C_o and C_{eq}. The formula (1) was:

$$Q = (C_o - C_{eq}) \cdot v / w \qquad (1)$$

where, Q is the amount sorbed (mg kg^{-1}), C_o is the initial P concentration (mg L^{-1}), C_{eq} is the equilibrium concentration (mg L^{-1}), w is the sample weight (g) and v is the solution volume (mL) of K_2HPO_4.

Statistical analysis: All data presented were the mean values of three replicates. The software of office excel and SPSS 15.0 were used for calculation and statistical analysis and Origin 8.0 was used to fit curves and calculate parameters.

RESULTS AND DISCUSSION

Soil characteristics: Soil samples were stony soil, stony soil, hydragric anthrosols and alluvial soil for S1, S2, S3 and S4, respectively. Hydragric anthrosols and alluvial soils were the accumulation of debris, alluvium and diluvial, they were dark brown to dark yellowish brown and were neuter and acidity respectively. The texture of alluvial soil was sandy loam to sandy clay, while the hydragric anthrosols contained more clay. Stony soil was gray to sallow and it was subacidity, which was mainly formed by cliff debris of coarse grain and phenocryst of granite, it had more sand than hydragric anthrosols soil and alluvial soil.

The physical/chemical properties of four soil samples were summarized in Table-1. It indicated that these soils collected from different land use patterns had different soil texture. For example, S1 and S2 were sandy texture with sand content exceeding 50 %, S3 and S4 generally were silt clay texture with silt content exceeding 40 % and clay exceeding 30 %. All soils were generally acidic with pH (water) ranged from 4.48 to 7.45 (Table-2). The pH of NaF solution ranged from 8.38 to 9.17, and S3 had a higher value indicated that soil planted paddy rice contained mineral constituents with surface hydroxyl ions, which were exchanged by the fluoride ion[12]. The organic matter content displayed a significant differences and the sequence was S3 > S4 > S2 > S1. Avail-P ranged from 14.73 to 23.50 mg kg^{-1} and the sequence was S4 > S2 > S1 > S3, which may be partly a consequence of fertilization. Such as S4 collected from vegetable field that applied more fertilize. Fe-P and Ca-P contents in S3 and S4 were more than S1 and S2. It indicated soils in the paddy rice and vegetable fields had more stored P which could be as a support for Avail-P. Crystalline iron oxides extracted by dithionite-citrate-bicar-bonate extraction (Fe_d) was the dominant forms of iron oxide in these soils and ranged from 5.53 to 5.37 g kg^{-1}. The low content of non-crystalline iron extracted by ammonium-oxalate (Fe_o) indicated that there were less amounts of both oxides and microcrystalline iron oxides in these soils[13] (Table-1). The low values of Fe_o/Fe_d ratio also indicated most Fe was existed as crystalline Fe-oxides.

Phosphate adsorption isotherm: Fig. 1 was the phosphorus sorption isotherm of different land use pattern soils. The phosphorus sorption data were well described by the Langmuir equation (median R^2 = 0.95), the Freundlich equation (median R^2 = 0.81) and the Temkin equation (median R^2 = 0.89), respectively. The equations were as follows:

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TABLE-1
PROPERTIES OF DIFFERENT LAND USE SOILS

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Properties	S1	S2	S3	S4
pH	6.07 ± 0.35	6.45 ± 0.47	7.45 ± 0.32	4.48 ± 0.55
pH (NaF)	8.41 ± 0.32	8.38 ± 0.25	9.17 ± 0.46	8.91 ± 0.32
OM (g kg⁻¹)	19.61 ± 0.56	23.201 ± 0.61	26.39 ± 0.48	25.211 ± 0.56
Avail-P (mg kg⁻¹)	16.92 ± 5.23	20.67 ± 3.45	14.73 ± 4.28	23.50 ± 7.24
Fe-P (mg kg⁻¹)	136.40 ± 40.23	65.38 ± 18.76	167.29 ± 28.20	189.17 ± 31.05
Al-P (mg kg⁻¹)	10.11 ± 1.02	18.49 ± 2.18	17.69 ± 3.45	11.13 ± 0.76
Ca-P (mg kg⁻¹)	32.99 ± 4.55	29.12 ± 6.58	476.27 ± 38.12	260.86 ± 26.15
CEC (cmol$_c$ kg⁻¹)	14.32 ± 2.15	17.01 ± 1.85	14.60 ± 1.79	16.12 ± 2.04
Sand (2-0.02 mm %)	55.46 ± 4.58	52.48 ± 7.28	16.16 ± 6.43	22.69 ± 6.46
Silt (0.02-0.002 mm %)	32.37 ± 4.32	35.42 ± 4.78	41.08 ± 4.56	44.08 ± 5.24
Clay (< 0.002 mm %)	12.17 ± 3.34	12.10 ± 3.45	42.76 ± 12.35	33.23 ± 10.28
Fe$_t$ (g kg⁻¹)	5.42 ± 0.64	6.79 ± 0.63	5.99 ± 0.58	6.54 ± 0.70
Al$_t$ (g kg⁻¹)	16.98 ± 1.235	17.21 ± 1.61	23.94 ± 1.57	22.88 ± 2.03
Mn$_t$ (g kg⁻¹)	0.12 ± 0.02	0.31 ± 0.02	0.63 ± 0.42	0.27 ± 0.03
Fe$_d$ (g kg⁻¹)	4.69 ± 0.52	5.37 ± 0.71	4.53 ± 0.76	4.93 ± 0.64
Al$_d$ (g kg⁻¹)	0.23 ± 0.14	0.29 ± 0.01	0.17 ± 0.02	0.18 ± 0.02
Mn$_d$ (g kg⁻¹)	0.05 ± 0.01	0.17 ± 0.02	0.18 ± 0.02	0.04 ± 0.01
Fe$_o$ (g kg⁻¹)	0.45 ± 0.02	0.57 ± 0.01	0.83 ± 0.11	0.95 ± 0.02
Al$_o$ (g kg⁻¹)	0.071 ± 0.01	0.05 ± 0.01	0.37 ± 0.01	0.10 ± 0.01
Mn$_o$ (g kg⁻¹)	0.05 ± 0.01	0.24 ± 0.01	0.28 ± 0.02	0.03 ± 0.01

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TABLE-2
PARAMETERS OF FITTING EQUATIONS

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Sample	Langmuir			Freundlich			Temkin		
	Q$_{max}$	k	R²	F	n	R²	B	K	R²
S1	91.26	1.21	0.97	38.20	0.40	0.84	48.33	17.46	0.96
S2	71.20	2.16	0.98	36.51	0.33	0.82	44.12	12.31	0.94
S3	325.11	0.98	0.87	121.15	0.52	0.75	159.69	62.88	0.86
S4	185.96	2.68	0.97	99.11	0.35	0.84	115.61	24.58	0.80

Langmuir equation: $\quad Q = \dfrac{Q_{max} \cdot k \cdot C_{eq}}{1 + k \cdot C_{eq}}$ (2)

Freundlich equation: $Q = F + C_{eq}{}^n$ (3)

Temkin equation: $Q = B + k \cdot \ln C_{eq}$ (4)

where, Q was the amount sorbed (mg kg⁻¹), Q$_{max}$ was the Langmuir sorption maximum (mg kg⁻¹); C$_{eq}$ was the equilibrium concentration (mg L⁻¹); k was a constant related to bonding energy (L mg⁻¹ P); F and B were adsorption capacity constant (mg kg⁻¹).

The fitted parameters about the Langmuir, Freundlich and Temkin equations were given in Table-2. The coefficient of determination (R²) for the Langmuir equation was slightly higher than the Freundlich and Temkin equations, which was consistent with the finding of Worachart Wisawapipat[2] for Thai upland soils, Hartone[14] for Indonesian soils. However, there was some inconformity with the trend in some soils for which phosphorus sorption data were described better by the Freundlich equation[15-18].

Values of Q$_{max}$ ranged from 71.20 to 325.11 mg kg⁻¹ for these soils, the F and the B which were also a parameter of the amount of P sorption capacity ranged form 36.51 to 121.15 mg kg⁻¹ and 12.31 to 62.88 mg kg⁻¹, respectively. The sequence of Q$_{max}$, F and B of soils were S3 > S4 > S1 > S2 (Table-2). S3 and S4 had greater sorption capacity than S1 and S2 reflecting the farmland planted paddy rice and vegetable providing more

adsorption sites. The k coefficient relating to the bonding energy of P adsorption ranged from 0.98 to 2.68 L mg⁻¹, while the Freundlich n coefficient, which was also an indicator of bonding energy ranged from 0.33 to 0.52. The sequence of k and n were not consistent with the sequence of Q$_{max}$, F and B. These were no systematic differences in k and n coefficients for the different land type patterns, which were possibly due to the difference of parent materials or their phosphorus adsorption surfaces.
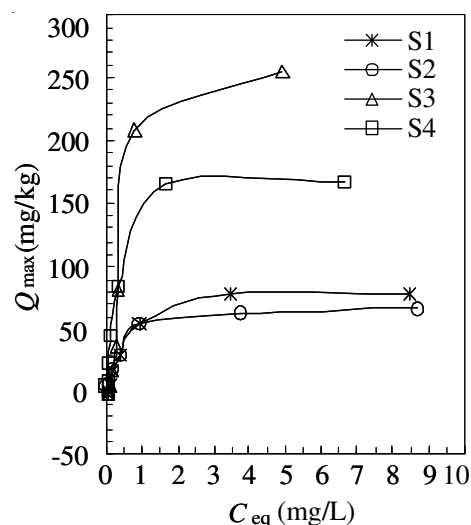

Fig. 1. Phosphorus sorption isotherm of different land use pattern soils

Phosphate sorption coefficients in relation to soils properties: Phosphorus sorption coefficients Q_{max}, F and B had highly significant (P = 0.05) positive relationship with pH (NaF), Ca-P, clay, Al_t and Al_o (Table-3). These relationships were closed and these soils properties which can be routinely determined by soil surveys could be used with confidence to predict the sorption capacity of different plant soils, it was similar to others reports[2]. Multivariate stepwise regression analysis and regression function indicated that 92-99 % of the Q_{max}, F and B for these soils can be estimated by a combination of some of these properties (Fig. 2). This indicated that Al_o and Clay provided much of the P sorption capacity and sorption energies, while pH and Ca-P were important influence factors. The regression functions were as follow formulas:

$$Q_{max} = 57.08 + 0.42(Ca\text{-}P) + 188.73\ (Al_o)\ (R^2 = 0.99)\ (5)$$
$$F = -3.39 - 0.05\ (Ca\text{-}P) + 3.49\ (Caly)\ (R^2 = 0.99)\quad (6)$$
$$B = -1063.97 + 131.99\ (pH\ (NaF)) + 36.04\ (Al_o)\ (R^2 = 0.99)\ (7)$$
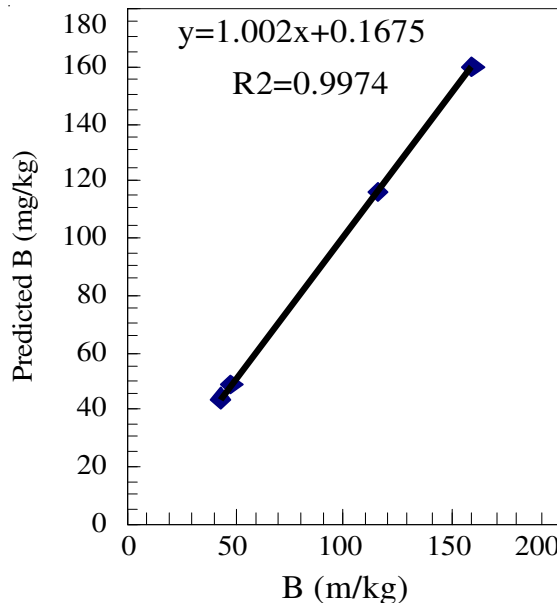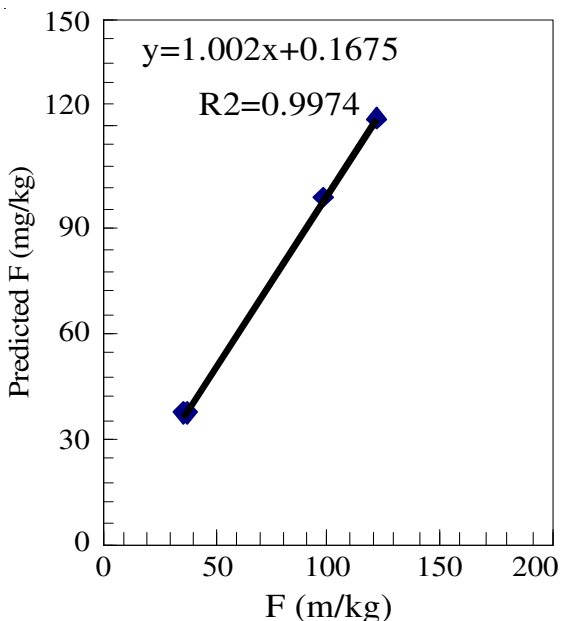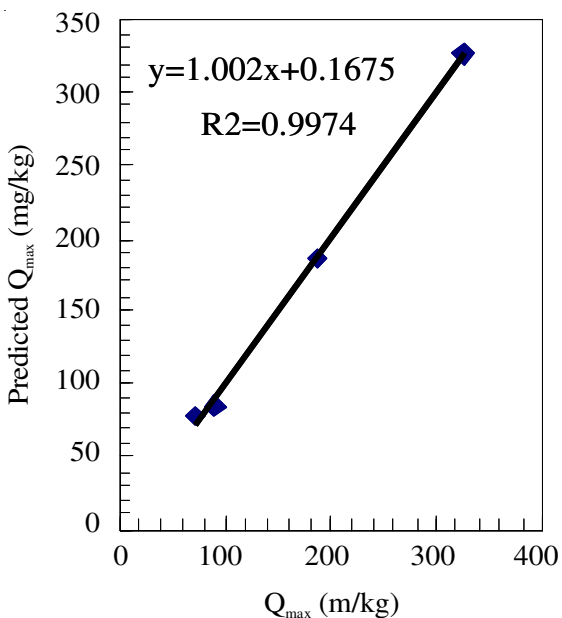

Fig. 2.　Relationship between Q_{max}, F and B predicted from regression equations and the observed values for different land use pattern soils

According to Table-3 and formula (7) the pH (NaF) was highly effective in phosphorus adsorption and the predicting phosphorus sorption capacity which was consistent with the findings of others[17,19-22]. The close relationship of Q_{max} with Al_o indicated that amorphous of poorly crystalline Al oxyhydroxides provided much of the phosphorus sorption, which was consistent with the finding of many authors for highly weathered soils[14,17,23-25]. However in this experiment the Fe oxyhydroxides had significant effect on the sorption capacity, which was different with previous work[26-28].

	TABLE-3					
	PEARSON CORRELATIONS ADSORPTION PARAMETERS					
Properties	Q_{max}	k	F	n	B	K
pH	0.353	-0.806	0.679	0.692	0.182	0.558
pH (NaF)	0.972*	-0.153	0.998**	0.689	0.999**	0.887
OM	0.787	0.188	0.861	0.372	0.845	0.686
Avail-P	-0.437	0.993**	-0.152	-0.857	-0.263	-0.628
Fe-P	0.675	-0.030	0.783	0.437	0.746	0.537
Al-P	0.267	-0.250	0.110	0.308	0.178	0.387
Ca-P	0.994**	-0.265	0.977*	0.769	0.995**	0.943
CEC	-0.420	0.827	-0.251	-0.751	-0.315	-0.511
Sand	-0.888	-0.088	-0.985*	-0.495	-0.958*	-0.755
Silt	0.737	0.356	0.895	0.243	0.845	0.569
Clay	0.927*	-0.015	0.997**	0.581	0.981*	0.812
Fe_t	-0.103	0.777	0.066	-0.527	0.006	-0.215
Al_t	0.918*	0.013	0.995**	0.558	0.976*	0.799
Mn_t	0.866	-0.338	0.768	0.731	0.818	0.894
Fe_d	-0.681	0.708	-0.565	-0.841	-0.612	-0.715
Al_d	-0.805	0.127	-0.878	-0.574	-0.856	-0.688
Mn_d	0.324	-0.343	0.146	0.398	0.222	0.456
Fe_o	0.713	0.384	0.886	0.212	0.830	0.533
Al_o	0.952*	-0.594	0.817	0.938*	0.879	0.997**
Mn_o	0.404	-0.398	0.218	0.480	0.298	0.535
*,**. Correlation is significant at the 0.05 and 0.01 level						

Conclusion

Soils collected from *Chinese chestnut* woodland (S1) and *Phyllostachys edulis* woodland (S2) were stony soils, while from paddy rice farmland (S3) and vegetable farmland (S4) were hydragric anthrosols and alluvial soils, respectively. They had different soils texture, S3 and S4 were clay texture while S1 and S2 were sandy texture. All soils were generally acidic and pH ranged from 4.48 to 7.45. Fe-P and Ca-P contents in S3 and S4 were higher than S1 and S2. Crystalline iron oxides were the dominant forms of iron oxide in these soils. Surface soils in Fushi watershed exhibited a wide range of phosphorus sorption capacity values and the sequence of sorption capacity of soils was S3 > S4 > S1 > S2. The Langmuir, Freundlich and Temkin models can be used to describe and calculate phosphorus sorption data, with R^2 ranged from 0.75 to 0.98. The parameters Q_{max}, F and B had a highly significant positive relationships with pH (NaF), Ca-P, clay, Al_t and Al_o. Multivariate stepwise regression analysis and regression equations indicated that about 92 %-99 % of the phosphorus sorption capacity maximum could be estimated by the combination of Ca-P with Al_o, Ca-P with clay and pH (NaF) with Al_o for these soils. The conclusion of phosphorus predicting formula of adsorption capacity could be useful for the management of farmland use patterns and fertilizer application. It was also helpful for the planning of environmental management agencies and environmental assessment.

ACKNOWLEDGEMENTS

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