Phosphate Sorption Characteristics and External P Requirements of Selected South African Soils

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Abstract

The Transkei is the largest consolidated area in South Africa where land is held by small-holder farmers but little is known about the extent of phosphate fixation in the region. This study was conducted to determine the phosphate sorption properties and external P requirements (EPR) of selected soils from the Transkei region, South Africa and to relate derived sorption values to selected soil parameters. The P sorption maxima and EPR values varied widely ranging from 192.3 to 909.1 mg P kg^{-1} and from 2 to 123 mg P kg^{-1} soil, respectively. Citrate dithionite bicarbonate-extractable aluminum explained most of the observed variations in P sorption. About 43% of the soils were found to be moderate P fixers and may need management interventions to ensure adequate P availability to crops. The single point sorption index accurately predicted the EPR of the soils obviating the need to use multiple point sorption isotherms. The results suggested that the use of blanket phosphate fertilizer recommendations may not be a good strategy for the region as it may lead to under-application or over-application of P in some areas.

Keywords: External P requirement, P-sorption, Single point sorption test, Citrate dithionite bicarbonate-extractable aluminum, South Africa

1 Introduction

The sorption of phosphate by oxides of iron and aluminum, and amorphous materials in soils is a major contributing factor to reduced effectiveness of added phosphates necessitating larger applications of fertilizer P to achieve good crop yields (WARREN, 1994). Phosphate sorption studies on soils from KwaZulu-Natal and Mpumalanga provinces, South Africa have shown that highly weathered soils have high sorption capacities ranging from 500 to 1197 mg P kg^{-1} soil (BAINBRIDGE et al., 1995; HENRY and SMITH, 2002). The highest P fixers were weathered red or yellow-brown clays with high oxalate (amorphous) aluminum content, and especially those with a humic-horizon. The Transkei is the largest consolidated area (4, 365, 263 ha) in South Africa where land is held by smallholder farmers (VAN AVERBEKE et al., 2008). Little is, however, known

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on the extent of P retention by soils in this region of South Africa despite the common occurrence in the region of soils with potential for high P fixation (BÜHMANN et al., 2006a).

Phosphorus sorption relationships are commonly used in the determination of the external phosphorus requirement (EPR) of crops. According to FOX (1981) EPR is the concentration of P in solution that is non-limiting to plant growth. For most crops, the amount of P in equilibrium with 0.2 mg P l^{-1} (P$_{0.2}$) has been shown to be the threshold over which no response to P is observed (BECKWITH, 1965; IYAMUREMYE et al., 1996; NZIGUHEBA et al., 1998). The P requirements, estimated in this manner aim at building up the status of soil phosphorus by a single application to a level which, thereafter, only requires maintenance application to replenish losses owing to plant uptake, removal by erosion or continuing slow reactions between phosphate and soil (HENRY and SMITH, 2003). No information could be found on the EPR of soils in the Eastern Cape Province, South Africa. Such information is, however, necessary to guide P fertilizer recommendations to ensure that crop yields are not compromised due to under-fertilization and that ground water is not polluted with P transported from over-fertilized soils.

Though phosphorus sorption relationships have been used successfully to assess the preliminary fertilizer requirements, the labour and time involved in constructing P sorption curves make it too expensive for routine soil testing laboratories. HENRY and SMITH (2003) proposed a single point sorption test procedure for obtaining an index of the P requirement in soils that avoids the need for constructing multiple point sorption isotherms. It was, therefore of interest to determine if the single point sorption procedure could be used as an index for estimating the P requirements of soils in the Eastern Cape. The objectives of this study were, therefore: (i) to quantify and compare the P sorption characteristics of selected soils from the Transkei region of the Eastern Cape, South Africa, and (ii) to relate the P sorption characteristics of the soils determined from Langmuir adsorption equations with single point sorption test values and other soil parameters.

2 Materials and Methods

2.1 Soil preparation

Surface soil samples (0-15 cm) were collected from cultivated farmers' fields from four districts (Elliotdale, Mthata, Lusikisiki and Mt. Fletcher) in Transkei, South Africa (Table 1). The districts were selected to represent low (0-600 meters above sea level (masl)), medium (700-1100 masl) and high (1500-3000 masl) altitudes. The soils were air dried and ground to pass through a 2mm sieve.

2.2 Soil characterization

Soil pH was measured in water and 1.0 M KCl (soil: solution ratio of 1:2.5) using a pH meter with a glass and reference calomel electrode (Model pH 330 SET-1, 82362) after the soil suspensions were shaken for 30 minutes and left standing for 1 hour. Electrical conductivity was measured in water (1:2.5 soil:water ratio) using a conductivity meter (Model Cond.330i/SET 82362). Organic C and N were determined by dry combustion

Table 1: Selected chemical properties of soils used in the study.

Properties	Sampling Sites and Grid References						
	Ntlonyana 31°46'27"S 28°38'16"E	Ncihane 32°00'04"S 28°42'33"E	Qweqwe 31°41'42"S 28°42'09"E	Qunu 31°46'27"S 28°38'16"E	Chevy Chase 30°50'54"S 28°32'12"E	Bethania 30°39'41"S 28°16'45"E	Flagstaff ND[‡]
pH H_2O	5.0	4.9	5.6	5.5	4.6	5.6	4.7
pH KCl	4.3	4.1	4.9	4.9	3.9	4.9	4.0
Total P (g kg^{-1})	0.18	0.18	0.21	0.14	0.17	0.18	0.42
Total N (g kg^{-1})	1.93	0.87	0.81	0.70	0.83	0.16	1.30
Organic C (g kg^{-1})	25.7	11.3	12.3	10.4	15.4	3.97	21.9
Bulk density (kg m^{-3})	1351	1449	1471	1492	1515	1698	1429
Exchang. acidity (cmol (+) kg^{-1})	0.93	0.83	0.07	0.10	1.27	0.10	1.73
CEC (cmol (+) kg^{-1})	16.5	11.3	15.8	7.4	6.3	4.6	16.2
% sand	21.1	39.0	53.2	40.6	74.7	54.7	21.8
% silt	56.4	45.2	30.3	38.5	12.8	28.0	45.2
% clay	22.5	15.8	16.5	20.9	12.5	17.3	33.0
Soil Form [*]	Klapmuts	Cartref	Glenrosa	Westleigh	Hutton	Hutton	Inanda
Corresponding WRB Soil units[†]	Planosol	Luvisol	Cambisol	Acrisol	Ferralsol	Ferralsol	Ferralsol

[*] : South Africa Soil Classification Working Group (1991); [†] : World Reference Base (2006); [‡] : data not available.

using a LECO TRUSPEC C/N auto-analyzer (LECO CORPORATION, 2003). Total P was estimated following wet digestion with H_2O_2/H_2SO_4 (OKALEBO et al., 2002). Exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ were extracted with 1.0 M ammonium acetate at pH 7 (OKALEBO et al., 2002) and determined by atomic absorption spectrophotometer. Exchangeable acidity (Al^{3+} + H^+) was extracted with 1.0 M KCl and titrated with 0.05 M NaOH (OKALEBO et al., 2002). Cation exchange capacity was estimated by the summation of exchangeable cations and exchangeable acidity.

Amorphous Fe and Al (Fe_{ox} and Al_{ox}) were determined in 0.2 M acidified ammonium oxalate adjusted to pH 3.0 with oxalic acid (WARREN, 1994). Dithionite citrate bicarbonate-extractable Fe and Al (Fe_{CDB} and Al_{CDB}) were determined by the method of MEHRA and JACKSON (1960) as cited by AGBENIN (2003). Exchangeable Al and Fe (Al_{KCl} and Fe_{KCl}) were extracted with 1.0 M KCl as outlined by OKALEBO et al. (2002). The extracts were separated by centrifuging at 3000 rev min^{-1} for 10 min and filtered with Whatman No.42 filter paper to get a clear solution. Al and Fe in all the extracts were measured by atomic absorption spectrophotometer (table 2). All analyses were done in triplicate. Particle size analysis was done by the pipette method as described by KETTLER et al. (2001).

Table 2: Forms of Al and Fe in soils used in the study.

Site	Soil form South African Soil Classification[*]	World Ref. Base[†]	Exchangeable Al (mg kg^{-1})	Exchangeable Fe (mg kg^{-1})	Oxalate Al (g kg^{-1})	Oxalate Fe (g kg^{-1})	Dithionite Al (g kg^{-1})	Dithionite Fe (g kg^{-1})	Crystaline Al (g kg^{-1})
Ntlonyana	Klapmuts	Planosol	12.50	11.00	0.41	3.47	2.28	9.24	1.87
Ncihane	Cartref	Luvisol	19.03	9.70	0.42	3.49	1.68	10.12	1.26
Qweqwe	Glenrosa	Cambisol	0.00	3.63	0.11	0.33	0.51	5.55	0.40
Qunu	Westleigh	Acrisol	0.77	3.47	0.12	0.27	1.31	9.91	1.19
Chevy chase	Hutton	Ferralsol	48.73	10.40	0.77	0.66	3.00	12.73	2.23
Bethania	Hutton	Ferralsol	0.00	3.30	0.18	0.69	1.56	13.20	1.38
Flagstaff	Inanda	Ferralsol	76.27	3.20	3.54	3.94	5.70	50.50	2.16

[*]: South African Soil Classification Working Group (1991); [†]: World Reference Base (2006)

2.3 Phosphate sorption isotherms

Three replicate 3.0 g, air-dried and milled ($<$2 mm), soil samples were weighed into 50 ml centrifuge tubes and suspended in 30 ml of 0.01 M $CaCl_2$ of supporting electrolyte containing 0 to 100 mg P l^{-1} as KH_2PO_4 with increments of 10 mg P l^{-1} . Three drops of toluene were added to each container to inhibit microbial activity. The tubes were then stoppered and shaken on an end-to-end shaker for 24 hours at a constant temperature of 25 $\pm$ 1°C at 100 oscillations per minute. Following equilibration, the soil suspensions were centrifuged at 3000 rev min^{-1} for 10 minutes and filtered through Whatman No. 42 filter paper to obtain a clear solution. Phosphorus in the supernatant was then determined by the molybdate-ascorbic acid method (MURPHY and RILEY, 1962). The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution (FOX and KAMPRATH, 1970). The sorption data were then fitted to the linearized form of the Langmuir equation viz:

$$\frac{C}{S} = \frac{1}{S_{max} \times b} + \frac{C}{S_{max}} \tag{1}$$

where C is the equilibrium P concentration (mg L^{-1}), S is the total amount of P sorbed (mg kg^{-1}), b is a constant related to the binding energy (L mg^{-1}) and S_{max} is the adsorption maximum (mg kg^{-1}).

Soil external P requirements were determined by substituting the desired P concentration into the fitted Langmuir equations (DODOR and OYA, 2000).

2.4 Single point sorption test

The single point sorption test (SI) was determined as described by HENRY and SMITH (2006). Simply, 50 ml of solution containing 10 mg P l^{-1} as KH_2PO_4, in 0.002 M $CaCl_2$, and three drops of toluene were added to 2 g of air dried soil ($<$ 2 mm). The suspensions were shaken for 24 hours on an end-to-end shaker, rotating continuously at 100 oscillations per minute. Following equilibration the suspension was centrifuged at 5000 rev min^{-1} for 10 minutes and then filtered through Whatman paper No 42. Phosphorus in the clear supernatant was determined colorimetrically by the molybdenum

blue method (MURPHY and RILEY, 1962). The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution. The single point sorption index was calculated as the amount of P sorbed expressed as a percentage of the added P (HENRY and SMITH, 2003).

2.5 Statistical analysis

Relationships between P sorption parameters, and P sorbed at equilibrium with 0.2 mg P L^{-1} ($P_{0.2}$), with selected soil chemical properties were done with simple regression and correlations and tested for significance at p = 0.05 using the GenStat statistical software (LAWES AGRICULTURAL TRUST, 2005). The contribution of soil properties to sorption parameters were examined using the maximum r^2 improvement stepwise model-building procedure (SAS INSTITUTE INC., 2001).

3 Results

3.1 Phosphate sorption

Sorption behavior was adequately described by the linearized Langmuir sorption equation with coefficients of determination (r^2) values > 0.95 observed for all the soils studied. Sorption isotherms for the seven soils showed that the soils differed considerably in sorption characteristics (Table 3). Sorption maxima ranged from 192.3 to 909.1 mg P kg^{-1} and sorption affinity constant ranged from 0.051 to 0.786 l mg^{-1}. The amount of P required to maintain a soil solution concentration of 0.2 mg P l^{-1} ($P_{0.2}$) ranged from 2 to 123 mg P kg^{-1} soil (Table 3) and as expected the trend was similar to that of the sorption maxima. Values for the single point sorption test (SI) expressed in percentage ranged from 9.5 to 86.5% (Table 3) and were highly and significantly correlated with S_{max} (r = 0.92), sorption affinity constant (r = 0.812), and external P requirement (r= 0.93).

Table 3: Phosphate sorption parameters of the different soils used in the study.

Site	Soil form South African Soil Classification*	World Ref. Base†	Linearized Langmuir equation $S = S_{max}bC/(1 + bC)$ S_{max}	b	R^2	SI	EPR ($P_{0.2}$)	EPR ($P_{1.0}$)
Ntlonyana	Klapmuts	Planosol	526.3	0.247	0.978	49.4	25	104
Ncihane	Cartref	Luvisol	476.2	0.158	0.965	48.1	15	65
Qweqwe	Glenrosa	Cambisol	204.1	0.051	0.959	9.5	2	10
Qunu	Westleigh	Acrisol	192.3	0.122	0.985	25.5	5	21
Chevy Chase	Hutton	Ferralsol	555.6	0.269	0.974	79.2	28	118
Bethania	Hutton	Ferralsol	285.7	0.095	0.965	33.5	5	25
Flagstaff	Inanda	Ferralsol	909.1	0.786	0.983	86.5	123	400

S = Total sorbed P (mg kg^{-1}), S_{max} = sorption maxima (mg P kg^{-1}), b = sorption affinity constant (L mg^{-1}), C = equilibrium P concentration (mg L^{-1}), SI = Single point sorption test (%), EPR = external phosphate requirement (mg P kg^{-1})
*: South African Soil Classification Working Group (1991); †: World Reference Base (2006)

3.2 Relationship between phosphate sorption parameters with soil properties

The regression of P sorption maxima on selected individual soil properties showed that Al_{CDB}, Fe_{CDB}, Al_{KCl}, pH, Al_{crys} and Fe_{crys} explained 89%, 69.8%, 83.9%, 79.7%, 62.8%, and 40.5%, respectively of the variations in S_{max} (Table 4). Using the stepwise multiple regression procedure (p = 0.05), a combination of organic carbon, Al_{KCl}, Al_{CDB} and Al_{ox} explained 93.2% of the variation in S_{max} of which 87.8% of the variation was explained by Al_{CDB} alone. These results suggested that the different forms of Al were primarily responsible for P sorption in the soils. The addition of soil organic carbon to the Al_{CDB} model only marginally increased the variation in S_{max} explained by the two parameters to 91.1%. The functions best fitting the data were:

$$S_{max} = 85.87 + 150\, Al_{CDB} \quad (R^2 = 0.878)$$
$$S_{max} = 46.73 + 128\, Al_{CDB} + 78.73\, C \quad (R^2 = 0.911)$$

where; S_{max} = Adsorption maximum, CDB = citrate dithionate bicarbonate, C = organic carbon.

**Table 4:** Relationships of sorption maxima (S_{max}) with selected soil variables.

Variable (x)	Functions best fitting data	R^2
pH$_{water}$ (1 : 2.5)	$Y = 195560 e^{-1210lx}$	0.797
Al_{KCl}	$Y = -0.04x^2 + 10.99x + 257.91$	0.839
Al_{ox}	$Y = 117.75x^2 + 627.34x + 164.93$	0.855
Fe_{ox}	$Y = 44.03x^2 - 67.60x + 316.33$	0.607
Al_{CDB}	$Y = -23.04x^2 + 310.05x - 115.20$	0.894
Fe_{CDB}	$Y = -0.26x^2 + 28.96x + 107.95$	0.698
Al_{crys}	$Y = 95.87 e^{0.8836x}$	0.628
Fe_{crys}	$Y = 275.13 e^{0.025lx}$	0.405

Y = sorption maxima, KCl = potassium chloride, ox = ammonium oxalate, CDB = citrate dithionate bicarbonate, crys = crystalline

3.3 Relationship between single point sorption tests (SI) with adsorption maxima (S_{max}) and external P requirement (EPR) $P_{0.2}$

The single point sorption test (SI) values were closely related to the adsorption maxima (S_{max}) and external P requirements (EPR) (Figure 1a and b) with R^2 values > 0.90. The functions best fitting the data were: $S_{max} = 0.059\, SI^2 + 4.232\, SI + 115.5$ ($R^2 = 0.967$) and EPR $= 0.028\, SI^2 - 1.233\, SI + 13.28$ ($R^2 = 0.994$).

Figure 1: Relationships between the single point sorption test (SI) and Langmuir adsorption maxima (S_{max}) (a), and the external P requirements (EPR) (b) for the soils studied.

$$S_{max} = 0.059SI^2 + 4.232SI + 115.5$$
$$R^2 = 0.967$$

$$EPR = 0.028SI^2 - 1.233SI + 13.28$$
$$R^2 = 0.994$$
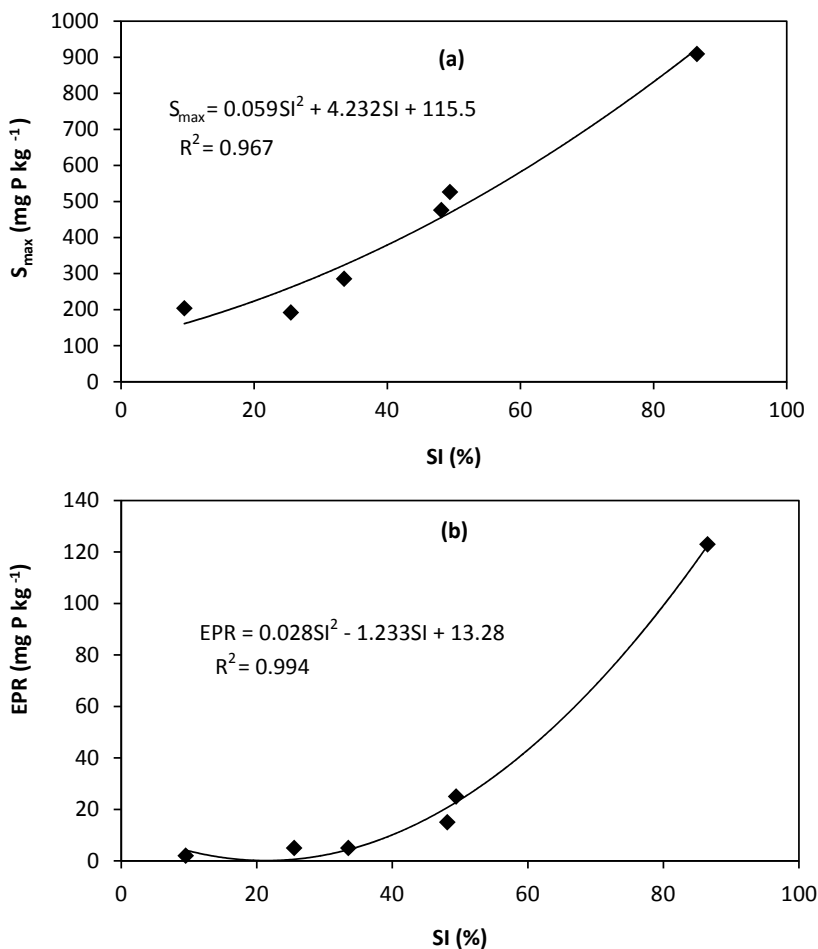
4 Discussion

The soils varied widely in their extent of P sorption as reflected by the ranges in adsorption maxima (S_{max}) and sorption index (SI) (Table 3). Soils collected from Qweqwe, Qunu, Ncihane and Bethania had low P sorption values and thus could be categorised as low P sorbers whereas soils from Ntlonyana, Chevy Chase and Flagstaff are moderate sorbers based on the scale of phosphate sorption of JUO and FOX (1977). Soils from Chevy Chase, Bethania, and Flagstaff were all classified as Ferralsols but they differed substantially in the extent to which they fixed phosphorus indicating that soils belong-

ing to the same form will not necessarily fix P to the same extent or have similar P fertilizer requirements. BÜHMANN et al. (2006b) observed similar P sorption trends for soils of the Lusikisiki area, Eastern Cape Province, South Africa and suggested that for optimum P recommendations soil P fertilization assessments need to be made at field scale level.

The observed differences in sorption parameters were largely explained by the variations in the amounts of Al in the soils. However, as revealed by stepwise multiple regression analysis most of the variation in S_{max} (87.8%) was explained by Al_{CDB} alone with only a marginal increase of 3.3% when soil organic C was included in the model. Our findings are in agreement with those of AGBENIN (2003); HENRY and SMITH (2002) and DUF-FERA and ROBARGE (1999) who also observed that Al_{CDB} had greater influence on P retention than other Al forms in the tropical soils they studied. The observed dependence of P sorption on Al_{CDB} suggested that citrate dithionite bicarbonate extractable Al is the single most important soil parameter that could be used for indicating the potential for soil P sorption in the area. The equation: $S_{max} = 85.87 + 150\ Al_{CDB}$ could therefore be used for estimating P sorption in the region after validation using a wider range of soils. Organic C was not significantly correlated with any of the P sorption parameters but together with Al_{CDB} explained 91 % of the variations in S_{max}. This suggested possible active participation of organic matter in governing P sorption in the experimental soils, possibly through Al-organo complexes as suggested by HAYNES and SWIFT (1989).

The amounts of added P required to maintain a concentration of 0.2 mg P L^{-1} ($P_{0.2}$) in solution (EPR) were generally lower than ranges reported in other studies (WARREN, 1994; IYAMUREMYE et al., 1996; MEHADI and TAYLOR, 1988; DODOR and OYA, 2000). DUFFERA and ROBARGE (1999) for example reported values ranging from 50 to 201 mg P kg^{-1} for surface samples from non-cultivated and non-fertilized areas in Ethiopia. Only Flagstaff soil with an EPR of 123 mg P kg^{-1} fell within this range while others such as Qweqwe, Qunu and Bethania had very low EPR values indicating possible early P saturation for these soils following repeated applications of P fertilizers. This could lead to elevated P levels in the soil solution which in time could contribute to the eutrophication of freshwater bodies. For purposes of water quality protection, the United States Environmental Protection Agency (USEPA) has recommended a maximum level of 1 mg P L^{-1} in surface runoff (US ENVIRONMENTAL PROTECTION AGENCY, 1986). External P requirements (EPR) calculated based on this criterion for the different soils ranged from 10 to 400 mg P kg^{-1} equivalent to 20 to 800 kg P ha^{-1} (Table 3). Given the low usage of fertilizers in sub Saharan Africa estimated at 8 kg nutrients ha^{-1} (MORRIS et al., 2007), these results suggest that unless rates of fertilizer use increase substantially, it will take some time before the application of fertilizer poses a significant threat to water quality in the region. Therefore, in the short term emphasis should be placed on ways of minimizing P fixation so as to increase P use efficiency, especially for soils such as Flagstaff, Chevy Chase and Ntlonyana with relatively high P fixing capacities.

The close association between SI with EPR ($R^2 = 0.994$) suggested that the SI function (EPR $= 0.028SI^2$ - 1.233SI $+ 13.28$) could be used to predict the external P requirement ($P_{0.2}$) for soils in the region most of which seem to have low to moderate P sorbing capacities. HENRY and SMITH (2003) also found high coefficients of determination ($R^2 = 0.98$) in the relationship between SI and $P_{0.11}$ for low to moderate sorbing soils of the tobacco growing areas of Kwa-Zulu Natal. They also concluded that SI can be used advantageously as a time saving measure to obtain an index of the external P requirement of soils instead of having to produce full P isotherms.

5   Conclusions

The seven soils studied varied widely in their capacities to sorb P with four of the soils classified as low P fixing and the remaining three (43%) as moderate P fixers. The latter category may need management interventions to ensure that P availability to crops is not compromised. The contrasting differences in the P fixing capacities of the soils suggested that the use of blanket phosphate fertilizer recommendations may not be a good strategy for the region as it may lead to under-application or over-application of P in some areas with the attendant consequences of compromised crop yields or freshwater quality. The differences in P sorption observed between the different soils were largely explained by variations in their citrate dithionite bicarbonate-extractable aluminum contents indicating that this parameter could be used for indicating the potential soil P sorption in the area. The results further showed that the single point test function could successfully be used to predict the external P requirements for the soils in the area obviating the need to use multiple point sorption isotherms.

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