PHOSPHORUS AND POTASSIUM QUANTITY/INTENSITY PROPERTIES OF SELECTED SOUTH AFRICAN SOILS (KWA-ZULU-NATAL) AND THEIR CORRELATION WITH SELECTED SOIL PARAMETERS

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Abstract There is no general single state function which describes the uptake of phosphorus (P) or potassium (K) by crop or escape in agro-ecosystem as a function external application. It is however proposed that quantity intensity relations have a potential of explaining such a paradigm. Extrapolating parameters from Quantity/Intensity (Q/I) parameters is laborious and technically complex, which makes them not suitable for routine analysis. A study of eleven soil samples was conducted to evaluate parameters which might correlate with Q/I parameters, and further evaluate influential soil properties on the Q/I parameters for both P and K using soils from different bioresource groups in KwaZulu-Natal, South Africa. It was found that pH measured in water could explain 71% variance in P sorption maxima. For K, it was found that EC accounted for 74% variance in K intensity (ARo), and 76% on the amount of K adsorbed (ΔKo). For both P and K no single parameter could uniformly and consistently explain the variance in Q/I parameters. It was concluded that although there is no single parameter which can uniformly explain Q/I parameter for both P and K, there is a potential for their modeling, using routinely determined parameters.
Keywords: *crop response, extractable nutrients, mechanistic soil test*

Introduction

Describing the state of ion in soil system, by deriving a state function which describes an uptake by roots or escape in ecosystems as a function of quantity of that particular ion is a task which has eluded natural scientists for a while. It is currently proposed that describing status of phosphorus or potassium at equilibrium by quantity intensity relations is mechanistically sound , compared to extraction based indices(Jordan-Meille et al., 2012). This is commonly supported by poor ability of extraction based indices to explain nutrient uptake (Jackson et al., 1997; Shirvani et al., 2005; Hue and Fox, 2010; Wiedenfeld and Provin, 2010; Anthony et al., 2013). Such discrepancies do not appear to be inherent errors between soil-plant relations rather soil-nutrient interactions which are poorly presented by the extractable or exchangeable phosphorus and potassium respectively as currently termed (Beckett, 1964; Fox and Kamprath, 1970).

Phosphorus can be explained by L-type isotherm, which forms when P is specifically retained at the exchange sites through the formation of inner sphere complexes. L-type isotherms are characterized by solid high affinity for a solute, with a curve resembling a logarithmic function (Tan, 2010). Constant partitioning isotherm (C-type isotherm) occurs commonly in soils where P is retained by formation of outer sphere complexes commonly found in high sandy soils (Tan, 2010). The C-type isotherms are well defined within low

ranges of initial P equilibrating solution, whereas L-type isotherms retain their form over high concentration ranges of equilibrating solution. This is because the solute that conform to C-type adsorption with the adsorbent, are commonly retained non-specifically. For L-type isotherm solutes are specifically retained on the adsorption sites. For this reason L-type isotherms are typical in soil with high sorption maxima (Qmax).

In order to extrapolate parameters which are useful in describing P dynamics in soils, the aforementioned isotherms are commonly linearized commonly using the Langmuir model (Bolster and George, 2006). The slope of the linear equation is proportional to the P buffering capacity (Dodor and Oya, 2000). This enables the use of the equation to calculate the amount of fertilizer required to raise P concentration at equilibrium (C) to desired levels based on crop needs (Fox and Kamprath, 1970). From the linearized equations parameters such as Qmax can be interpolated and these are important in indicating the potential of phosphorus escaping the agro-ecosystems.

Isotherms have also been applied to study potential of K at equilibrium (Beckett, 1964; Becket, 1971). The K sorption isotherm is characterized by two parts; at lower concentrations it curves asymmetrical to the x-axis, and second portion is linear (Shirvani et al., 2005). The slope of the linear portion corresponds to the buffering capacity. The intensity is described by the activity of K over activity (Ca + Mg) treated as single units, and extrapolated from the linear portion where Sorption ($\Delta K = 0$) and commonly termed activity ratio (ARo) (Beckett, 1964). The axiomatically assumption of conformation to ratio law as explained by Schofield (1947) is used.

There are few studies that have evaluated P and K Q/I parameters in combination. Despite the comprehensiveness of the Q/I studies, they remain confined to research due to their laborious nature. Therefore, it is necessary to evaluate simple parameters which might assist in modeling these parameters. The objectives of the current study were to: 1) Evaluate P and K Q/I properties on selected KwaZulu-Natal soils in South Africa under contrasting land uses and agro-ecological zones (bioresource groups). 2) Evaluate soil parameters that are routinely determined that correlate with Q/I parameters without necessarily assuming causal relationships. 3) Evaluate the combination of parameters which are the main drivers of Q/I parameters of the soils using a multiple regression model.

Methods and materials

Source of soil

Eleven soils were collected from various locations in KwaZulu-Natal (KZN), South Africa (*Table 1*). Soil samples were collected from different agro-ecological zones (bioresource groups) selected to obtain soils with different properties under different land uses. Soil samples collected were classified according (Soil-classification-working-group, 1991) Bioresource classification was taken from (Camp, 1995).

Table 1. Soil forms according to South African classification system, land use and bioresource group where the soil used for the experiment were sampled

Soil form[1]	WRB[††]	Abbreviation	Land use	Bioresource group[‡]	description
Sepane-A	Luvisols	Se1	Experimental Site	17	Lowlands
Griffin-A	Lixisol	Gf1	Unfertilized maize	3	Lowlands
Griffin-A	Lixisol	Gf2	Unfertilized maize	1	Coastal plains
Clovelly-A	Arenosol	Cv	Forestry	5	Mistbelt

Shortlands-B	Nitisols	Sd	Fallow and bare	6	Mistbelt
Swartland-C	Luvisols	Sw	Permanent pasture	6	Mistbelt
Vilafontes-E	Acrisols	Vf	Grassland	8	Highland
Hutton-B	Ferralsol	Hu	Grassland	8	Highland
Inanda-A	Acrisol	Ia	Forestry	1	Coastal plains
Sepane-A	Luvisol	Se	Permaculture	1	Coastal plains
Cartref-E	Acrisol	Cf	Grassland	1	Coastal plains

ⱡ Soil forms are adopted from South African Soil Classification Systems and the – A represents the horizon which was sampled for further analysis

‡Bioresource group: it's a natural resource classification system that is used in the province of KwaZulu-Natal in South Africa. Whereby, rainfall, vegetation land capabilities and suitability are used as mapping units.

††International classification systems (WRB reference group)

Soil preparation, analysis and characterization

Soils were air dried on polystyrene trays, and grinded to pass through <2mm mesh. Total nitrogen and carbon, sample density, extractable phosphorus, exchangeable K, Ca, Mg, acidity, Zn, Mn and Cu were determined by the Fertilizer Advisory Services of the KwaZulu-Natal Department of Agriculture and Forestry and Fisheries (hereinafter CEDARA). The pH in water was determined at a soil to solution ratio of 1:2.5. Electrical conductivity was determined using the same solution ratio, and pH in sodium flouride (NaF) was determined at a NaF concentration of 0.01M using soil to solution ratio of 1:40. The pH meter model PHM 210 with standard glass electrode was used to measure both pH in water and NaF.

Extractable aluminium (Al_d) and iron (Fe_d) in the soil samples were extracted by dithionate-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960). Poorly crystalline form of these elements (Al_o and Fe_o) were extracted using acid ammonium oxalate (Jackson et al., 1986). Organic carbon was determined using dichromate oxidation (Walkely, 1947).

Phosphorus sorption isotherms

Five gram portions of air-dry soil were equilibrated with 50 ml of graded P solutions ranging $1–140$ mg l^{-1} P (1, 2, 4, 10, 20, 40, 80, 120 and 140 mg l^{-1} of P), in 0.01M of $CaCl_2$ as a supporting electrolyte. The contents were shaken for 16 hours, and equilibrated for 2 hours, followed by centrifugation and filtered using Whatman No1 filter paper into a storage bottle. The phosphorus in the supernatant was determined by molybdate-ascorbic acid method (Murphy and Riley, 1962).

Phosphorus sorption parameter derivation

From the logarithmic function (Q vs C) slope and intercept of the equation were noted, where Q = P initial – P equilibrium. The sorption data were then fitted into a linearized form of Langmuir Equation 1:

$$\frac{C}{Q} = \frac{1}{Q_{max} \times b} + \frac{C}{Q_{max}} \qquad \text{(Eq.1)}$$

Where C: is equilibrium concentration; Q: amount of P sorbed; Qmax: maximum amount of P that a soil can retain; and b: is constant related to binding affinity.

Phosphorus buffering capacity was taken as the slope of linear function. Soil external phosphorus requirements were determined by substituting the desired P concentration (0.2 mg l^{-1}) into the linearized form of Langmuir equation.

Potassium Q/I relations

Five gram portions of air-dry soil were equilibrated with 50 ml of graded K solutions with a range of 0 -200 mg l^{-1} K (0, 10, 30, 50, 80, 120, 200 mg l^{-1} of K), in 0.01M of CaCl as a supporting electrolyte. The contents were shaken for 2hours, and equilibrated for 24 hours (Beckett, 1964), followed by centrifugation and filtered using Whatman No.1 filter paper into a storage bottle. Potassium, calcium and magnesium in the supernatant were analyzed by atomic adsorption spectrometer (Varian AAS 220).

Potassium Q/I parameters

The ΔK (adsorbed K) was calculated as the difference between initial and final K concentration at equilibrium and ΔK was plotted against ARe which was calculated using Equation 2.

$$ARe = \frac{aK}{\sqrt{(aCa + aMg)}} \qquad \text{(Eq.2)}$$

Where ARe: is the activity ratio of K at equilibrium; and aK:, aCa: and aMg: refer to the activity coefficient of K, Ca and Mg, respectively at equilibrium, which were calculated using Debye-Huckel equation presented as Equation 3.

$$loga = \frac{0.509 \times z^2 \times \sqrt{I}}{1 + 1.5 \times \sqrt{I}} \qquad \text{(Eq.3)}$$

Where Z: is the valence of an ion; and I: ionic strength calculated using Griffin and Jurinak (1973), simple regression Equation 4.

$$I = 0.013 \times EC \ (m\Omega \ Cm^{-1}); n = 27 \ and \ r = 0.996 \qquad \text{(Eq.4)}$$

From linear function of ARe vs ΔK, KBC is presented by the slope of the function, ARo is extrapolated from the equation when ΔK = 0, and ΔKo is extrapolated from the equation when ARe = 0. The Gibbs Free energy of exchange (–ΔG) was calculated using Equation 5.

$$-\Delta G = RT \ln ARe \qquad \text{(Eq.5)}$$

where R: is universal gas constant in Joules; T absolute temperature (K).

Correlations and regressions

Multiple regression equation is commonly expressed as Equation 6.

$$Y = \beta \times x_1 + \alpha \times x_2 + \cdots + \Omega \times x_n + E \qquad \text{(Eq.6)}$$

Where Y is an independent variable; β; α; and Ω are weight coefficients of X1……Xn; and E refers to the error due to the noise in the data (although this coefficient was omitted in this work). All regressions and correlations were performed by Microsoft Excel data analysis addon (2010).

Results

Soil physicochemical properties

Soils used showed a great variety in their physicochemical properties (*Table 2*). Generally Swartland soil form (Sw), had the highest total cation content, whereas Cartref soil form (Cf) had the lowest. Extractable P and K were highest in Sepane soil form (Se1) and lowest in Cartref. Of particular interest were the soils that are of the same family i.e, Se1, and Se and Gf1 and Gf2. Differences in these soils were that Se1 was sampled from University of KwaZulu-Natal Ukulinga research farm, with a history of high intensive fertilization and Se was sampled from a permaculture site. Also Gf 1 and Gf 2 belong to the same family, under same land use (subsistence maize farming), but differ with respect to bioresource group (*Table 1*).

In these soils, intrinsic properties such as sample density were similar with values of 1.13 and 1.14 g ml^{-1} for Se1 and Se, respectively. For Gf1 and Gf values were 0.92 and 0.90 g ml^{-1}, respectively (*Table 2*). Organic carbon was fairly constant between these soils with values of 2.05 and 2.13 % for Se1 and Se, respectively. For Gf1 and Gf2 organic carbon content was 5.80 and 5.21%, respectively. Amount of AMBIC extractable P was five times higher in Se1 compared to Se, with values of 28 and 5 mg L^{-1} of P respectively, exchangeable K on these two soils showed similar trends with exchangeable K in Se1, almost three times higher than in Se, with values of 331 and 107 mg L^{-1} of K, although the total cations were similar with values of 19.0 and 19.17 cmol L^{-1} for Se1 and Se respectively (*Table 2*).

P sorption isotherms

All of the studied soils exhibited L-type isotherm (*Figure 1*). Slope ΔQ/C followed this order (from highest to lowest): Ia> Hu > Vf > Sd > Gf 2 ≈ Se ≈ Gf1 > Cv > Sw > Se1 > Cf. Major differences as with physicochemical properties were obtained between Se and Se1, with Se having a notably steeper slope compared to Se1. The Q/I slope of Gf1 and Gf2 were approximately equal (*Figure 1*).

The Cf had the least steep slope. It is worth noting that Cf and Se beyond 30 mg l^{-1} of P of the equilibrating solution relationship between Q and C did not conform to the trend either (C-type or L-type isotherm), hence shorter trend lines.

Table 2. *Physicochemical properties of the soils used, the second column of the table gives the type of extracting solution for nutrient analysis, whereas it refers to the electrolyte material used measure pH.*

		Se1	Gf1	Gf2	Cv	Sd	Sw	Vf	Hu	Ia	Se	Cf
EC (Ms Cm^{-1})		1.21	0.62	0.95	0.75	0.72	0.86	0.75	0.56	0.17	0.19	0.11
pH	Water	5.79	5.03	4.84	5.20	5.11	5.92	5.30	5.20	4.78	6.85	6.77
pH	KCl	4.78	4.12	3.80	4.09	4.32	4.92	4.13	4.30	3.82	5.47	4.83
pH	NaF	7.56	10.5	8.85	7.80	9.22	7.74	7.75	7.97	8.06	7.77	7.71
density (g ml^{-1})		1.13	0.92	0.90	0.93	0.94	1.13	1.11	0.91	0.74	1.14	1.45
O.C (%)		2.05	5.80	5.21	3.44	0.65	2.69	1.64	0.94	6.28	2.13	0.45
clay (%)		28.00	33.0	59.00	42.00	65.00	42.00	36.00	62.00	42.0	35.00	8.00
Al (mg L^{-1})	oxalate	3.13	21.8	14.18	5.32	6.41	0.29	1.23	6.33	0.52	0.23	0.03
Fe (mg L^{-1})	oxalate	9.81	15.4	16.59	8.32	6.46	7.28	3.75	11.35	1.84	0.64	0.18
Al (mg L^{-1})	citrate dithionate	2.33	10.2	8.75	2.71	3.23	0.69	1.11	2.32	0.89	0.17	0.01
Fe (mg L^{-1})	citrate dithionate	11.83	21.7	36.61	16.85	31.04	16.84	13.59	22.83	2.95	1.84	0.26
P (mg L^{-1})	extractable	28.00	10.0	11.00	9.00	4.00	5.00	7.00	3.00	15.0	5.00	5.00
K (mg L^{-1})	exchangeable	331.0	65.0	83.00	145.0	24.00	187.0	116.0	42.00	41.0	107.00	48.00
Ca (mg L^{-1})	exchangeable	2212.	274.	327.0	986.0	154.0	2258.	730.0	288.0	105.	2051.0	352.0
Mg (mg L^{-1})	exchangeable	845.	93.0	106.	260.0	147.	917.	333	277.0	59.0	1040.00	100.00
Total cations(cmol l^{-1})		19.0	4.09	6.48	7.97	2.52	19.3	7.06	4.30	4.34	19.17	2.80
Exch Acidity(cmol l^{-1})		0.17	1.79	3.76	0.54	0.48	0.09	0.39	0.48	3.23	0.10	0.10
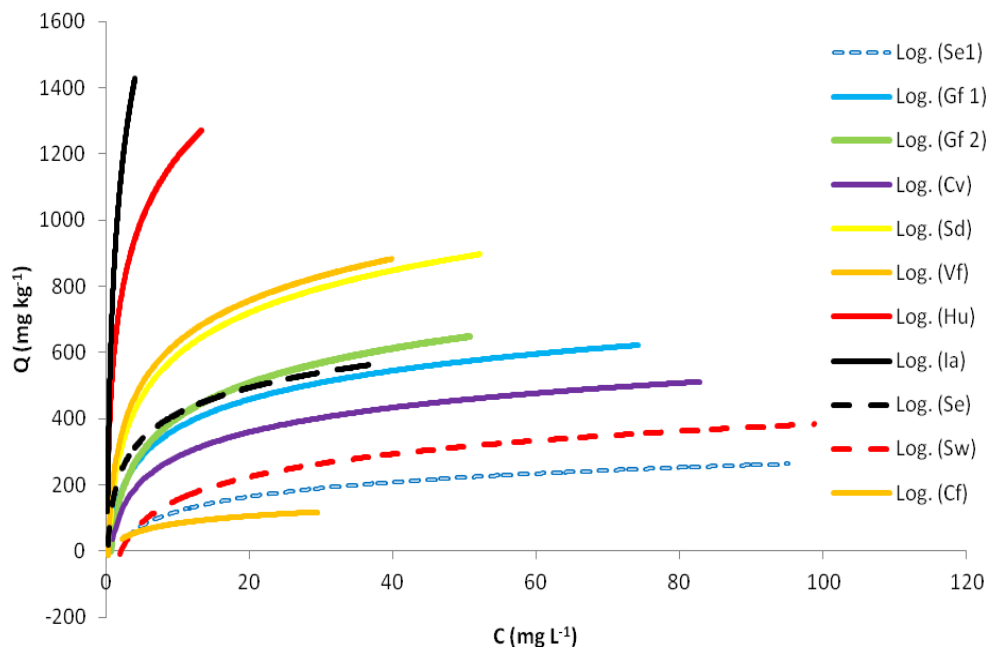
Figure 1. *Phosphorus amount of P remaining in the equilibrium (C) vs P amount sorbed (Q) from unprocessed data*

P-sorption coefficients

Table 3 shows that there was a concurrent change in equilibrium P concentration (C) and amount of P adsorbed (Q) with changes in P external application, this is parameterized by high $r^2 > 0.8$. The Ia slope was almost two times steeper than the second steepest slope (Hu), while it was almost 15 times steeper than the least steepest slope (Cf).

Table 3. *Phosphorus Q/I parameters derived from equilibrium concentration (C) vs amount of P sorbed (Q).*

Profile	Log function		
	r^2	Slope	Intercept
Se1	0.973	63.64	-264.07
Gf1	0.97	124.96	83.80
Gf2	0.91	151	55.35
Cv	0.99	106.93	38.89
Sd	0.94	184.09	168.83
Sw	0.97	99.58	74.266
Vf	0.93	181.82	212.31
Hu	0.98	274.63	559.16
Ia	0.97	454.17	793.12
Se	0.86	112.79	155.76
Cf	0.83	31.54	11.02

The amount of P sorbed at equilibrium when concentration of P in soil solution at equilibrium was equal to zero (intercept coefficient) was highest in the order of Ia > Hu > Vf > Sd > Se > Gf1 > Sw > Gf2 > Cv > Cf > Se1. It is worth noting that Se1 at equilibrium P is not sorbed, but is released even when P concentration in soil solution is zero, hence the negative value.

Linearized Langmuir coefficients

The difference in maximum amount of P that the studied soils could hold was observed as Ia> Hu > Vf > Sd > Gf1 = Gf2 > Cv > Se > Se1 > Cf. The strength at with active sites hold P (b) showed an almost reverse trend to that of the amount of P that soils sorb at equilibrium when soil solution P is equal to zero. Note that Se1 had the highest b coefficient and Ia had the lowest (*Table 4*).

Table 4. Phosphorus Langmuir sorption parameters.

	r2	Qmax (mg kg^{-1})	b (l mg^{-1})	EPR$_{0.2}$ (mg P kg^{-1})†
Se1	0.93	238.09	0.99	39.35043
Gf1	0.97	769.23	0.969	124.8758
Gf2	0.93	769.23	0.876	114.6776
Cv	0.99	555.55	0.944	88.23001
Sd	0.99	909.09	0.345	58.6784
Sw	0.98	500	2.83	180.7152
Vf	0.96	1111.11	0.7	136.4521
Hu	0.98	1428.57	0.185	50.97116
Ia	0.99	1666.66	0.1	32.67961
Se	0.99	344.82	0.158	10.56254
Cf	0.99	172.41	0.917	26.71962

†EPR$_{0.2}$ external phosphorus requirements to achieved equilibrium concentration of 0.2 mg l^{-1}.

All of the studied soils (*Table 4*) conformed to linearization using Langmuir model (Equation 1), with correlation coefficients ($r^2 > 0.95$) except for Se1, and Gf2 for which both had an r^2 of 0.93 (*Table 4*).

Regression characteristics of P sorption paramters and selected soil variables

A 74 % variance in the slope of logarithmic function (Q vs C) was explained by sample density where n = 11 (*Table 5*). Sample density was also able to explain 52% variance in the amount of P that soil can hold when C = 0 mg of P L^{-1} of solution. A 71% variance in Qmax (mg kg^{-1}) was explained by pH measured in water. Also sample density could explain 74% variance in Qmax. 32% variance in Langmuir constant related to binding affinity (b) could be explained by sample density. It is worth noting that pH measured in NaF had a correlation coefficient 0.89 with oxalate extractable Al.

Table 5. correlation (r^2) between selected soil parameters and phosphorus Q/I parameters

	pH water	pH NaF	Al oxalate	sample density
Slope	-0.59	0.05	-0.07261	-0.74

Intercept	-0.39	-0.0049	-0.14	-0.52
Qmax	-0.71	0.169	0.088	-0.74
b	0.16	-0.094	-0.036	0.32
pH NaF	-0.478	1	0.89	-0.42

No P sorption parameters correlated with oxalate extractable or pH measured in NaF. The pH measured in water and sample density through multiple regression models accounted for 72% variance in sorption maxima and 74% variance in the slope of (Q vs C) (*Table 6*).

Table 6. Interpolated multiple regression equation for Qmax and Slope for the studied soils

parameter	regression equation	r2
Qmax (mg kg^{-1})	$= 581 \times pH\ (water) - 2418 \times sample\ density$	0.72
slope	$= 169 \times pH\ (water) - 759 \times sample\ density$	0.74

Potassium Q/I

Intensity parameter as Quantified by ARo was highest in Se1 and lowest in Se. It was observed to occur in the order Se1 > Gf1 > Gf> Cv > Vf > Sw > Hu > Cf > Ia > Sd > Se (*Table 7*).

Table 7. Potassium Q/I parameters.

	ARo (moles l^{-1})$^{0.5}$	Δko (cmolc kg^{-1})	KBC (mmol kg^{-1}/mmol l^{-1})	-ΔG (J mole^{-1})
Se1	0.00220	-0.0443	20.14	13.89
Gf1	0.00116	-0.0203	17.47	15.34
Gf2	0.00098	-0.0172	17.61	15.73
Cv	0.00076	-0.0133	17.42	16.29
Sd	0.00006	-0.0009	14.53	21.99
Sw	0.00064	-0.0146	22.78	16.69
Vf	0.00073	-0.0131	17.92	16.39
Hu	0.00049	0.0070	14.40	17.32
Ia	0.00027	0.0036	13.25	18.64
Se	0.00005	-0.0012	25.29	22.60
Cf	0.00035	-0.0041	11.86	18.09

The same trend of ARo was true for Gibbs free energy of enthalpy. Potassium buffering capacity occurred in the order of Se > Sw > Se1 > Vf > Gf 2 > Gf1 > Cv > Sd > Hu > Ia > Cf. Although there were differences in soils of the same family such as Se1 and Se, and Gf1 and Gf2, they were not as tremendous as ARo differences, where ARo in Se1 was almost 50 times higher than in Se (*Table 7*). However, it was interesting to note that KBC for Se1 was 20.139 and for Se was 25.287 mmol kg^{-1}/mmol l^{-1}. There were minor differences between Gf1 and Gf2 in all four evaluated K Q/I parameters (*Table 7*). The amount of K sorbed when ARo = 0 was highest in Hu and lowest in Cf.

Generally, the electrical conductivity (EC) correlated well with three of the four K Q/I parameters i.e., ARo, ΔKo and $-\Delta$G, with r^2 of 0.74, 0.76 and 0.62, respectively (n = 11). A 89 % variance in potassium buffering capacity (KBC) was explained by total cations (cmol L^{-1}). Extractable P accounted for 81% in ARo variances, and exchangeable K accounted for 78%. The EC accounted for 66% variance in exchangeable K and 46% variance in extractable P (*Table 8*).

Table 8. correlation (r^2) between selected soil physic-parameters and phosphorus Q/I parameters

	EC	Extractable P	exchangeable K	Total cations
ARo	0.74	0.81	0.78	0.33
Δko	-0.76	-0.76	-0.84	-0.47
KBC	0.3	0.09	0.57	0.89
-ΔG	-0.62	-0.55	-0.53	-0.06
EC		0.46	0.66	0.32
Exch P			0.7	0.33
Exch K				0.79

Exchangeable P and extractable K showed a correlation coefficient of 0.7 (n = 11).

From *Table 9*, it is clear that 91% variance in ARo can be explained by EC and extractable P, whereas 81% variance in KBC can be accounted for by total cations, and 87% variance in ΔKo can be accounted for by EC and exchangeable K.

Table 9. Interpolated multiple regression equation for ARo, KBC and ΔKo.

	EQUATION	R^2
ARo	$= 5.34 \times 10^{-4} \times EC + 4.57 \times 10^{-5} \times extractable\ P$	0.91
KBC	$= 1.47 \times Total\ cations$	0.81
ΔKo	$= 5.56 \times 10^{-4} \times EC + 3.5 \times 10^{-6} \times exch\ K$	0.87

Discussion

Genesis, morphology and land use can be applied successfully to explain some of the differences that were obtained from physicochemical properties presented in *Table 2*. Low content of native fertility from the Cf soil can be explained by low clay %, hence high sand percentage. Sandy soils tend to have to low active sites, which either retain P or K, thus low CEC (Zhang et al., 2002) and (Yuan et al., 1967). This notion is perhaps supported by the highest total cations which were observed in Se1 and Se soils. A true exception to this proposition is Sd soil, which had the highest clay %, yet the lowest extractable P, exchangeable K and total amount of cations. This anomaly can be explained by the land use of this soil form, as it was bare and fallow (Chase and Singh, 2014). This land use might have caused continuous leaching without replenishment.

Land use had a marked effect on Se1 and Se, although they are of the same soil family and bioresource group), their fertility statuses were different as parameterized by extractable and exchangeable nutrients. These differences could be accounted for by heavy fertilization on Se1 compared to Se. There were no physical differences as

parameterized by density, clay and O.C contents. This can be attributed to the fact that soil morphologic properties are subject to soil genesis. Morphological differences were also noted with soils of the same family but different bioresource group i.e., Gf1 and Gf2, notably the high clay percentage in Gf2 (58%) compared to 33% in Gf1. The Gf1 soil was sampled from a high rainfall area in KwaZulu-Natal mist-belt, compared to Gf2 which was sampled from Umbumbulu (coastland). Under relatively high rainfall, clay is moved from the upper horizon through elluviation and illuviation processes; translocation is directly proportion to rate and intensity of rainfall events (Phillips, 2007). Since top soils were used for this study, the translocation process as a function of rainfall can thus account for clay differences. This proposition is perhaps further supported by high exchangeable acidity in Gf2 compared to Gf1 with values of 3.76 and 1.79 cmol L^{-1}, respectively (*Table 2*). This may also occur due to the leaching of basic cations (Ca^{2+}, Mg^{2+} and K$^+$) under high rainfall, thus leading to an increase in acidity (H$^+$, Al^{3+}) (Gillman and Sumpter, 1986). Genesis, and morphological properties play a crucial role in explaining variance of state equations at equilibrium of nutrients.

Soil solution pH is considered a major variable with respect to P sorption. This is mainly because P is retained at pH-dependent sites of hydroxyl-oxides (Parks, 1965) under low pH, where H$^+$ ions are dominating the solution, surface charges become more net positive and decrease as the pH increases due to increase in OH$^-$. Since P in soil solution is available as PO$_4^-$, soil ability to retain P decreases with an increase in OH$^-$ due to the reduction in electrostatic potential at the plane sorption as the net charge becomes less positive (Arai and Sparks, 2001; Wang et al., 2008).

The Ia soil had the lowest pH of 4.78 in water and 3.82 in KCl This explains the highest Qmax of Ia (1667 mg kg^{-1}) and highest resistance in change of equilibrium concentration of P as parameterized by slope of 454 mg kg^{-1}/mg l^{-1} (*Table 3*). This was further supported by r^2 of 0.71 between Qmax and pH in water. There are other factors of consideration with regards to amount of P sorbed such as oxalate extractable Al, clay content and mineralogy and ionic strength (Ullah et al., 1983; Martinez et al., 1996; Liu et al., 2011). Ullah et al. (1983) obtained a direct correlation between clay content and P sorption so that P sorption increase with an increase in clay %, and this can be used to explain the P sorption dynamics in Cf as it had 8% clay content, contrary to 62% clay content in Hu, and as such it had the lowest Qmax value and lowest resistant to external application as parameterized by slope.

It is however apparent that although soil characteristics that affect P sorption are well defined, the degree by which they affect P sorption is not constant, it varies with genesis, morphology and land use. Thus there is no single parameter which can be predefined with regards to the quantifiable degree by which it will affect P sorption. It has been previously proposed that extractable Al either by citrate dithionate or oxalate can account for up to 88% variance in Qmax (Gilkes and Hughes, 1994; Gichangi et al., 2008) . This is contrary to the obtained results showing that 8% variance can be accounted for by oxalate extractable Al in this study. Nonetheless, use of intrinsic properties such as soil density seem to be more beneficial as it was observed in this study that density accounted for 74% variance in both Qmax and slope. Such parameters can be perhaps used to develop pedotransfer functions over a wide variety of soils, although demarcation might be necessary.

Potassium intensity property as parameterized by ARo (aK/(aCa + aMg)) ranged from 0.0022 to 0.000048 √moles l^{-1} in Se1 and Se respectively. Low ARo implies depletion of K for plant uptake (Beckett, 1964). Sharma et al. (2012) suggested a

threshold ARo of 0.002 $\sqrt{moles}$ l^{-1} as an ARo level which is not limiting to plant growth (*Table 2*). Except for Se1, all other soils were below this threshold; noteworthy beings Gf1, Gf2, Sd, Se and Cf. Low levels of K in Gf1 and Gf2 can be ascribed to continuous K mining, as subsistence farmers do not commonly apply potash fertilizer. The Sd low levels are probably due to continuous leaching as earlier explained. While the limited exchange sites Cf might account for low ARo observed in this soil. Gibbs free energy of enthalpy ΔG followed a similar trend as ARo. Zhang et al. (2011) concluded that –ΔG of 14 kJ mol^{-1} is not limiting to plant growth and development. From *Table 7* is is notable that only Se1 was above this threshold (-14 kJ mol^{-1}), while Se had lowest free enthalpy energy of -23 kJ mol^{-1}.

Potassium buffering capacity (KBC) is a measure of ease by which soil ARe is depleted or replenished, so that soils of higher KBC are more capable of replenishing lost K but they are more resistant to the increase in ARe due to external application of K sources, while the reverse is true for soils with low KBC (Bertsch and Thomas, 1985). Leroux (1966) concluded that the slope (KBC) of ARe vs ΔK remains constant for different levels of K fertilizer. This explains the slight difference between Se1 and Se (20 and 25 mmol kg^{-1}/mmol L^{-1} for Se1 and Se respectively)(*Table 7*) considering that with other parameters ARo and –ΔG they were on the opposite ends of spectrum, with Se1 having the highest and Se being the lowest of the 11 studied soils. This notion extends well between Gf1, and Gf2 with KBC of 17.4 and 17.6 mmol kg^{-1}/mmol l^{-1} for Gf1 and Gf2, respectively (*Table 7*), this perhaps further enforces the notion that KBC is a constant intrinsic property. The Cf soil had the lowest KBC, due to high sand content.

Electrical conductivity explained 74% variance in ARo while it explained 76% variance on ΔKo and 62% variance of ΔG (*Table 8*). Griffin and Jurinak (1973) observed that EC had 0.99 correlations with ionic strength from 27 agricultural soil samples. Sparks et al. (1990) demonstrated the crucial role that ionic strength plays in K dynamics on multicationic solutions, as K dynamics are dependent on other cations in soil solution given that they simultaneously exchange on the exchange sites. This can be used to explain the correlation of EC with these parameters in the present study. Another correlation of noteworthiness is that of KBC and total cations (0.89), exchangeable K and ARo (0.78) and extractable P and ARo (0.81), although these might not be causal correlations, rather covariates of same processes. Multiple regression equations showed that EC and extractable P accounts for 91% variance in ARo (*Table 9*). Total cations accounted for 81% variance in KBC, and the combination of EC and exchangeable K accounted for 87% variance on ΔKo (*Table 9*).

Conclusion

The physicochemical properties of the studied soils can be linked to their morphology, genesis and land use. In particular, the differences between Se1 and Se land use had a dominating role in fertility parameters such as extractable nutrients, also on P and K Q/I parametes. This study also found that P sorption is a function of various processes operating at different dimensions. For the studied soils, pH can be identified as accounting for most of the variance observed in P sorption maxima. Combination of parameters is needed to explain P dynamics, and these changes from soil to soil. Electrical conductivity can account for most of the K sorption parameters. The findings

of this study provide an opportunity for a potential of modeling both K and P Q/I parameters by use of simple regression models.

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