EVALUATION OF EXTRACTION BASED FERTILIZER RECOMMENDATIONS

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DECLARATION

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Signed: Date: 16 February 2016

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I, the candidate's supervisors have approved this dissertation for submission

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Professor A.T. Modi (Supervisor)

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GENERAL ABSTRACT

There is a need to improve methods by which nitrogen, phosphorus and potassium are currently recommended. There is a considerable lack of mechanistical justifications for the methods used to recommend these nutrients. Lack of mechanistical justification can be attributed mainly to the disregard of nutrient (N, P and K) dynamics. Also the difficulty in incorporating these dynamics on fertilizer recommendation programs has compromised the mechanistical basis of extraction based approaches. The aim of the study was to evaluate these conventional (extraction based fertilizer recommendations) methods used to recommend these nutrients, by comparing their performance to the alternative approaches provided in this study. This evaluation was carried out through several studies, and a review of literature. From literature review it was apparent that there is indeed a need for revision of these methods. Their lack in mechanistical, technical and practical justification was considered and critically analyzed. It was proposed that alternative P and K recommendations can be achieved through quantity/intensity (Q/I) relations (amount of a respective nutrient in solution relative to the amount of nutrient adsorbed). It was also proposed that N recommendations can be improved by integrating mineralizable N. It was also concluded that these alternative approaches can routinely in a cost effective manner be determined.

The first chapter evaluated P and K Q/I relations in several South African soils. Parameters of K dynamics were derived from activity ratio diagrams and these were used to explain K dynamics. Phosphorus sorption curves were linearized by Langmuir equation, and parameters derived therefrom were used to evaluate P dynamics. It was found that pH measured in water had a correlation coefficient (R^2) of 0.71 with P sorption maxima. It was also found that electrical conductivity could account for 76% variance in K intensity parameter. It was suggested that these correlations could be exploited further to empirically model these crucial parameters. Thus, these correlations provide a possibility of determining these parameters routinely.

Pot trials were also conducted to evaluate the crop response, when P or K was made with the alternative approaches using maize and potato as test crops. Conventional extraction approach recommended higher P rates, and the P uptake between the two methods was not significantly improved. The extraction based approach recommended lesser K rates and K uptake was significantly higher under the alternative approach. The impact of integrating mineralizable N on N recommendations was also evaluated under control conditions. It was found that although alternative N recommendation approach recommended lesser N rates the N uptake was not significantly reduced. In fact the non-significant trend was that N uptake was higher when N recommendations were made with an alternative approach. From these initial pot trials only one nutrient was allowed to vary and the rest were kept constant at optimum levels. The second set of pot trials were carried out (parallel to the previous one), and on this set, all three nutrients were allowed to vary per experimental units. On these NPK was recommended with alternative approach and compared to the conventional approach. The results obtained were similar to those obtained when N, P or K were allowed to vary individually. It was also suggested that total carbon can be used to assess the validity of these approaches. This was based on the consistent inverse correlation that was obtained between total carbon and P or K.

Field trials were also conducted at Ukulinga research farm Pietermaritzburg and Wartburg, using maize and potato as test crops. The lack of concurrent response from nutrient uptake was also observed here similar to the observations already made in pot trials. These were characterized by conventional method recommending higher rates of N and N uptake not concurrent with the rates. It was also found that there was a poor correlation between applied fertilizer and extraction based intensity parameters, with R^2 ranging between 0.005 – 0.011, compared to R^2 of Q/I parameter which was 0.98 for both P and K. This poor correlation was evident between nutrient uptake and total biomass. Yield of both maize and potato at both sites was higher when recommendations were made by alternative approaches, and yield grade of potatoes was also improved when the recommendations were made by alternative approach. Total biomass of maize was also significantly improved when the recommendations were made by the alternative approach. Earlier,

observation with regards to correlation of total carbon and nutrients was also observed under field conditions. This suggested that this is an important parameter to evaluate fertilizer recommendation program. It was concluded that recommending P and K with Q/I relations, and integrating mineralizable N on N recommendations is more mechanistically, technically, theoretically and practically justified compared to the conventional method.

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LIST OF ABBREVIATIONS AND ACRONYMS

Acronym	Definition
ARe	Activity ratio of K to Ca + Mg
ARo	Activity ratio of K to Ca + Mg when amount
	K adsorbed = 0
EBFR	Extraction Based Fertilizer
	Recommendations
KBC	Potassium Buffering Capacity
PBC	Phosphorus Buffering Capacity
PRF	Phosphorus Requirement Factor
Q/I	Quantity/Intensity
S/OC	Soil/ Organic Carbon

CONCEPTUALIZATION AND STUDY OBJECTIVES

Background and Research Problem

Synthetic fertilizer is an expensive and a necessary input for agricultural production. Projected population increase is expected to put pressure on both fertilizer demand and prices. Efficiency in the use of nutrients needs to improve in order to maintain sustainability. It is currently estimated that use efficiency of Nitrogen (N) is less than 50%, while for phosphorus (P), it is less than 10%, and close to 40% for potassium (K) (global averages). These low recovery rates, can be partially attributed to plant-nutrient relations and management (timing and placement of fertilizer). Nonetheless, there is a significant portion of inefficiencies which can be attributed to soil-nutrient relations (Roberts 2008).

Quantification of soil-nutrient relations is accomplished by soil testing. Currently soil test is routinely carried out by extractants and or chelating agents (Jordan-Meille et al. 2012). Use of extractants lacks mechanistical justifications and it is incomprehensive and empirical (Evangelou et al. 1994). Errors of this approach receive limited analysis from scientific community, except for the inconsistence of extraction based approaches (EBFR) (Jordan-Meille et al. 2012; Bai et al. 2013; Toth et al. 2014). The inconsistence of EBFR can be quantified in terms of the rates of fertilizer that they recommend, and from such observations great discrepancies have been obtained. For example, Jordan-Meille et al. (2012), for the same soil sample, and same soil – crop situation, received more than three-fold differences in fertilizer rates recommendations. Such differences are mainly attributed to the use of different extractant and or different recommendation philosophies.

There are several underlying errors enclosed within EBFR, and these are commonly overlooked for various reasons. For example, if we limit soil testing to advising fertilizer rates required for optimal crop growth, we would expect that the amounts of either P or K quantified are those that directly influence crop growth (intensity parameter). However, this

is not the case as extractant performance is not only limited to this pool; other pools which are not readily available are extracted in the process (Kamprath & Watson 1980; Abdu 2006). Expectedly, these quantities are not always reflective or concurrent with crop response (Ogaard et al. 2002; Woods et al. 2006; Sharma et al. 2012). Another inherited error of this approach is a lack of function that explains changes in soil solution nutrient levels with application rates (buffer capacity) (Hue & Fox 2010). The lack of this parameter is compensated for by the general coefficient that seeks to relate soil test to application rates. For example, Leikam et al. (2003), for P recommendations reported that a factor of 18 is used in Kansas State University for determining the fertilizer rates. The interpretation of this factor is that for every 20.17 kg/ha of fertilizer P applied there will be one unit increase in soil P

Years of research in soil chemistry, have revealed that nutrient status in soil solution can be comprehensively presented by the use of quantity/intensity (Q/I) relations for P and K (Beckett 1964; Fox & Kamprath 1970; Jalali 2007b; Hue & Fox 2010). This approach is considered more comprehensive compared to EBFR. Comprehensiveness is due to the way intensity parameter is presented and the consideration of buffer capacity. Also, N recommendations are unsatisfactory, and the recommendation rates can be improved by integrating potential mineralizable nitrogen (Rice & Havlin 1994). It is worth acknowledging that N mineralization studies are more laborious than the currently used rates-yield functions.

It is a conventional approach in soil fertility studies to focus on one nutrient. For this study all three primary macronutrients were considered. The primary aim of this study was to compare crop response between two fertilizer recommendation strategies i.e., NPK recommended by conventional approach and NPK recommended by an alternative approach where P and K recommendations are derived from Q/I relations and N rates are adjusted for mineralizable N.

Hypothesis and Objectives

It was generally hypothesized that the alternative NPK recommendation strategy presented in this study is more mechanistically justified than its conventional counterpart. It was further hypothesized that if the Q/I relation for P and K recommends lower rates of fertilizer, crop growth will not be negatively affected; and if it recommends more rates crop growth will be significantly and positively affected. It was further hypothesized that adjusting N application rates for mineralizable N would not negatively affect crop response. The specific objectives of the study were to:

- Evaluate phosphorus and potassium quantity/intensity relations in a range of South African soils in KwaZulu-Natal, and evaluate routinely measured parameters that correlate with Q/I parameters.
- Evaluate relations between the conventional extraction based indices with quantity/intensity indices.
- Compare conventional methods and alternative methods of recommending N, P and K on crop response (maize and potatoes)
- Evaluate whether crop growth parameters and nutrient uptake correlate better with Q/I indices or conventional indices.
- Evaluate crop response parameter that is less subjective and can be conclusively ascribed to changes in nutrient dynamics.

Thesis Structure

The thesis is written in a paper format. The contents of its chapter are indicated below.

Chapter 1 reviews literature, with a focus on shortcomings of current indices used to index phosphorus and potassium availability. Problem solution for these indices is also reviewed. A possibility of improving nitrogen recommendations is also reviewed.

Chapter 2 evaluates some of Q/I properties of selected soils. This chapter addresses the first objective, by evaluating correlations between Q/I parameters and other easily measured soil

properties. It also sought to show the practicality of predicting these Q/I parameters routinely by the use of regression equations.

Chapter 3 is a short-term glasshouse study which addresses objective two and partially objective three. It has two parts, the first part compares maize and potato responses when P is recommended by Q/I relations and by extraction; the second part is a similar comparison done for potassium.

Chapter 4 is a second short-term glasshouse study that addresses objective three, and partially addressing objective 5. It also has two parts: the first parts compares maize and potato response to two N recommendations approaches i.e., when N rates are adjusted for mineralizable N, and when no adjustments are made; the second part holistically compares two NPK recommendation strategies, i.e., when N is adjusted for mineralizable N, and when P and K are recommended by Q/I relations, and responses of maize and potatoes are compared to conventional NPK recommendations. Objective 5 is partially addressed by evaluating response parameters in these two crops that has a consistent relationship with all three macronutrients.

Chapter 5 is similar to the second part of chapter 4, but under field conditions it reports growth parameters and nutrient uptake. This chapter addresses objectives 3 and 4 by evaluating coefficient of determination between nutrient uptake and the intensity parameter as explained by either Q/I relations, or extraction based approach.

Chapter 6 is a field trial that reports yield and yield components of maize and potato, and nutrient removal by grains or tubers. It addresses objective 3 and 5. It was also intended to evaluate the parameter proposed in chapter 4 to be less subjective, thus suitable for use in evaluating crop response as to whether it holds true under field conditions.

Chapter 7 is a general discussion. It discusses the significance of all the chapters as they relate to the primary and main objectives. It also recommends future work on this subject

References: Provided at the end of Literature review.

CHAPTER 1

TOWARDS MECHANISTICALLY SOUND FERTILIZER RECOMMENDATIONS: A REVIEW

General Process of Nutrients Recommendation and Its Shortcomings

There is positive relationship between crop yield and fertilizer application rates. This relationship can presented as a mathematical function; this function can be utilized in its rudimentary form to recommend fertilizer rates, as it is done for nitrogen. Recommendations made in this way can be interpreted as the amount of fertilizer required to achieve given yield. There are underlying assumptions with the use of application ratesyield function, and these can be summarized as follows: 1) Fertilizer rates effectiveness is independent of sites, implying that the amount of fertilizer effectiveness will be standard in all soil. 2) Homogeneity between the sites used to develop calibration and sites which fertilizer is recommended for, thus the end users sites. 3) External applications represent the only nutrient pool which affects crop growth. Because these assumptions have technical limitations Mehlich (1984), Olsen et al. (1954), Mehlich (1953), and Bray and Kurtz (1945) proposed that phosphorus and potassium levels in soil can be extracted by various chelating agents and the levels of either P or K in the aliquot should be representative of soil nutrient status. Such proposition was a great leap forward compared to rates-yield functions. Soil test-yield functions were hypothetically insensitive to soil with a consistence performance across different soils. Colwell (1967b), Colwell (1967a) and Colwell and Esdaile (1968), were among the first soil scientists which evaluated the concept of soil test as it relates to crop yields. The conclusion of these studies can be summarized by equation 1 (Colwell 1967a).

$$Y = P_0 \delta_0 + P_1 \delta_1 + P_2 \delta_2 + P_3 \delta_3 \tag{1}$$

Where Y is the yield, P_0 P_3 are coefficients, δ are orthogonal polynomials of fertilizer rates ranging from 0 to 3 × relative application rate.

Since equation 1 by interpretation still represents yield as a function of fertilizer application rate and this already has been established to be insufficient. "General" equation 2 is thus used to relate application rates with soil test.

$$P_k = q_k + r_k T^{1/2} + S_k T, \dots K = 0, 1, 2, 3,$$
(2)

Where T is the soil test, k is the order of polynomial; q and r are regional parameters.

Equation 3 represents a final interface of this equation, as currently applied in Kansas State University to recommend phosphorus (Leikam et al. 2003), equation 4 represents a yield function used to recommend potassium in South Africa (Manson et al. 2011).

$$P = (20 - T) \times 18 \tag{3}$$

$$P = (R - T) \times 2.5 \tag{4}$$

Where P refers to the application rates, T soil test, and R target soil test

Equation 4 can be interpreted as follows; for every 2.5 kg of K /ha applied the will be a standard increase in exchangeable K by one unit. This conform to both assumption 1 and 2 of rates—yield function. Since the standard change between calibration sites and sites which fertilizer rates are recommended for is assumed, also the effectiveness of fertilizer is assumed to be independent of site. This is a major challenge EBFR, and various strategies have been evaluated to circumvent this conundrum. For example Hue and Fox (2010), suggested that P buffer coefficient as obtained from single point sorption can be used to supplement equation 3 and 4. So that the rate of change of soil test is site specific as it supposed to be so. Similar approach is used here in South Africa in Kwa Zulu-Natal soil testing station (Johnston et al. 1991), whereby readily measured soil parameters are

correlated with buffer function, and a mathematical function derived therefrom is used to present a specific rate of change in soil test for a given site.

Even if the factor that relates changes in soil tests with external fertilizer application rates is accounted for and made specific, an error of soil testing and correlating with yield remains uncheck. This error originates from calibration process, during calibration processes soil cores are collected after harvesting and tested for nutrients and these are the soil tests that used to develop yield—soil test function and this seem to be a common practice for both P and K (Bray 1944; Colwell 1967a; Colwell 1967b; Jackson et al. 1986; Bhandal & Malik 1988; Eckert 1994; Andreis & McCray 1998; Fageria et al. 2010).

Interpretation of a function from this approach is as follows; the fertilizer rates recommended to achieve desirable yields are determined by soil test values at harvest. The justification for this practice remains unclear, because deployed functions for recommendations are based on application rates and coefficient of standardization. So that critical or targets test must have been in the first place derived from standardizing coefficients and application rates, to maintain the validity of the function when it is used to derive application rates for end users. Also from a crop physiology perspective this practice makes no sense. Since most crops cease nutrient uptake as they enter reproductive stage (Bender et al. 2012). Thus any relation observed at this point remains solely empirical with no causal relationship between soil test and yield. The practice of collecting soil cores at the harvest is also illogical from soil science perspective, as at this stage nutrients have already underwent several changes and some have leached. Thus there is no causal relationship observed is empirical.

The issue of soil core collection can be circumvented by defining the nutrient levels using the functions which are used to derive application rates, since the rates during calibration are known and the soil test remains unknown. This approach might be useful in ensuring that what is recommended for end user is based on description of nutrient level which has already been described and evaluated under field conditions. For example calibrating with

equation 4 where T is an unknown and it is derived based on rates and a coefficient of standardization, is more theoretically sound in terms of deployment, than calibrating with cores collected at harvest. Overall there is no relationship between recommendations made for end users with nutrient indices used for calibration. Thus it seems EBFR lacks mechanistically justifications for fertilizer application—soil tests; also soil tests—yield and indices of calibration—with indices used for recommending fertilizer to end users.

Limitations of Indexing Phosphorus with Extractants

The controversial use of extractants to index available P or K also extends to the mode of action of extracting solutions. The extractants are purportedly quantifying the amount of labile nutrients, and labile pool has been defined as soil nutrients in immediate equilibrium with soil solution (Fixen & Grove 1990). The performance and mode of action of these have been reviewed extensively, and some are given on Table 1 (Fixen & Grove 1990; Haby et al. 1990; De la Horra et al. 1998; Brown et al. 1999; Kleinman et al. 2001).

Table 1: Selected extractants used to index phosphorus and potassium availability in soils

Names	Composition					
Phosphorus extractants (Fixen & Grove 1990)						
AMBIC-DTPA	$1M NH_4HCO_3 + 0.05 M DTPA pH = 7$					
Bray P 1 and 2	$0.03 \text{ M NH}_4\text{F} + 0.025 \text{ or } 0.1 \text{ M HCl}$					
Mehlich II	$0.015 \text{ M NH}_4\text{F} + 0.2 \text{ M CH}_3\text{COOH} + 0.2 \text{ M}$					
	$NH_4Cl + 0.012 M HCl$					
Olsen	0.5 M NaHCO ₃ – pH 8.5					
Troug	$0.002 \text{ M H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4 - \text{pH } 3$					
Potassium ext	Potassium extractants (Haby et al. 1990)					
Ammonium acetate	1 M CH3COONH4 - pH = 7					
Bray and Kurtz P1	$0.025 \text{ M HCl} + 0.03 \text{M NH}_4\text{F} - \text{pH} \sim 2.6$					
Mehlich I	$0.05 \text{ M HCl} + 0.0125 \text{ M H}_2\text{SO}_4$					
Olsen	$0.5 \text{ M NaHCO}_3 - \text{pH} \sim 8.5$					

The general mode of action of P extractants can be summarized as follows; 1) extractants index P by solubilizing Fe-, Al- or Ca bound P, as it is the case with acid based extractants, such as Troug (Table 1). 2) Flouride and certain organic anions reduces the activity of Al, Fe or Ca, and liberate P retained by these ions. 3) Dilute acid through hydrolysis can break up organic P ester bonds thereby quantifying organic P 4) Bicarbonate can displace adsorb P, complex Ca thus leading to indexing of Ca bound P (Fixen & Grove 1990). For limiting this discussion, we would assume that these extractants truly index labile P, other complications such as pH of extractant will be overlooked as well, the inconsistence performance of these extractants across soils with different properties will be overlooked, interested reader is referred to Kleinman et al. (2001), Hue and Fox (2010)and reference therein. We will limit our focus to phosphorus and later to potassium fundamental chemistry.

Upon adding P, some will be retained specifically, through formation of inner sphere complex (Arai & Sparks 2001); and non-specifically through precipitation-dissolution reactions (Zhang et al. 2002). The latter poses no complications as far as indexing with extraction is concerned. Formation of inner sphere complexes, can be either bidentate binuclear or monodentate mononuclear, depending on the number of oxygen atom bonded to phosphorus in pH dependent sites (Arai & Sparks 2001). If P is retained through monodentate mononuclear mechanism, the mechanistic validity of using extractants to index P is intact. Since P retained in this form is readily reversible (Fixen & Grove 1990). However, certain portion of P that is adsorbed is irreversible fixed (sorption hysteresis), existence of sorption hysteresis of P seem to be much more common than its nonexistence (Okajima et al. 2012). Therefore even if extractants were truly indexing labile pool these fundamental processes are unlikely to be accounted for. Thus, a true labile pool as it truly affects crop growth is unlikely to be accounted for, and asymmetries between crop response and soil tests are inevitable.

Practical use of extraction based indices has shown similar limitation. Preliminary experimentation on soil test – crop response can be mainly attributed Colwell and Esdaile (1968), Colwell (1967a) and Colwell (1967b). Correlation between soil test and yield

parameters were given attention later by Holford (1980). Even from these initial results it was clear that something was wrong with these indices. For example: Holford (1980), used soil test and wheat yield data that has been reported by Colwell and Esdaile (1968). Holford evaluated relationship between Bray P1 and 2, Olsen P, and Colwell P extracting solutions, with wheat yield. The variance in wheat yield that could be accounted for by these extractants were low, ranging between 40 and 62% for Colwell P and Bray P2 respectively, and for Bray P1 and Olsen P extractant were 56 and 51% respectively. These were improved by incorporation of buffer parameter (Holford 1980). It is worth acknowledging there are many physical, chemical and biological variables affecting soil nutrient dynamics and plant uptake on multiple sites. As a result many of assumed relationships do not always account for the existing relationship.

Much later Colwell said "an ambitious research project was developed, called the National Soil Fertility project (South Australia), to establish relationships between soil fertility, as measured with fertilizer experiments and a wide range of other variables in soils.....But unfortunately despite much work the project failed to show many of the expected relationships so that for many it ended with disappointment" (Colwell 1994). Perhaps this suggests that use of extractants did not produce the much anticipated superior results. Such poor correlation have not improved yet for example; Andreis and McCray (1998) reported R^2 of 0.35 between sugar cane yield component and Bray extractable P, also Dodd and Mallarino (2005) showed similar low correlation coefficient between relative yield of maize and extractable P. There are several other studies where P extractants have failed to explain variance in yield components (Grigg 1972; Cox & Lins 1984; Jackson et al. 1986; Jackson et al. 1997; Otto & Kilian 2001; Wiedenfeld & Provin 2010; Shama et al. 2012; Anthony et al. 2013). Soil test - crop response studies are voluminous and citation made here are insignificant compared to the massive literature presented on this subject. We evaluate instances where there has been a positive response, and poor response and draw our conclusion therein.

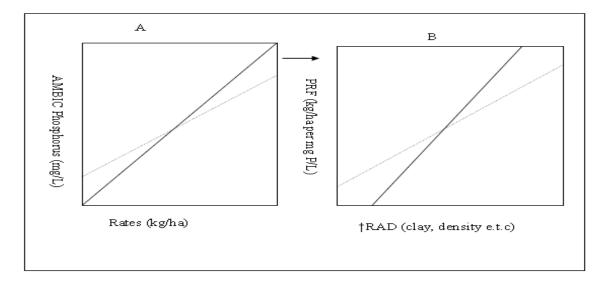
The ability of various P extractants to account for yield response varies greatly. Schlindwein et al. (2011) reported that Mehlich 1 or 3 extracted P can account for 82% to

99% in yield variance of maize, wheat, barley and soybean, when other growth limiting factors are held constant at optimum levels. Similar results were reported by (Hue & Fox 2010), whom reported that 91% to 99% of maize yield variance can accounted for by Troug P (extraction by weak acid (0.01M HCl) or Olsen P respectively. On the contrary (Jackson et al. 1997), illustrated that Olsen P can only account for 45% variance in the maize yields, similar results have been confirmed by Shama et al. (2012) and Cox and Lins (1984) on sorghum and maize respectively. The differences in responses can be attributed to several factors, such as initial P concentration, climatic condition, or experimental errors. If these factors are significant, questioning the repeatability and linearity of the extractant is refuted.

Experimental setup, specifically homogeneity within experimental units seems to be the main factor which affects correlation coefficient between soil test and crop response. For example, Jackson et al. (1997) conducted their experiment between 1986-1995 in 54 different field plots, and the correlation coefficient was 0.45. Contrary to Schlindwein et al. (2011) whom they conducted their experiment on 2 field sites during one growing season and their attain correlation coefficient of up to 0.99. Although this observation statistically is to be expected, it however poses a challenge when the data points are rendered insignificant due to the lack of homogeneity. Therefore, it is essential to maintain homogeneity in the calibration sites for these methods to be accurate, and by extension, the calibration derived from these sites can only be used to recommend for soils that fall within that homogeneity. In South Africa there are 73 soil forms, with over 160 soil families, distributed in various bioresource groups and units. This setup implies that an impossible number of calibration experiments will have to be developed for a representative combination in order for a technical sound recommendation can be made. Specificity is one of the many challenges facing extraction based strategy.

Extraction based strategy only gives information about plant available P, thus separate calibrations are required to establish the amount of fertilizer required to raise soil tests to sufficiency range. The amount of P required to raise the soil test by 1 unit varies with soil. Currently in a local soil testing station Kwa Zulu-Natal Department of Agriculture Fisheries

and Forestry (CEDARA) the following method was used to establish PRF (Johnston et al. 1991; Manson et al. 2011) Figure 1 summarizes the process.



 \dagger RAD: readily available data. Slope of Figure 2.2 A = PRF.

Figure 1: Typical protocol followed when determining phosphorus requirement factor. Figure 1a demonstrates relationship (soil test/fertilizer rates) which is used to derive PRF. This relationship cannot be routinely performed for every soil sample. Figure 1b is used where PRF is correlated with routinely measured soil parameters. It is the equation that is derived from this relationship that is used to compute PRF for individual soils. Solid line presents (1:1) ($R^2 = 1$), dotted line demonstrate the errors.

Different soil forms were used to setup a pot trial; three application rates were selected to develop a linear regression between application rates and soil test (represented by figure 2.2 A). The slope of the line (kg ha⁻¹ per mg P L⁻¹) represents the amount of P from the fertilizer required to change soil test by one unit on each soil. However, to develop the final interface another soil property which is readily tested such as clay, or bulk density is used to model PRF. The final amount of P required to raise a soil test based on pre-established optimum levels for a given crop, is calculated using Equation 5, 6, and 7 equation 5 gives an example of PRF equation taken from Johnston et al. (1991).

$$PRF = e^{(1.026 - 0.02 \times clay\%)}$$
 (5)

$$\Delta P = R - T \tag{6}$$

$$EXR = \Delta P \times PRF \tag{7}$$

Where ΔP refers to P deficit based on target soil test (R) and soil test (T), and EXR refers to external requirements of fertilizer to raise soil to desired levels.

Only 56% of the variance in PRF is accounted for by clay in this scenario (Figure 2). This value seems unacceptably low for the management of such crucial and expensive commodity, at the same rate it seems loose with regards the negative impact that P has on the quality of open water bodies. Further model predicting ability seems random beyond 58% clay, and 20 PRF units.

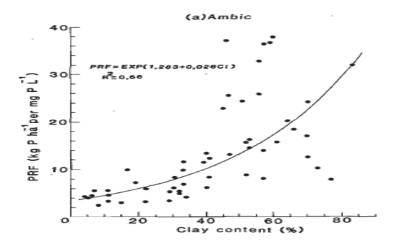


Figure 2: Relationship between PRF and clay (Johnston et al. 1991)

The problem with PRF seems universal, from the survey conducted by Cox (1994) on 13 different laboratories in the United States, he received P recommendations ranging from 26-120 kg/ha for the same sample. These discrepancies are similar to those that have been reported by Jordan-Meille et al. (2012) for European soil laboratories. The need for developing technical sound P recommendations is essential.

Potential Problem Solution for Phosphorus Recommendations

Phosphorus sorption curves provide the most comprehensive information regarding P dynamics in soil system. From the linearized P sorption equations such as Langmuir, information about the P buffering capacity, P affinity, maximum P sorption, and P

concentration at equilibrium can be extrapolated and interrelated (Taylor et al. 1996; Mesquita et al. 2002). Phosphorus sorption can be used to make P recommendations (Fox & Kamprath 1970; Dodor & Oya 2000; Gichangi et al. 2008; Hue & Fox 2010). External P requirements (EPR), are applied with an objective of increasing P concentration at equilibrium to concentration considered not liming for that particular crop (Hue & Fox 2010). Buffering capacity is utilized to relate the change in unit of equilibrium concentration with external applications. Use of P sorption is mechanistically justified, because it incorporates buffering capacity in recommendation procedure. Furthermore, it mimics the changes in soil solution due to external applications.

Limitations of Indexing Potassium with Extractants

Potassium indexing with extractants has shown similar limitations. It lacks mechanistic justifications, and detached from principles of potassium chemistry. Similar to phosphorus, an extractant intent is to quantify labile pool (Haby et al. 1990). Labile pool for it is defined as potassium retained in exchange sites plus potassium in soil solution. Mode of action for K extractant is relatively standard compared to that of P. Cations such as NH₄⁺ or Na⁺ are used to replace K⁺ on exchange sites, and amount analyzed from the aliquot is purportedly representative of K levels in soil as they are likely to influence crop growth. This index has not always been successful in explaining changes in crop response (Panique et al. 1997; Ogaard et al. 2002; Buczko & Kuchenbuch 2011). Such poor correlations perhaps might be expected considering K chemistry. Sole use of K levels in soil is incomprehensive because of the exchanges that occur between K and other cations (Evangelou et al. 1994). Further there is an issue of nonexchangeable which might contribute to soil solution K levels especially in young soils where smectite is a dominant mineral (Datta 2007; Lee & Gibson 2012).

Plants obtain K directly from the soil solution as K⁺ ions, the K in solution is in a state of dynamic equilibrium with exchangeable K that is held at the exchange sites, further; K in both solution and exchange sites is at equilibrium with other cations such as Ca²⁺ or Mg²⁺ (Schofield 1947). Once the equilibrium between soil solution K and exchangeable K is

perturbed it is restored within minutes to hours. Non-exchangeable K constitutes the second pool of K in the soil, contrary to the former, non-exchangeable K is slowly available, and commonly considered non-significant to crop growth especially to crops with short growing seasons (annual or crops with lesser growing seasons).

It is proposed that non exchangeable lattice K reaches equilibrium with soil solution within several hours or weeks once the equilibrium is disturbed (Trolove 2010), from this proposition lattice K might be significant to crop growth. The conventional notion of that crop response is exclusively accounted for by exchangeable K as extracted by ammonium acetate commonly with a pH adjusted to 7 as originally suggested by Bray (1944), is challenged by the presence of non-exchangeable K (Miller 1968; Becket 1971; Sparks 1987a; Datta 2007; Lee & Gibson 2012). Several researchers have observed poor correlation between soil tests and yield also K rates and yield (Panique et al. 1997; Ogaard et al. 2002; Buczko & Kuchenbuch 2011) (Figure 3 and Table 4). These observations are prominent in soil with smectite as dominant mineral in clay fraction due to release of K from the interlayers. Lee and Gibson (2012) have observed the poor correlation even on pot trials under control conditions. Also the poor correlation between soil tests and nutrient uptake are prominent (Woods et al. 2006) (Figure 4)

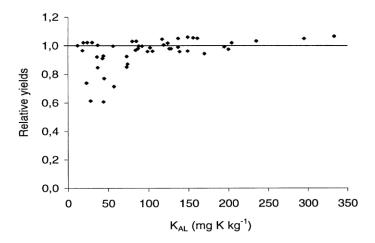


Figure 3: relative yields of timothy grass species in relation to NH4oAc extracted K (Ogaard et al. 2002)

It is worth acknowledging that there is a significant number of trials which responded to K especially those with kaolonitic mineralogy (Farina et al. 1992; Eckert 1994), however there is a still a number of trials which seem independent to soil K tests (Figure 4).

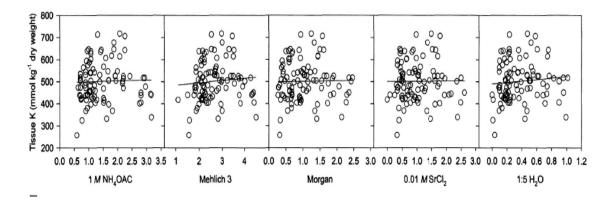


Figure 4: Tissue K content of turfgrass in relation to K as extracted with different extractions (Woods et al. 2006)

Ogaard et al. (2002) used a simple mass balance equations Equation 8, 9 and 10 to quantify unaccounted K in a fertilized agro-ecosystem as reflected by crop K uptake. Their results concerning this pool conclusively demonstrated that it was highly significant and relevant to K uptake, hence yields can be hardly explained if it is excluded.

$$K_{uptake} - K_{fertilizer} = K_{soil}$$

$$K_{NH_4OAc-S1} - K_{NH_4OAc-S2} = K_{NH_4OAc}$$

$$K_{soil} - K_{NH_4OAc} = K_{reserves}$$
(8)
(9)

Where K reserves is non exchangeable K, S1 and S2 are two different season (Autumn and Spring)

There are various other extractants that are being used to index labile K (Table 1). Extraction of other pools of K has been attempted (Becket 1971; Trolove 2010; Carey et al. 2011). An ideal extractant will be an extractant which extracts K from all pools that

actively affect crop growth, if an extractant over or under extract elemental K that actively affects crop growth calibrations being developed will be inaccurate, hence future recommendations. Although it is known that there is K unaccounted for, its extraction, kinetics and dynamics has eluded researchers thus far. It is not known how much of this K is released by the soil and at what rate, not so successful attempts have been made in quantifying rates and quantities (Guzel et al. 2006; Datta 2007; Ghiri et al. 2011; Lee & Gibson 2012). It is therefore clear that difficulties associated with extraction of K poses challenges.

It was on the basis of these challenges that (Bear et al. 1945; Bear & Toth 1948) after observing these poor response they proposed that concentration of K in soil solution does not matter but the ratio of K to Ca and Mg in soil exchange complex and similarly they cited several studies whereby crop did not respond to K applications. This conclusion was confirmed by (Graham 1959) at the time (Gladbach et al. 2005) and (Schonbeck 2000) recently. They proposed that an ideal soil should be consist of 5% K, 10% Mg, and 65% Ca, and fertilizer recommendations should aim at maintaining this balance. This hypothesis hasn't yielded much result (Figure 5). Even on other parameters such as Ca:Mg this theory does not hold true (Figure 5).

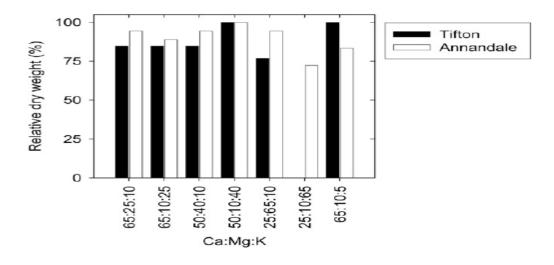


Figure 5: Relative dry weight response of Tifton and Annandale to different basic cation saturation ratios

Based on the literature extraction based strategies, are empirical, rudimentary and unpredictable. Potassium soil tests seem to manifest similar poor correlation with crop response (Panique et al. 1997; Ogaard et al. 2002; Woods et al. 2006; Buczko & Kuchenbuch 2011; Lee & Gibson 2012). It therefore, seems that the use of extractants to quantify P or K is faced with both theoretical and technical limitations, as well as practical and application limitations. This practice is currently justified on the basis of its cost effectiveness, and its empirical yet poor correlations with crop response, beyond this, justification for its validity remains hugely unconvincing.

Potential Problem Solution for Potassium Recommendations

Soil is a polycationic systems, cations such as K⁺, Mg²⁺, Ca²⁺, Al³⁺ are at equilibrium with each other (Schofield 1947; Evangelou et al. 1994). The relevance of equilibrium to explain K dynamics cannot be overstated; it forms the basis of Gapon's and Vanselow classical exchange equation. Exchange between cations and surface of the adsorbent surface occur simultaneously with various combinations such K-Ca-Mg, K-Na-Ca or K-Na-Mg, hence the term ternary mixture (Sparks et al. 1990). Thus, in order to account for K intensity and buffer capacity the exchange between K and other cations is needed to be accounted for, because capacity and intensity do not only depends on K levels. Binary systems (two ion exchange system), have been studied extensively (Sposito 1981), and they seem applicable to ternary exchange systems (Becket 1971; Ninh et al. 2009). Woodruff (1955) Proposed that K-Ca (binary system) interactions can explain K availability, modifications have been applied to Woodruff's theory to incorporate Mg thus K availability can be explained by the activity of (Ca+Mg) as a single unit. The assumption of using Ca and Mg as reference cation is that their activity is dominant in soil exchange system, and it has been shown that in acidic soils where activity of Al3+ and H+ is significant the K-Ca+Mg binary system is not sufficient in explaining K dynamics in soil system (Tinker 1964b; Tinker 1964a), by extension; it can be expected to be also not a good predictor of K potential in sodic soils where Na⁺ activity is significant in soil exchanges system.

Fundamental K chemistry can be utilized to describe K status in soil through quantity/intensity (Q/I) relations (Becket 1971; Evangelou et al. 1994). The Q/I relations seem to be more mechanistically justified as they consider exchange dynamics between K and Ca+Mg. It has also been shown by (Tinker 1964a) that for acidic soil these relations can be modified to account for Al³⁺ activity. There are several studies which have demonstrated mechanistical potential of Q/I relations in explaining K uptake by variance in crops (Zarrabi & Jalali 2008; Hosseinpur & Tadayon 2013).

Improving N Recommendations

Nitrogen in soil is present in both organic and inorganic form, over 98% of total N is in organic matter (Allen et al. 2007). N is taken up by plants mainly in inorganic forms NO₃⁻ and NH₄⁺, with the former being the common form in which plants meet their N demands, except under anoxic conditions where the latter becomes the crucial form. Despite the inorganic forms of N being the major source of N, their instability, characterized by the rapid transition from one form to the other, and high rates of immobilization and leaching; have made an efforts to develop an appropriate soil tests to index their availability a discouraging task (von Wiren et al. 1997). One of the most common index that is currently in use to quantify nitrate is the pre-sidedress soil nitrate test, which is performed by collecting soils and analyzing for nitrate a week before planting. It remains a significant variable in accounting for yield variances in the field (von Wiren et al. 1997; Scharf 2001; Zebarth et al. 2001). This test is more suitable for crops with short growing seasons such as cabbage or spinach (Heckman et al. 2002). Another index commonly used is the analysis of the plant tissue; this is considered a true reflection of N dynamics as affected by soil and atmosphere. However, this index has limitations especially since the corrective action can only be taken in the following season, considering the rate of N dynamics the value of this index is questionable (Schroder et al. 2002). Therefore, it can be concluded that contrary to K and P intensity factor of N as affected by inorganic constitutes has its limitations and challenges to be used as basis of N indexing. With regards to N managements, N

mineralization (Nm), remains an essential process in accounting for N dynamics, and useful index for N recommendation.

Nitrogen mineralization is the process of transforming organic N into plant available forms. According Bundy and Andraski (1993) organic N can replenish between 0.25–1.50 kg of N ha⁻¹ in one day. Considering that maize during the first three weeks after emergence (stage V6-V10) its N uptake is less than 0.5 kg of N ha⁻¹ day⁻¹ even at the peak of N uptake relative to growth stage (stage R5), maize do not exceed 1.5 kg N ha⁻¹ day⁻¹ (Schroder et al. 2002), it is clear that Nm can meet N maize demands under suitable conditions, when potentially mineralizable N content is high, and environmental conditions conducive for N mineralizing organisms. It is thus, worth an effort to quantify this process, to minimize any further economic losses and environment N footprint from agro-ecosystem. Nitrogen mineralization can be either studied directly in the field, or through laboratory incubation, also field indices of Nm have been developed, and extraction based strategy have been developed to correlate certain portion of extractable N to more direct studies of Nm such as incubation or field mineralization studies (Havlin et al. 1993).

The most common in situ methods for studying N mineralization its either buried bags, or ion exchange resins (Stanford & Smith 1972), and N extracted from the material at various time intervals represents Nmin. However, this method is only suitable for research. Laboratory incubations are also commonly used to study N mineralization. An amount of soil at optimum conditions (water and temperature) is incubated either aerobically or anaerobically for a given amount of time and N released during that period is taken to be N mineralization potential of a soil (Rice & Havlin 1994), also this method is not suitable for routine analysis. Since field and incubation study used quantify potential nitrogen mineralization are not suitable for routine use, a third method has emerged, whereby N is extracted by various extraction commonly 2M KCl, and N extracted by KCl is correlated to incubation studies indices (Aimian 1992). However, the use of this approach has been limited by inaccuracies.

There are several factors that affect N mineralization (Chen et al. 2002), biotic factors such as microbial biomass and activity, abiotic factors such as climatic conditions, anthropogenic factors such as fertilization natural factors such as soil properties. Arguably these many factors can be reduced to four factors i.e., (1) Substrate quality (C/N) (2) Moisture (3) Substrate accessibility and (4) Temperature (Rice & Havlin 1994). Direct mineralization studies are not possible to be used as a routine nitrogen recommendation tool. Such direct methods include field studies of mineralization (Rice & Havlin 1994), incubation studies (Cabrera et al. 2005), greenhouse studies and chemical extraction indices (Rice & Havlin 1994). Mineralizable N can be determined by the method of Stanford and Epstein (1974) (equation 11).

$$N_{\min} = N_0 (1 - e^{-kt})$$
 (11)

Whereby N_{min} = mineralizable N; N_0 = mineralizable pool ; K = rate constant adjustable for moisture and temperature and t = time.

Once N_{min} is determined, N application rates can be adjusted using equation 12 (Rice & Havlin 1994).

N recommendation = a (yield goal) – b (application rate) – c (
$$N_{min}$$
) (12)

Thus Rice and Havlin (1994) proposal to integrate can be used as a tool for improving N recommendations.

Practicality of Problem Solutions

One of the fundamental prerequisite for soil test is that it must be carried out with a reasonable ease and be guided by financial feasibility. To this end we propose that alternative soil tests proposed here within can meet these requirements. This can be either achieved by the use of mid or near infrared spectroscopy (M/NIR), or use of soil inference systems. Several studies have been conducted on the use of M/NIR, it has been shown that this tool can be used to predict several soil physicochemical properties such as organic carbon, texture analysis, exchangeable and extractable nutrients (Chang et al. 2001; Meyer

et al. 2005; He & Song 2006). Use of soil inference systems as recently reviewed by McBratney et al. (2002), also shows the potential of using easily measurable soil parameters and correlating them with the complex soil parameters. Thus, these potential two approaches have a potential of predicting P and K Q/I parameters and mineralizable N with relative ease in a cost effective manner. Considering the rate at which fertilizer prices are increasing, financially feasibility of a soil test might be redefined, what is currently considered not financially feasible is likely to not remain so.

Conclusions

There is an urgent need to shift our current fertilization approach. The entire process of extraction based fertilizer recommendation is riddled with controversies. The calibration process for these indices is empirical, thus critical values therefrom lacks mechanistic justifications. Soil extractants used to quantify P or K are inconsistence, therefore unable to provide technically sound indexes. Relations used to recommend application rates are inferred, thus not site specific. There is no evidence that predefined critical values, relates to recommendation made for end-users. These fundamental challenges that currently characterize extraction based fertilizer recommendation approach can be overcome by using quantity intensity relations to recommend P or K. This alternative approach seem comprehensive and theoretical justifiable. There is also a room for the improvement in N recommendations, by integrating mineralizable N. All these proposed improvements can be achieved, with relative ease and financially feasibility. Through utilizing emerging technologies in soil testing such as mid or near infrared spectroscopy. Alternatively; our improving computation power can benefit soil testing through development of soil inference systems.

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CHAPTER 2

PHOSPHORUS AND POTASSIUM, QUANTITY/INTENSITY PROPERTIES OF SELECTED SOUTH AFRICAN SOILS (KWAZULU 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 crops or escape in agro-ecosystems as a function of external application. It is however proposed that quantity intensity relations have a potential of explaining such a paradigm. Extrapolating parameters from Quantity/Intensity relations (Q/I) 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 soil electrical conductivity 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 a mechanistically sound approach, compared to extraction based strategies (Jordan-Meille et al. 2012). This is commonly supported by extraction studies poor correlation with crop response compared to Quantity/Intensity (Q/I) parameters (Jackson et al. 1997; Shirvani et al. 2005; Hue & Fox 2010; Wiedenfeld & Provin 2010; Anthony et al. 2013). Differences in response are commonly attributed to the comprehensiveness of Q/I relations, in simulating the soil solution changes with external application. Sorption isotherms enable quantification of changes in concentration of a soil solution with regards to a particular ion as influenced by the quantity of the adsorbent with the extent and rate of change coordinated by buffering capacity (Beckett 1964; Fox & 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 (Tan 2010). L-type isotherms are characterized by solid high affinity for a solvent, 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. 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 & George 2006). The slope of the linear equation is proportional to the P buffering capacity (Dodor & 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 & 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 the 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 (Δ 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 Kwa-Zulu 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 Kwa-Zulu Natal (KZN), South Africa (Table 1), sampling depth was 0-15 cm. 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	Luvisols	Se1	Experimental Site	17	Lowlands
Griffin	Lixisol	Gfl	Unfertilized maize	3	Lowlands
Griffin	Lixisol	Gf2	Unfertilized maize	1	Coastal plains
Clovelly	Arenosol	Cv	Forestry	5	Mistbelt
Shortlands	Nitisols	Sd	Fallow and bare	6	Mistbelt
Swartland	Luvisols	Sw	Permanent pasture	6	Mistbelt
Vilafontes	Acrisols	Vf	Grassland	8	Highland
Hutton	Ferralsol	Hu	Grassland	8	Highland
Inanda	Acrisol	Ia	Forestry	1	Coastal plains
Sepane	Luvisol	Se	Permaculture	1	Coastal plains
Cartref	Acrisol	Cf	Grassland	1	Coastal plains

¹ Soil forms are according to South African Soil Classification Systems.

[†]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, with geographical description given on the last column. ††International classification systems (WRB reference group)

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).

Soil preparation, analysis and characterization

Soils were air dried on polystyrene trays, and grinded to pass through <2mm mesh. Total carbon was determined by LECO CNS analyzer. Extractable phosphorus and exchangeable K were extracted by ammonium bicarbonate EDTA. Exchangeable Ca, Mg, acidity were extracted with 1M KCl, and these were determined by the Fertilizer Advisory Services of the Kwa-Zulu 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 & Jackson 1960). Poorly crystalline form of these elements (Al_oandFe_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 CaCl₂ 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

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

Where C: is amount of P remaining at equilibrium (mg l⁻¹); Q: amount of P sorbed (initial – amount of P equilibrium (C)); 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.

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 CaCl₂ as a supporting electrolyte. The contents were shaken for 2 hours, 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 using 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.

$$ARe = \frac{aK}{\sqrt{(aCa + aMg)}}$$
 (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.

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

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

$$I = 0.013 \times EC (dS m^{-1}); n = 27 \text{ and } r = 0.996$$
 (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 $\Delta K = 0$, and ΔK o is extrapolated from the equation when ARe = 0. The Gibbs Free energy of exchange ($-\Delta G$) was calculated using Equation 5.

$$-\Delta G = RT \ln ARe \tag{Eq.5}$$

where, R: is universal gas constant in J/mol; T absolute temperature (K).

Correlations and regressions

Multiple regression equation is commonly expressed as equation 6.

$$Y = \beta \times x_1 + \alpha \times x_2 + \dots + \Omega \times x_n + E$$
 (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

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 $\Delta Q/C$ followed this order (from highest to lowest): Ia> Hu > Vf > Sd > Gf 2 \approx Se \approx 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)

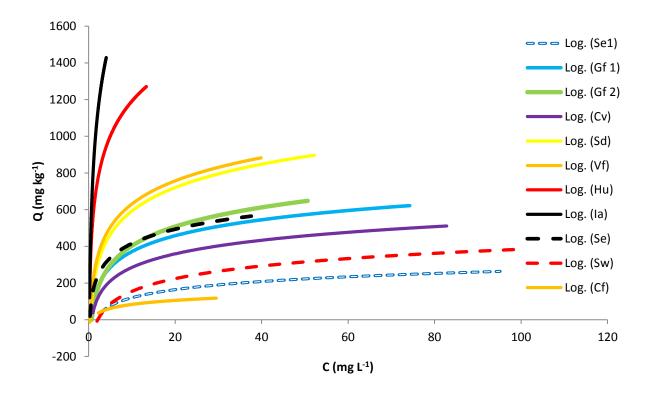


Figure 1. Phosphorus Quantities/Intensity relations of studied soil

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.

Parameter	Method	Se1	Gf1	Gf2	Cv	Sd	Sw	Vf	Hu	Ia	Se	Cf
EC (Ms Cm ⁻¹)	Water	1.21	0.62	0.95	0.75	0.72	0.86	0.75	0.56	0.17	0.19	0.11
рН	Water	5.79	5.03	4.84	5.20	5.11	5.92	5.30	5.20	4.78	6.85	6.77
рН	KC1	4.78	4.12	3.80	4.09	4.32	4.92	4.13	4.30	3.82	5.47	4.83
рН	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
SOC (%)	Dichromate	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
Basic cations(cmol 1 ⁻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

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 Q vs C curve.

Profile	Log fi		
	r^2	Slope	Intercept
Se1	0.97	64	-264
Gfl	0.97	125	84
Gf2	0.91	151	55
Cv	0.99	107	39
Sd	0.94	184	169
Sw	0.97	100	74
Vf	0.93	182	212
Hu	0.98	275	559
Ia	0.97	454	793
Se	0.86	113	156
Cf	0.83	32	11

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 adsorbed was in the order of 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 Sw had the highest b coefficient and Ia had the lowest (Table 4).

Table 4. *Phosphorus Langmuir sorption parameters*.

			Qmax (mg		
Soil form	r^2	1/Qmax	kg ⁻¹)	1/bQmax	b (1 mg ⁻¹)
Sel	0.93	0.0042	238.09	0.0416	0.99
Gf1	0.97	0.0013	769.23	0.0126	0.969
Gf2	0.93	0.0013	769.23	0.0114	0.876
Cv	0.99	0.0018	555.55	0.017	0.944
Sd	0.99	0.0011	909.09	0.0038	0.345
Sw	0.98	0.002	500.00	0.0566	2.83
Vf	0.96	0.0009	1111.11	0.0063	0.7
Hu	0.98	0.0007	1428.57	0.0013	0.185
Ia	0.99	0.0006	1666.66	0.0006	0.1
Se	0.99	0.0029	344.82	0.0046	0.158
Cf	0.99	0.0058	172.41	0.0532	0.917

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)	imes 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 in the order of Se1 > Gf1 > Gf> Cv > Vf > Sw > Hu > Cf > Ia > Sd > Se (from highest to the lowest) (Table 7).

Table 7. Potassium Q/I parameters.

	ARo (moles 1 ⁻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 1-1. 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, Δ Ko 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
Δ ko	-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 Δ Ko can be accounted for by EC and exchangeable K.

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

	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
ΔΚο	$= 5.56 \times 10^{-4} \times EC + 3.5 \times 10^{-6} \times exch K$	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 & Singh 2014). This land use might have promoted run-off and erosion.

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 Gfl 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 (Ca²⁺, Mg²⁺ and K⁺) under high rainfall, thus leading to an increase in acidity (H⁺, Al³⁺) (Gillman & 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 PO₄³⁻, 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 & 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 r² 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 & 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 √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 being 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 $-\Delta G$ 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 & 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 $-\Delta G$ 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 Δ Ko and 62% variance of Δ G (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. Potassium 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 Δ Ko (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 parameters. 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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CHAPTER 3

COMPARISON OF QUANTITY/INTENSITY AND EXTRACTION BASED FERTILIZER RECOMMENDATION STRATEGY ON GROWTH, AND NUTRIENT UPTAKE OF MAIZE AND POTATO

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Abstract

The aim of this study was to compare the effect of two fertilizer recommendations strategies on crop response. Phosphorus and potassium quantity/intensity relations were derived from the sorption isotherms. These were used to recommend fertilizer (experimental model approach) and were compared with a conventional laboratory extraction based method. Conventional method recommended higher phosphorus amounts than the experimental approach, but phosphorus uptake and crop growth between the two approaches were not significantly different. Conventional method recommended lesser potassium levels, potassium uptake and crop growth was significantly lower than where potassium was recommended by experimental approach. It is concluded that the quantity/intensity approach recommendations are more justified than the conventional ones.

Key words: Soil Test, Sorption Isotherms, Mechanistic Fertilizer Recommendations

Introduction

Total expenditure on fertilizer (NPK) relative to other farm inputs (seeds + lime + insecticides + pesticides) is currently estimated at 46%, and the total cost in crop production can be as high as 13% (Plastina 2015). At the same rate there are rising concerns regarding non-point pollution of fertilizer inputs.

Soil testing is currently the only method by which fertilizer can be quantitatively recommended. Use of extractants to quantify a particular nutrient especially K and P is a traditional approach by which the objective of nutrient indexing is accomplished. Mechanistic soundness of fertilizer recommended using extraction based strategies is questionable due to the lack of correlation between crop response and soil test (Rice & Havlin 1994; Shirvani et al. 2005; Romheld & Kirkby 2010). This incomprehensiveness include but not limited to the use of inductive logic to infer the amount of nutrient required to raise a soil test, in South Africa it has been applied by Johnston et al. (1991), and Johnston et al. (1999). Extraction based approach is empirical in nature and commonly

lacks mechanistic justification. Empirical nature of this approach is characterized by the overlook of fundamental soil properties which govern the ultimate concentration of a nutrient in soil solution. Extraction based strategy lacks consistence for example Jordan-Meille et al. (2012) found that in Europe from the same soil sample there can be 3 fold differences in P recommendation. These inconsistencies are ascribed mainly to different "philosophies" used to recommend fertilizer by different institutions.

Defining an ion state in soil system at equilibrium using isotherms has been proposed to be a mechanistically sound strategy. Fox and Kamprath (1970) proposed to apply P fertilizer with the objective of raising equilibrium P concentration to levels that are not limiting to crop growth. Equilibrium P concentration are regulated by the buffering capacity (slope of P sorption isotherm), so that External P requirements can be presented as a function of buffering capacity and equilibrium concentration. From this approach amount of fertilizer required to raise an equilibrium P concentration (external P requirements) can be calculated if the equilibrium concentration that is not limiting to plant growth is known, thus this approach can be provide an alternative fertilizer application strategy (Dodor & Oya 2000). Similar works has been done for K by Beckett (1964) and Samadi (2012). Intensity parameter in K equilibria studies is defined by the activity ratio of K to Ca and Mg treated as single unit, similar to P the external K requirements is then expressed as a function of buffering capacity and intensity parameter.

There are limited studies which have been conducted to contrast the effect of recommending fertilizer using either extraction based strategies or equilibria based approach. The study main objectives were to compare the effect of fertilizer strategy on maize and potato growth and evaluate the impact that a recommendation strategy might have on the uptake of N, P, and K.

Materials and methods

The soil used for this pot trial was locally classified as Cartref soil form, according to the world reference base for soil resource it can be classified as Acrisol (Fey 2010). This soil was selected because of it low initial native fertility. Only top soil was used for this experiment (0-15cm), previously this soil was under natural grasslands. The soil was sieved

to pass through <2mm mesh. The experiment was conducted at the University of KwaZulu-Natal, Pietermaritzburg Campus (29°36"S, 30°23"E) under glasshouse conditions with maximum and minimum temperatures of 26°C and 16°C, respectively.

Q/I based recommendations were based on sorption isotherms. These were developed by the batch equilibration technique as described by Fox and Kamprath (1970) and Beckett (1964) for P and K respectively, also given in detail on Chapter 2. External P requirements (mg kg⁻¹) were calculated based on Langmuir linearized equation targeting equilibrium concentration of 0.05 mg L⁻¹ and 0.18mg L⁻¹ for maize and potato respectively, as these are assumed to be levels not limiting for respective crops. Both these critical equilibrium concentration levels were taken from Hue and Fox (2010). The K recommendations were applied to target intensity parameter of 0.02 mol/L^{0.5} as suggested by Beckett (1964).

For extraction based approach; P was extracted by ammonium bicarbonate – EDTA solution (locally known as AMBIC). Applications are based on the difference between target and soil test P value multiplied by a purport buffer capacity value relating application rates with soil test, a parameter which is locally known as phosphorus requirements factor (PRF). The PRF's for individual soils are calculated using Equation 1 (Johnston et al. 1991).

$$PRF = 31.37 \times ("sample density")^2 - 94.13 \times "sample density" + 73.5$$
 (Eq.1)

Where sample density is mass/volume of soil sample passed through 2mm sieved and expressed in (g ml⁻¹), and PRF is in kg ha⁻¹/mg L⁻¹. So that it can be interpreted as the amount of fertilizer per area of land required to raise soil test by 1 mg L⁻¹, for further reading see Johnston et al. (1991). Similar approach was adopted for recommending K, except that a value of 2.5 is inductively applied to relate the amount of fertilizer required to raise soil test by one unit. The actual quantities of fertilizer applied are given in Table 1.

Table 1. Quantities of fertilizer recommended by two methods used in this study

Nutrient and method†	Maize (mg 2kg ⁻¹)‡	Potato (mg 2kg ⁻¹)‡
Phosphorus (Q/I)	70	150
Phosphorus (CEDARA)	130	200
Potassium (Q/I)	1000	2000
Potassium (CEDARA)	600	1300

[†] single superphosphate was used for P recommendations and 2:3:4 was used for K recommendations; N and P applications were adjusted accordingly considering amounts applied by 2:3:4. ‡ To convert fertilizer application rates from kg ha⁻¹ to mg kg⁻¹; bulk density of the soil was used to calculate mass of soil in 1 ha assuming 30cm depth (top soil), and the values obtained therefrom were converted to 2 kg of soil in a pot.

The treatments were setup so as to observe variance due to a particular nutrient when other nutrients are at optimum levels. For potassium; 1) was applied experimental when P and N were optimal (Ke), 2) no K applied N and P applied optimal (Ko) 3) K applied conventional P and N applied optimal (Kc). Same treatment structure was adopted for P.

Maize cultivar EST: 1902 (border row king), and certified Mnandi cultivar potato tuber seeds were planted. Three seeds of maize were planted initially on the 3rd of November 2014, after 5 weeks (08/ December/2014) the first 2 plants were harvested 1cm above the ground, and one plant was left behind. On the 8th week (31/December/2014) the remaining plant was harvested 1cm above ground. For potato one seed was planted per pot and the trial was harvested on the 8th week 1cm above ground, the trial was replicated three times. Both maize and potato were harvested at establishment stage.

Plant height was measured using 1 meter long tape measure, chlorophyll content was measured using spud meter (3 readings were averaged for each plant). The plants were kept for 48 hours in 70°C and thereafter biomass was determined. Same plant material used for biomass determination was digested in the CEM microwave digester MARS 6 (CEM Corporation) using concentrated nitric acid. After digestion was complete, samples were prepared for analysis for K by AAS, and P was analyzed in an UV spectrometer using

method of Murphy and Riley (1962). Nutrient uptake was taken as an amount of nutrient multiplied by biomass.

Statistical analysis was performed using Genstat statistical software (Version 12.1; 2009). One way analysis of variance (ANOVA) was conducted by running a full model across treatments. Mean separation was done using the least significant difference (LSD) at p=0.05. Additional 10 soils that have been reported on Chapter 2, were used to asses certain correlations.

Results

Soil Properties

Physicochemical properties of the soil were typical for a sandy soil, as characterized by low clay content, and low buffering capacities for both P and K (Table 2).

Table 2. Selected properties of the soil used for pot trials

Parameters	
pH (KCl)	4.80
clay (%)	8.00
AMBIC extractable P (mg L ⁻¹)	5.00
NH ₄ OAc exchangeable K (mg L ⁻¹)	48.23
Phosphorus buffer capacity (Q/I derived) (mg kg-1/mg L ⁻¹)	31.54
Potassium buffer capacity (Q/I derived) (mmol kg ⁻¹ /mmol L ⁻¹)	11.86
Equilibrium P (Q/I derived) (mg L ⁻¹)	0.00521
Potassium activity ratio (Q/I derived) (moles L ⁻¹) ^{0.5}	0.000352

It is worth noting in this instance that C (mg L⁻¹) (Q/I derived) and AMBIC extractable P (mg L⁻¹) parameters represent the same factor (intensity parameter) and they are indices which inform about the plant available P. For K, the intensity factor is NH₄OAc exchangeable K and ARo for extraction and Q/I relations respectively. Buffer coefficients are parameters which inform about the rate of change of the intensity with the amount of

fertilizer applied. It is worth noting that for extraction based approach this value for K recommendation it is assumed to be 2.5 in all soils, and for P it is calculated using (Eq.1).

Effect of P Fertilizer Recommendation Strategy on Growth Parameters

Different P recommendation strategies i.e., Q/I approach and extraction approach had no significant effect on growth parameters of maize (Table 3). Numbers of leaves of maize harvested after 8 weeks were the only parameters which were significantly affected by P recommendation strategy (Table 2).

Table 3. Plant growth parameters as affected by P fertilizer recommendation strategy

Crop	Fe	rtilization Strat	egy	Statistical para	meters
	Pc†	Pe‡	Po§	LSD $(p = 0.05)$	<i>P</i> -value
			Biomass (g pot	·1 <u>)</u>	
maize1††	8.473	8.434	8.177	0.28	0.075
maize2‡‡	11.25	11.57	11.1	0.81	0.41
potato	12.35	12.97	11.7	1.11	0.082
			<u>CCI</u>		
maize1††	27.73	28.03	28.93	68	0.87
maize2‡‡	19.7	18.03	24.43	46	0.066
potato	38.1	23.2	38.7	8.64	0.007
			Height (cm)		
maize1††	48.7	53.7	43	10	0.2
maize2‡‡	66.3	65	62	16	0.8
potato	46	49.3	34	11.32	0.036
			Leaf number		
maize2‡‡	4	3.33	2	0.67	<.001
potato	7	7	5	3.05	0.26

†phosphorus applied based on extraction based conventional approach; ‡ Phosphorus applied based on quantity/intensity relations, § no phosphorus was applied, N and K were applied at optimal and constant rates; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks.

Potato biomass was significantly higher than that of control when P was recommended by an alternative approach (Table 3). Chlorophyll content index (CCI), was significantly affected by recommendation strategy, with the mean of Pe significantly lower than that of Pc which was equal to that of Po (Table 3). Plant height was significantly affected by fertilizer recommendation strategy with both Pe and Pc significantly higher than

control, though not significantly different from each other. Fertilizer recommendation strategy had no significant effect on leaf numbers of potato at 95% significant level (Table 3)

Effect of P Fertilization Strategy on Uptake of Macronutrients

Uptake of nitrogen on maize harvested after 5 and 8 weeks was significantly affected by P fertilizer recommendation strategy with P values of 0.004 and 0.029 respectively (Table 4), however no effect was observed on potato. Mean separation reveals that Po was significantly higher than both Pe and Pc. P uptake of maize harvested after 5 weeks was significantly affected by P recommendation strategy with Pe significantly lower than Pc. However, after 8 weeks P uptake of Pe was not significantly different from that of Pc. P recommendation fertilizer strategy had no significant effect on P uptake of potato. P recommendation strategy had no significant effect on K uptake of either maize or potato.

Table 4. P recommendation effect on uptake of primary essential nutrients

Crop	Fertilization Strategy			Statistical parameters				
	Pc†	Pe‡	Po§	LSD $(p=0.05)$	<i>P</i> -value			
		N uptake (mg pot ⁻¹)						
maize1††	14.69	13.89	19.84	2.84	0.004			
maize2‡‡	13.47	12.3	19.05	4.8	0.029			
potato	46.8	46.3	48.8	12.7	0.88			
		P uptake (mg pot ⁻¹)						
maize1††	9.41	6.39	4.63	3	0.021			
maize2‡‡	5.5	4.84	3.63	1.91	0.12			
potato	12.4	13.1	8.9	4.09	0.27			
	K uptake (mg pot ⁻¹)							
maize1††	36.3	33.1	36	13.39	0.84			
maize2‡‡	41.6	40.7	30.3	19.88	0.366			
potato	41.6	56	53.8	36.96	0.62			

†phosphorus applied based on extraction based conventional approach; ‡ Phosphorus applied based on quantity/intensity relations, § no phosphorus was applied, N and K were applied at optimal and constant rates; †† maize harvested after 5 weeks (after cutting the maize was uprooted from the pots to avoid regeneration); ‡‡ maize harvested after 8 weeks

Effect of K Fertilization Strategy on Uptake of Macronutrients

Potassium recommendation strategy had a significant effect on biomass of both maize harvested 5 and 8 weeks and it had no significant effect on above ground biomass of potato after 8 weeks at p = 0.05. After 5 weeks of planting maize biomass of Kc was significantly higher than both Ke and Ko (Table 5). This trend did not hold up to the 8th week whereby the reverse happened with Ke significantly higher than Kc and Ko, and both Kc and Ko not significantly different from each other. Chlorophyll content index was significantly affected on both test crops and on both harvest dates of maize. CCI values were highest on this order Ko > Kc > Ke. Plant height was not significantly affected by K recommendation strategy. Leaf numbers of maize harvested after 8 weeks where K was recommended by extraction based approach was significantly higher than when K was recommended using Q/I relations, and there were significantly more leaves when K was recommended by Q/I relations compared to control. K recommendation strategy had no significant effect on the number of leaves on potato plants (Table 5).

Table 5. Potassium recommendation strategy effect on growth parameters

Crop	Fertilization Strategy			Statical parameters			
	Kc†	Ke‡	Ko§	LSD(p=0.05)	<i>P</i> -Value		
			Biomass (g))	_		
maize1††	8.473	7.807	7.99	0.3	0.004		
maize2‡‡	11.25	13	11.3	0.68	< 0.001		
potato	12.35	11.33	11.53	1.64	0.34		
			<u>CCI</u>				
maize1††	27.73	28.23	34.57	6	0.029		
maize2‡‡	19.7	14.7	20.2	1.4	<.001		
potato	38.1	30.7	42.6	8.03	0.03		
	Height (cm)						
maize1††	48.7	57	43.7	11.65	0.113		
maize2‡‡	64.5	70.5	66.7	17.39	0.71		
potato	46	32	39.7	20.93	0.33		
			Leaf numbe	<u>r</u>			
maize2‡‡	4	3.33	2	0.67	<.001		
potato	7	5.67	5.33	2.49	0.30		

†potassium applied based on extraction based conventional approach; ‡ potassium applied based on quantity/intensity relations, § no potassium was applied, N and P were applied at optimal and constant rates; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks.

Effect of K Fertilization Strategy on Uptake of Macronutrients

Potassium fertilization strategy had no significant effect on the uptake of nitrogen on both harvest dates of maize and potato (Table 6). P uptake of maize in both harvesting dates was significantly affected by K fertilization strategy at P = 0.05, (Table 6) P uptake was highest in Ko treatment and significantly so compared to Ke and Kc, it is worth noting that although on average in maize harvested after 8 weeks control treatment had a high P uptake it was not significantly different from that of Kc. Significant effects on K uptake were only evident during the first 5 weeks on maize, whereby Kc and Ke were significant higher than Ko. However after 8 weeks this trend disappeared and no significant impact was observed on the uptake of K by potato (Table 6).

Table 6. Effect of K recommendation strategy on uptake of primary essential nutrients

Crop	Fe	rtilization S	trategy		Statical Paran	neters
	Kc†	Ke‡	Ko§		LSD(p=0.05)	<i>P</i> -Value
			N uptake	(mg po	<u>ot⁻¹)</u>	
maize1	14.69	17.	.08	18.98	4.24	0.12
maize2	13.47	12.	.05	13.32	1.87	0.21
potato	46.8	4	7.1	54.4	12.71	0.32
			P uptake	(mg po	<u>t-1)</u>	
maize1	9.41	8	.75	13.06	3.57	0.051
maize2	55	6	.37	8.65	2.01	0.022
potato	12.4	1	4.5	20.5	12.21	0.32
_			K uptake	(mg pc	<u>ot⁻¹)</u>	
maize1	36.3	3	8.5	10.2	12.98	0.003
maize2	41.6	4	4.5	36.8	7.95	0.88
potato	41.6	4	7.9	34.3	12.95	0.29

†potassium applied based on extraction based conventional approach; ‡ potassium applied based on quantity/intensity relations, § no potassium was applied, N and P were applied at optimal and constant rates; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks.

No correlation was found between AMBIC extractable P and P remaining at equilibrium as determined by sorption studies (Q/I intensity) with $R^2 = 0.05$ (Figure 1). Nonetheless the slope of the curve reveals that 1 unit of P remaining at equilibrium is equivalent to 1003 units of AMBIC extractable. It is noteworthy that AMBIC extractable P for the soil used to conduct the pot trial was 5 mg L⁻¹, and P remaining at equilibrium was 0.0058 mg L^{-1} .

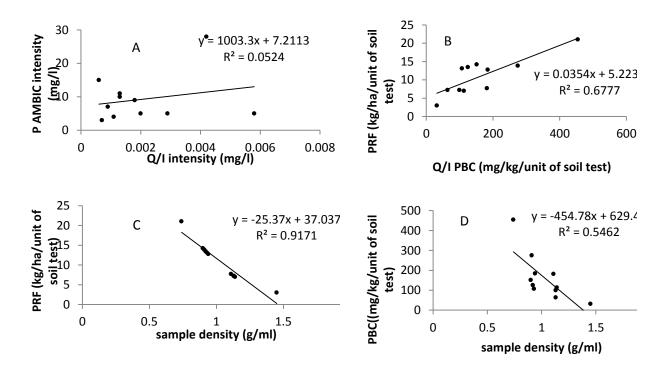


Figure 1. Correlation and linear equations between P (a) intensity of Q/I and extraction (b) capacity factor of Q/I (PBC) and extraction (PRF) (c) PRF and sample density and (d) PBC and sample density

There was an appreciable correlation between the P capacity factors of the two approach parameterized by $r^2 = 0.68$. One unit increase in the slope of sorption of curve (buffering capacity factor of Q/I relations) (PBC) is equivalent to 0.035 unit increase in phosphorus requirement factor (extraction based capacity factor) (PRF), (Figure 1B). Both

PRF and PBC had an inverse relationship with the sample density. For every 1 unit change in sample density there is 25 units change in PRF towards left hence negative value. Similarly for every one unit increase in sample density there is 455 units change in PBC towards left (Figure 1 c and d).

There was an agreement between potassium intensity parameters derived by the two approaches characterized by $r^2 = 0.61$. For every 1 unit increase in activity ratio (Q/I intensity; ARo) there is 113450 change in K exchangeable by NH₄OAc (Figure 2)

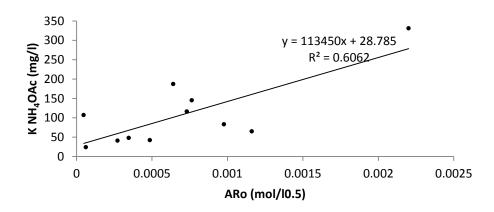


Figure 2. Relationship between K intensity of derived from NH₄OAc and Q/I intensity parameter

The NH₄OAc exchangeable K used for pot trials was 48 mg L⁻¹, and activity ratio was 0.000346 mol L⁻¹. It is worth noting that in CEDARA it is currently assumed that for every 2.5 kg/ha of K applied the will be 1 unit increase in NH₄OAc exchangeable K, for every soils, hence no comparison is possible between potassium buffering capacity as determined by Q/I relations and requirement factor associated with extraction approach.

Discussion

Higher P application rates recommended by extraction approach did not concurrently improve growth and P uptake by maize and potato (Tables 3 and 4). This implies that higher P rates recommended by conventional methods were unwarranted and non-beneficial. The artificially high P recommendation might be ascribed to the nature of

extracting solution. OH⁻ ions in an AMBIC solution can solubilize Fe and Al bound P (Kamprath & Watson 1980). Also carbonate (CO₃⁻²) in the solution can replace adsorbed P. This consequently makes the solution more ideal for highly weathered soils contrast to the sandy soil used for this experiment. Thus calibrating using this solution might cause artificially high soil test P values, based on non-universal P pools. Leading to inaccurately presented high target P values when extrapolated to soils whereby adsorbed P and metal bound P is low. This is in contrary to the sorption studies which mimic the changes in soil solution composition with external application of nutrients. Perhaps leading to more comprehensively presented intensity parameter and soil test, since the test is not directly dependent on metal-P or adsorbed P, but presenting an ultimate outcome in soil solution when the P comes in to contact with soil surface. It is worth acknowledging that the other 10 soils used in Chapter 2 might have behaved differently, since only one soil was used for pot trials.

This ultimately lead to two virtually different intensity parameter as supported by the poor correlation coefficient between the two intensity parameter with $r^2 = 0.05$ (Figure 1a). Since P recommendations made by Q/I relations achieved the same crop response with lesser P quantities it can be safely inferred that parameterizing P using this approach is perhaps more superior and more comprehensive, and might ultimately reduce unwarranted P application. It is also worth noting that although in this instance the P recommendations were unwarrantedly higher, the inverse of this is possible where P recommendations are compromisingly lower. Since the extraction is empirical in nature rather than comprehensively presenting mechanistic changes in P concentration in soil solution as affected by fertilizer inputs thus any error is possible.

Despite difference in intensity approaches there is considerable agreement between the capacity factor of the two approaches as parameterized by $R^2 = 0.68$ (Figure 1 b). Since the AMBIC buffering capacity (PRF) is derived from the sample density this implies that sample density has an effective role also in Q/I buffering capacity (PBC) perhaps supported by an appreciable correlation between PBC and sample density (Figure 1 d). The concurrent increase in phosphorus capacity with decrease in bulk density (increase in clay

content) is due to the increase in P sorption with an increase in clay content (Ullah et al. 1983). This implies that more P is required in clayey soils to raise the soil test by the same unit compared to sandy soils.

Greater amounts of K were warranted given their significance effect on biomass of maize harvested after 8 weeks (Table 5). Potassium optimum levels for the conventional method are based on NH₄OAc extractable K which reflects intensity parameter. For Q/I relations intensity parameter is derived from the activity ratio of K/(Ca + Mg). Significance of the latter approach is based on the ternary exchange between K-Ca-Mg especially in agricultural soils where these ions are dominating soil matrix (Sparks et al. 1990; Romheld & Kirkby 2010). Ohno and Grunes (1985); Welte and Werner (1963); and Jakobsen (1992) conclusively demonstrated that either K, Ca or Mg deficiencies are not exclusively dependent on the soil solution concentration. Interactions between the ions also play a crucial role, and this relationship is commonly antagonistic in nature, hence quantifying these ions by accounting for these interactions is mechanistically justified. Soil surface prefer divalent cations over monovalent cations, however this preference is not fixed, it is dynamic depending on the ratio of K:Ca:Mg, or even Na in sodic soils and Al in acidic soils (Agbenin & Yakubu 2006). The solution concentration is inversely correlated with the preference for a respective ion, so that when soils show higher preference for that particular ion its buffering capacity will be higher, and ultimately the effectiveness of fertilizer in increasing its concentration in solution will be lower. The preference commonly indexed by Gapon, or Vanselow selectivity coefficients is quantified by the same principle applied in this study to calculate KBC. This is in contrast to the traditional extraction methods, which overlooks these relations. The lack of any form of buffer coefficient for K as currently applied in various soil testing institution compromise any possibility of accuracy in the method. On a technical standpoint it is only buffer coefficient which has a capability of quantifying the rate of change in solution concentration per amount of fertilizer applied. Not accounting for K buffer capacity is not only evident in South Africa, even similar axiomatic assumptions of standard values in relating external applications with solution

concentration is evident in the United State; in Ohio States it has been reported by Vitosh et al. (1995), and in South Dakota it has been reported by Gerwing and Gelderman (2005).

Higher CCI values on both Ko and Po (Table 5) can be attributed to the classical virtual deficiency symptoms of these respective nutrients of intense green colour. Also using this logic seem to be in support that K applied using conventional approach was not sufficient, since CCI value of Kc was higher than that of Ke. Although caution might be needed with this line of reasoning since CCI values are closely correlated with N levels in leaves (van den Berg & Perkins 2004). However, N levels were the same across the treatments. The higher N uptake of both P and K controls might be attributed to the dilution effect.

Conclusions

On this study, use of Q/I relations to recommend P fertilizer is more effective and more efficient than the extraction based strategy. Higher values of K recommended by Q/I relations were more justified based on a crop response (biomass and uptake). Lack of buffer coefficients for K recommendations might be compromising the accuracy of K recommendations. Based on this trial using Q/I relations to recommend either P or K is more mechanistically justified.

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CHAPTER 4

MAIZE AND POTATO RESPONSE TO TWO CONTRASTING NPK RECOMMENDATION STRATEGIES: EXPERIMENTAL-THEORETICAL STUDY

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Abstract

There is an urgent need for accurate and consistent fertilizer recommendation approach. Use of extraction to index available P and K has been previously shown to be highly unreliable. Also it has been shown that integrating nitrogen mineralization on nitrogen recommendations, has a potential of improving nitrogen recommendations. Two parallel studies were established with the aim of comparing between two fertilizer strategies. The first study was to compare the effect of integrating nitrogen mineralization on N recommendations. No negative impacts were observed due to this integration. Second pot experiment in addition to N being recommended after integrating N mineralization; P and K were also recommended with an alternative strategy, which was derived from quantity/intensity relations. This NPK recommendation experimental approach (NePeKe) outperformed its conventional counterpart (NcPcKc).

Key words: Nitrogen mineralization, fertilizer recommendations, Quantity/Intensity.

Introduction

The use of extractions to index and calibrate phosphorus and potassium plant requirement as currently done is characterized by inaccuracies, lack of repeatability, specificity and inconsistences (Cox 1994; Eckert 1994; Sharpley 1994; Jordan-Meille et al. 2012). Such attributes 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. Despite the differences with the choice of extractant or "philosophy" of recommendations there are not much differences within the approaches of extraction based recommendations. It appears that the only attractive feature of the approach lies in its simplicity and low cost, beyond which no justifications can be made for its appropriateness.

Soils by nature have varying affinities for ions, also ions interact with each other in ways which ultimately changes the availability of a particular ion for plant uptake in final soil solution; such are but of many dynamics which cannot be sufficiently accounted for by extraction based approaches. Works on potassium demonstrated that K dynamics are determined among many factors by activity ratio of K to other counter cations in soil

solution, also by potassium potential, which is determined by soil physicochemical properties and management factors (Becket 1971; Sparks 1987b; Sparks et al. 1990). From such studies it can be expected that calibrating fertilizer recommendations on the basis of such mechanisms would emerge as it is theoretically more mechanistic, however the reverse is true. Similarly, phosphorus levels in soil solution have been demonstrated that they can be more comprehensively presented by use of P sorption isotherms (Fox & Kamprath 1970), however these approaches have not gain the popularity one would expect, one of the major reason for this sluggish adoption of these concepts is mainly believed to be their laborious nature, hence highly expensive to be adopted as routine methods.

Nitrogen recommendations are also consider inefficient as such about 70% of applied N is lost (Raun & Johnson 1999), although partially the inefficiency can be attributed to plant-N relations rather soil-plant relations. Rice and Havlin (1994) have suggested that subtracting mineralizable nitrogen from recommended nitrogen can improve inefficiencies. Mineralizable nitrogen has been shown to correlates well with N uptake under field conditions (Fox & Piekielek 1984). It is thus worth an effort to evaluate this index further.

There are several challenges associated with unsound fertilizer recommendations, such as over fertilization which might lead to unnecessary economic losses and negative environmental impacts, also under applying which might affect the final yield. Over applying one nutrient in respect to the other might also compromise other nutrients, through antagonistic reactions in either soil or plant.

The objective of a current study is to compare the response of plant growth and nutrient uptake under two different fertilizer recommendations approaches, i.e., conventional extraction approach and Q/I relations. The impact of subtracting mineralizable N from N recommendations is also a subject of interest in this study.

Materials and Methods

(Same as Chapter 3)

The soil used for this pot trial was locally classified as Cartref soil form, according to the world reference base for soil resource it can be classified as Leptosol (Fey 2010). The experiment was conducted at the University of KwaZulu-Natal, Pietermaritzburg Campus (29°36"S, 30°23"E) under glasshouse conditions with maximum and minimum temperatures of 26°C and 16°C, respectively.

Fertilizer Recommendations

Nitrogen mineralization potential of soil was determined after incubating soils anaerobically for 7 days, and amount of mineral of mineral N extracted by KCl as suggested by (Waring & Bremmer 1964). This value was integrated by subtracting it from the amount of N recommended by conventional method (Rice & Havlin 1994). Net mineralizable N was calculated by Equation 1 to be 20 mg kg⁻¹ of soil, and this value was subtracted from the initial recommendations made by conventional method and the actual amounts applied are given on Table 1.

$$N_{\min} = N_o \left(1 - e^{-kt} \right) \tag{1}$$

Where K is a mineralization rate constant taken to be $0.054~\text{week}^{-1}$ (Stanford & Smith 1972); No is a potentially mineralizable N (mg kg⁻¹); t is time (7 days); N_{min} is net mineralized N (mg kg⁻¹/week).

Q/I based recommendations were based on sorption isotherms (Same as Chapter 3). These were developed by the batch equilibration technique as described by Fox and Kamprath (1970) and Beckett (1964) for P and K respectively. External P requirements (mg kg⁻¹) were calculated based on Langmuir linearized equation targeting equilibrium concentration of 0.05 mg L⁻¹ and 0.18mg L⁻¹ for maize and potato respectively, as these are assumed to be levels not limiting for respective crops. Both these critical equilibrium concentration levels

were taken from Hue and Fox (2010). The K recommendations were applied to target intensity parameter of $0.02 \text{ mol/L}^{0.5}$ as suggested by Beckett (1964).

For extraction based approach; P was extracted by ammonium bicarbonate – EDTA solution (locally known as AMBIC). Applications are based on the difference between target and soil test P value multiplied by a purport buffer capacity value relating application rates with soil test, a parameter which is locally known as phosphorus requirements factor (PRF). The PRF's for individual soils are calculated using Equation 2 (Johnston et al. 1991).

$$PRF = 31.37 \times ("sample density")^2 - 94.13 \times "sample density" + 73.5$$
 (2)

Where sample density is mass/volume of soil sample passed through 2mm sieved and expressed in (g ml⁻¹), and PRF is in kg ha⁻¹/mg L⁻¹. So that it can be interpreted as the amount of fertilizer per area of land required to raise soil test by 1 mg L⁻¹, for further reading see Johnston et al. (1991). Similar approach is adopted for recommending K, except that a value of 2.5 is inductively applied to relate the amount of fertilizer required to raise soil test by one unit. The actual quantities of fertilizer applied are given in Table 1.

Table 1. quantities of fertilizer recommended by experimental approach and conventional approach for maize and potato

Nutrient and method†	Abbreviation in the text	Amount applied for maize (mg 2kg ⁻¹)‡	Amount applied for potato (mg 2kg ⁻¹)‡
N-conventional	N _c	90	150
N-experimental	N_e	70	120
P-conventional	P_c	130	200
P-experimental	P_e	70	150
K-conventional	K_c	600	1300
K-experimental	K_{e}	1000	2000

[†] LAN was used as N source, single superphosphate was used for P recommendations and 2:3:4 was used for K recommendations; N and P applications were adjusted accordingly considering amounts applied by 2:3:4. ‡ To convert fertilizer application rates from kg ha⁻¹ to mg kg⁻¹; bulk density of the soil was used to calculate mass of soil in 1 ha assuming 30cm depth (top soil), and the values obtained therefrom were converted to 2 kg of soil in a pot.

Treatment Structure

Two parallel pot trials were conducted. The first one was an N-based experiments when other nutrients are held at optimum constant levels. These are presented as N_e i.e., N is applied using experimental approach (integrating mineralizable N) and PK are at optimum levels. This treatment is compared to N_c i.e., N is applied using conventional approach similar to previous treatment P and K are at constant optimal levels. Control for this treatment is presented as N_o i.e., N is not applied, however, P and K are applied and are constant at optimal levels. Amounts of P that were considered optimum were 150 and 250 mg 2kg⁻¹ for maize and potato respectively. Potassium amounts that were considered optimum were 650 and 1350 mg 2kg⁻¹ of soil for maize and potato respectively.

The second pot trial was conducted to compare between the complete NPK fertilizer strategies. The conventional treatment is presented as $N_c P_c K_c$ i.e., N, P and K are applied using conventional method and abbreviated with $(N_c P_c K_c)$. This is compared to $N_e P_e K_e$ i.e., N, P and K are applied using experimental approach whereby P and K are applied using Q/I relations and N experimental is applied as outlined above. Control for this experiment is $N_o P_o K_o$ thus no fertilizer was applied on this treatment.

Pot Trial Planting and Data Collection

Maize cultivar EST: 1902 (border row king), and certified Mnandi cultivar potato seeds were planted on 2 kg soil. Three seeds of maize were planted initially on the 3rd of November 2014, after 5 weeks (08/ December/2014) the first 2 plants were harvested 1cm above the ground, and one plant was left behind. On the 8th week (31/December/2014) the remaining plant was harvested 1cm above ground. For potato one seed was planted per pot and the trial was harvested on the 8th week 1cm above ground, the trial was replicated three times. The pots were irrigated every second day after weighing to field capacity which was determined at -33 kPa suction pressure. Plant height was measured using 1 meter long tape measure, chlorophyll content was measured using spud meter (3 readings were averaged for

each plant). The plants were kept for 48 hours in 70°C and thereafter biomass was determined.

Plant Analysis and Statistical Analysis

Same plant material used for biomass determination was grounded on ball miller and digested in the CEM microwave digester MARS 6 (CEM Corporation) using concentrated nitric acid. After digestion was complete, samples were prepared for analysis for K by AAS, and P was analyzed in an using method of Murphy and Riley (1962). Nitrogen, Sulfur and total carbon were determined by LECO CNS analyser. Nutrient uptake was taken as an amount of nutrient multiplied by biomass.

Statistical analysis was performed using Genstat statistical software (Version 12.1; 2009). One way analysis of variance (ANOVA) was conducted by running a full model across treatments. Mean separation was done using the least significant difference (LSD) at p=0.05. 10 more soils were analyzed so as to evaluate certain correlations.

Results

Physicochemical properties of the soil were typical for a sandy soil, as characterized by low clay content, and low buffering capacities for both P and K (Table 2).

Table 2. Selected properties of the soils used for pot trials

Parameters	
pH (KCl)	4.80
clay (%)	8.00
AMBIC extractable P (mg L ⁻¹)	5.00
NH ₄ OAc exchangeable K (mg L ⁻¹)	48.23
Phosphorus buffer capacity (Q/I derived) (mg kg-1/mg L ⁻¹)	31.54
Potassium buffer capacity (Q/I derived) (mmol kg ⁻¹ /mmol L ⁻¹)	11.86
Equilibrium P (Q/I derived) (mg L ⁻¹)	0.00521
Potassium activity ratio (Q/I derived) (moles L ⁻¹) ^{0.5}	0.000352

It is worth noting in this instance that equilibrium P (mg L⁻¹) (Q/I derived) and AMBIC extractable P (mg L⁻¹) (Extraction based) parameters represent the same factor (intensity parameter) and they are indices which inform about the bioavailable P. For K, the intensity factor is presented by NH₄OAc exchangeable K and potassium activity ratio (ARo) for extraction and Q/I relations respectively. Buffer coefficients are parameters which inform about the rate of change of the intensity with the amount of fertilizer applied. It is worth noting that for extraction based approach this value for K recommendation it is assumed to be 2.5 in all soils, and for P it is calculated using (Eq.2).

Effect of Integrating Nitrogen Mineralization On Crop Response

Nitrogen fertilizer had a significant impact on most of the growth parameters measured (Table 3). Chlorophyll content index on maize of both conventional applied N (N_c) and N applied after adjusting for potential mineralizable N (N_e) were significantly higher than treatment where no N was applied (N_o) at p = 0.05 (Table 3). N_e and N_c were not significantly different from each other with means almost equal in maize after 8 weeks of planting. Potato CCI values were highly significantly impacted by integrating Nm with p < 0.001. Integrating N mineralization index in potato resulted in significant improvement on CCI values compared to applying N using conventional methods; it is worth noting that when N was applied using conventional methods on potato there was no significant difference between N_o and N_c (Table 3).

The amount of N uptake by potato was not significantly impacted by integrating N mineralization on N recommendations (Table 4); the means between the two fertilizer recommendations strategies were almost equal, with value of 34.59 and 35.57 mg pot⁻¹ (Table 4) for N_e and N_c respectively. The same was true for maize harvested after 8 weeks between N_e and N_c . Contrary to potatoes; maize harvested after 8 weeks both N application strategies, significantly improved N uptake by maize, as characterized by significantly higher means compared to the control. Nonetheless, the maize harvested after 5 weeks N uptake was significantly higher on N_c than N_e , and N uptake by Ne fertilization strategy was significantly higher than No (Table 4)at p=0.05. The P uptake was only significantly

impacted on maize harvested after 8 weeks. With both Ne and No significantly higher than Nc (Table 4). Similar trends were observed on potato whereby No was significantly higher than Nc, and not statistically different from Ne at p = 0.05. Potassium uptake as affected by N recommendation strategy was only significantly affected on Potatoes, where Ne was significantly higher than Nc and Nc was not statistically significant from K uptake of control pots. Total carbon content of plant material was significantly affected on maize harvested after 5 weeks, with control pots having a higher total C content than N treated pots, and N treated pots had means which were almost equal of 37.8 and 37.9 for Ne and Nc respectively (Table 4).

Table 3. The Effect of integrating nitrogen mineralization index on maize and potato growth parameters.

Crop	Fertilization strategy			Statistical pa	rameters
	Ne†	No‡	Nc§	LSD _{p=0.05}	Contrast
		<u>CCI</u>			
maize1††	26.7	20.4	27.7	8.54	ns
maize2‡‡	19.63	12.1	19.7	4.44	**
Potato	38.1	23.1	26.3	4.53	**
		Biomass (g)			
maize1††	7.877	7.817	8.473	0.44	*
maize2‡‡	12.47	10.83	11.25	0.815	**
Potato	12.15	11.7	12.35	0.58	ns
		Height (cm)			
maize1††	48.3	41	48.7	15	ns
maize2‡‡	83.3	51	66.3	12.12	**
Potato	50.5	37	46	7.93	*
		leaf number			
maize2‡‡	3.67	2.33	4	0.94	*
Potato	6.5	3.5	7	1.82	**

[†] Nitrogen applied after adjusting for potentially mineralizable nitrogen; ‡ No nitrogen applied, P and K were at optimum; § Nitrogen applied using conventional method thus no adjustments were made; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks; * P < 0.05; ** P < 0.01; ns i.e., not significant.

Table 4. Effect of integrating nitrogen mineralization index on uptake of primary macronutrients and carbon content.

crop	I	Fertilization strateg	У	Statistical parameters		
	Ne†	No‡	Nc§	$LSD_{p=0.05}$	contrast	
		N uptake (mg pot ⁻¹)			
Maize1††	11.08	10.87	14.69	0.54	**	
maize2‡‡	13.64	10.12	13.34	2.55	*	
Potato	43.2	38.3	46.7	7.82	ns	
		P uptake (mg pot-1))			
Maize1††	6.23	10	9.41	3.96	ns	
Maize2‡‡	9.54	9.56	5.53	3.1	*	
Potato	19.6	22.9	12.4	9.02	ns	
		K uptake (mg pot-1)			
Maize1††	31.7	35.3	36.3	16.3	ns	
Maize2‡‡	53.4	37.7	41.6	25.92	ns	
Potato	72.8	66.7	41.6	13.93	*	
	Tiss	sue carbon content	<u>(%)</u>			
Maize1††	37.79	40.48	37.9	0.66	**	
maize2‡†	36.28	36.76	37.7	2.42	ns	
Potato	34.69	33.48	35.57	2.37	ns	

[†] Nitrogen applied after adjusting for potentially mineralizable nitrogen; ‡ No nitrogen applied, P and K were at optimum; § Nitrogen applied using conventional method thus no adjustments were made; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks. ;* P < 0.05; ** P < 0.01; ns i.e., not significant

Effect of NPK Fertilization Strategy on Crop Response

Mechanistic nutrient recommendations must be based on all three essential nutrients i.e., N, P and K. Second part of this results section focuses on integrating mineralizable N and recommending P and K using Q/I relations, to form a single composite of NPK (experimental model). N and P amounts Table 1 were lower on experimental recommendations compared to conventional recommendations, and K applied was higher on experimental recommendations treatments compared to conventional recommendations.

NPK fertilization strategy caused no significant impact on the most growth parameters of maize at p = 0.05 (Table 5). Biomass of maize between NcPcKc and NePeKe was not significantly different from each other and both were significantly higher than NoPoKo.

Most of the observed growth parameters were equal between NePeKe and NcPcKc (Table 5). Plant height was the only exception, with NePeKe treated maize taller than and NcPcKc. Similarly on potato, biomass was not statistically different between NcPcKc and NePeKe. Chlorophyll content index on potato treated with NePeKe was higher than NcPcKc; this observation was consistent with the observation made earlier on Ne (Table 3 and 4).

Table 5. Effect of NPK fertilization strategy on maize and potato physiological growth parameters

crops]	Fertilization strate	gy	Statistical parameters		
Treatment	$N_c P_c K_c \dagger$	$N_eP_eK_e$ ‡	$N_oP_oK_o\S$	LSDp=0.05	contrast	
		<u>CCI</u>				
maize1††	27.7	25.9	24.9	6.94	ns	
maize2‡‡	19.7	19.4	14.7	7.91	ns	
potato	38.1	45.5	35.9	13.93	ns	
		Biomass (g)				
maize1††	8.473	8.193	7.773	0.29	**	
maize2‡‡	11.25	11.97	10.83	0.88	*	
potato	12.35	11.5	11.23	0.69	*	
		height (cm)				
maize1††	48.7	50.7	37.7	11.76	ns	
maize2‡‡	66.3	74.7	53	7.26	**	
potato	46	44.3	29.3	8.1	**	
		<u>Leaf Number</u>				
potato	7	5.33	3.67	1.88	*	

†phosphorus and potassium applied based on extraction based conventional approach using ammonium bicarbonate-EDTA and ammonium acetate respectively. Nitrogen applied based on conventional approach thus no accounting for potentially mineralizable N; ‡ Phosphorus and potassium applied based on quantity/intensity relations, and nitrogen applied after potentially mineralizable N was adjusted for; § no fertilizer was applied; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks;* P < 0.05; ** P < 0.01; ns i.e., not significant.

There were few significant impacts that were observed on nutrient uptake as a result of NPK recommendation strategies with most P values > 0.05 (Table 6). The only exception on this trend was maize K uptake which was significantly affected on both harvest dates. Also total carbon content of maize harvested after 5 weeks and potato was significantly affected (Table 6). The general trend observed with regards to total carbon in both maize

harvested after 5 and 8 weeks also on potatoes, was that control pots had higher total carbon content followed by NPK applied using conventional approach, and on pots that NPK was applied after integrating for mineralizable nitrogen and PK recommended based on Q/I relations had the lowest total carbon content on their tissues in both maize and potatoes.

Table 6. Effect of NPK fertilization strategy on uptake of primary macronutrients and C content of maize and potato.

crop]	Fertilization strates	gy	Statistical p	arameters
	$N_c P_c K_c \dagger$	$N_e P_e K_e \ddagger$	$N_o P_o K_o \S$	LSD _{p=0.05}	Contrast
		N uptake (mg pot	1)		
maize1††	14.69	14.94	11.8	5	ns
maize2‡‡	13.45	14.93	11.8	4.88	ns
potato	40.7	46.5	32.9	11.35	ns
		P uptake (mg pot	<u>1)</u>		
maize1††	9.41	8.32	4.93	4.51	ns
maize2‡‡	5.55	6.19	3.98	3.58	ns
potato	12.4	14.4	12.5	11.5	ns
		K uptake (mg pot	<u>1)</u>		
maize1††	36.3	43.7	17.7	17.93	*
maize2‡‡	41.6	44	16.2	12.34	**
potato	41.6	59.6	32.3	31.16	ns
	<u>Tis</u>	sue carbon conten	<u>t (%)</u>		
maize1††	37.9	37.27	40.67	2	*
maize2‡‡	37.7	36.34	41.01	4.11	ns
potato	35.57	33.86	40.13	4	*

†phosphorus and potassium applied based on extraction based conventional approach using ammonium bicarbonate-EDTA and ammonium acetate respectively. Nitrogen applied based on conventional approach thus no accounting for potentially mineralizable N; ‡ Phosphorus and potassium applied based on quantity/intensity relations, and nitrogen applied after potentially mineralizable N was adjusted for; § no fertilizer was applied; †† maize harvested after 5 weeks; ‡‡ maize harvested after 8 weeks;* P < 0.05; ** P < 0.01; ns i.e., not significant.

Selected Correlations Between Total Carbon with Nutrients Content and Biomass

Total carbon content of plant material is hardly reported on plant nutrition studies, however the trends in this instance were too persistent to ignore. From Table 6 both harvest times for maize we obtained significant results whereby total carbon was the significantly high (P < 0.05) in control pots followed by $N_c P_c K_c$, and $N_e P_e K_e$ had the lowest total carbon content (Table 6).

When nutrient content of maize (P, K and S) was plotted against total carbon showed an appreciable inverse correlation (Figure 1). This ranged from 0.92 to 0.40 for maize harvested after 5 weeks and potato respectively. In all assessed correlation, potato nutrient contents showed the least agreement with total carbon. While maize nutrient contents harvested after 5 weeks showed the highest correlation. Similar inverse relation with total carbon was obtained for potato and maize harvested after 8 weeks with r² of 0.33 and 0.74 respectively (Figure 2).

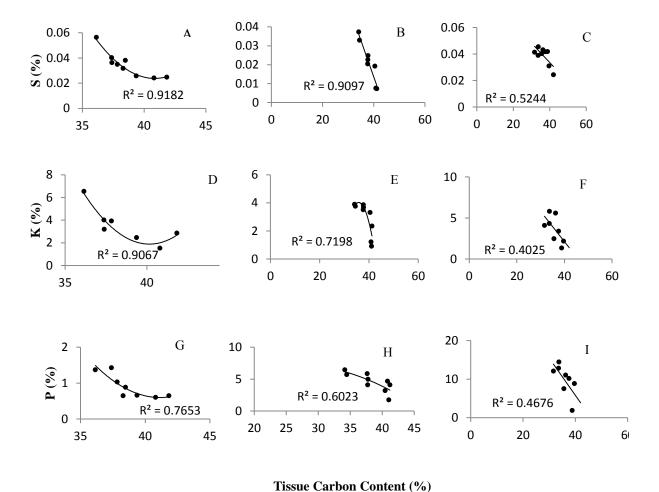


Figure 1: correlation between total plant carbon with various nutrients, for A, D and G maize harvested after 5 weeks. for B, E, and H for maize harvested after 8 weeks. For C, F and I for potato harvested after 8 weeks. With nutrients given on the y-axis, where, S, P and K refers to sulfur, phosphorus and potassium content respectively.

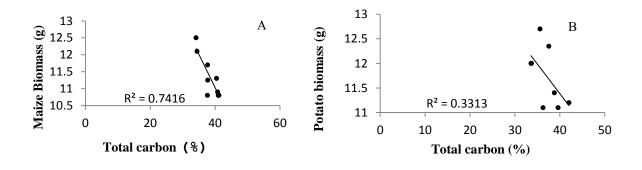


Figure 2: Correlation ship between total carbon with (A) maize biomass harvested after 8 weeks, (B) with potato biomass harvested after 8 weeks.

Discussion

Higher values of CCI on N treated pots are consisted with the observation that were made by van den Berg and Perkins (2004) on sugar maple leaves. They observed a positive correlation between N content and CCI. There were no negative impacts which were observed on both maize and potato growth parameter as a result of subtracting mineralizable N from N recommendations (Table 3), as it would have been so if N applied was below sufficiency. This might be because of two reasons. 1) Subtracting mineralizable N did not impact the growth of maize or potato, because even after subtracting mineralizable N from the recommendations the amount of N applied was still sufficient to not negatively impact crop growth. 2) mineralizable N actually compensated for the amounts of N that were subtracted on its account from initial recommendations hence no differences observed on most of the growth parameters between Ne and Nc. It is also possible that some N might have been used at a later given that plants were not harvested at maturity.

To this end it was proposed that mineralizable N subtracted from the initial recommendations actually compensated for N subtracted on its account. This proposal was supported by Table 3 using CCI, biomass and plant height of maize and CCI of potato. As it was observed that these parameters were lower in Ne compared to Nc on first harvest (5 weeks), and significantly so when we asses above ground biomass. This might be because of faster turnover of plant material (Gordon et al. 2000). This occurrence is characterized by accelerated turnover of biomass during earlier stage of establishment under high mineral N content. However, this is usually not sustained for longer periods. This is in support with observation made after 8 weeks when these parameters between Ne and Nc were not different in fact they were higher on Ne treatments compared to Nc. One of the many possible mechanisms driving high turnover might be because N fertilizer is readily soluble hence immediately available, hence higher turnover during establishment phase. This is in contrary to mineralizable N which is slowly available.

It was however observed that despite this improved establishments, after 8 weeks of planting both maize and potato showed some unconventional response to N fertilization strategy. Characterized by an inverse relationship between growth parameters and amount of fertilizer applied, this phenomenon was evident between Ne and Nc, since amount of N fertilizer on Nc treatments was greater than the amount of N fertilizer applied on Ne. The inverse relationship was observed on the above ground biomass of maize harvested after 8 weeks which was significantly higher on Ne treatment compared to Nc (Table 3). This trend was further observed on plant height of both maize and potato, and CCI of potato. This trend was consistent with the uptake of N by maize harvested after 8 weeks (Table 4).

The inverse relationship between growth and N uptake might be due to the priming effect (increase in nitrogen mineralization rate constant), hence increase in mineralized N which is subjected to the plant uptake. This might also contribute to higher turnover during earlier stages of growth as earlier proposed. This proposition can explain the observed occurrence in a sense that Ne received lower N fertilizer, subsequently priming effect was proportionally influenced relative to Nc (Jenkinson et al. 2006). Implying that mineralizable pool (No) is reduced to levels which are still relatively higher than Nc treatments, thus able to continuously and natively supply N in levels which are proportionally higher than Nc. The primed N is perhaps luxuriously consumed leading to initially higher turnover, then N uptake will steadily decline due to the reduction in N source, it is worth noting this is one of the justifications for split N application (Lopez-Bellido et al. 2005). Luxuriously consumed N does not concurrently improves growth on long term basis and associated parameters (Lipson et al. 1996). Luxuriously consumed N is also not metabolized into functional or structural components, nor does it lead to excess N uptake this is in agreement with observations made on N uptake of maize (Table 4). Luxury consumed N might be accumulated into nonstructural carbohydrates hence perhaps the reason for higher plant total carbon of Nc treatments (Table 4). Also this might support earlier made proposition about potentially mineralizable compensating for N withheld on its account on this study.

Higher P uptake on controls compared to Nc yet not statistically different from Ne on Table 4 contradicts most studies which have been conducted on N-P relations on agroecosystems, which have demonstrated that P uptake is proportional to amount of N fertilizer applied (Coblent et al. 2004). Nonetheless, several studies which have conducted mainly on natural ecosystem have demonstrated negative correlation between N:P ratio and P content (Gusewell 2004) this concept have been linked with nitrogen saturation (Aber 1992). Nitrogen to phosphorus ratio implies that at certain levels of P the plant response to P is independent of P concentration, rather it is determines by the ratio between N and P. So that if N concentrations relative to P increases hence N:P ratio, the P uptake is limited. Also potassium uptake of both maize and potato harvested after 8 weeks demonstrated similar patterns as P uptake where $N_e > N_e$ it is worth noting that even N_o on potato had higher K uptake compared to conventionally applied N treatments.

Mechanistic nutrient recommendations must be based on all three essential nutrients i.e., N, P and K. Second part of this discussion focuses on integrating mineralizable N and recommending P and K using Q/I relations, to form a single composite of NPK (experimental model). Growth parameters in this instance are subjective given that all three nutrients were variables, thus variances observed cannot be conclusively ascribed to a particular nutrient. In order to assess the effectiveness of fertilization strategy we considered uptake of the individual nutrients given on Table 6. Nitrogen uptake of maize harvested after 8 weeks showed trends which were similar to those observed on Table 4. With Ne > Nc, this instance N uptake by NePeKe was greater than NcPcKc, perhaps these observations support earlier made propositions, regarding priming effect of N fertilizer and its ultimate effect on long term basis.

Unconventional results were observed regarding P uptake, these were characterized by an average higher P uptake of both maize and potato when NPK recommendations were made by experimental compared to conventional approach. These results are in conflict with general fundamental relations considering that NcPcKc recommended higher P compared to NePeKe, but the reverse was true for the P uptake. This observance was ascribed to Gusewell (2004)proposition of N:P ratio. That the relative increase of N must concurrently

increase with P, the consequences of unbalanced ratios between N and P include reduced P uptake (Gusewell 2004). This might be the case considering that N:P ratio of NePeKe treatment for maize was 1:1, while for NcPcKc was 3:5 (Table 6.1). The proposition is true for potatoes with N:P under NePeKe being 4:5 while for NcPcKc is 3:4.

Despite the possibilities of perturbed ratios, it is also apparent that higher P recommendations made by conventional were unnecessarily high, since P uptake was not improved under NcPcKc. The artificially high P recommendation might be ascribed to the nature of extracting solution. OH⁻ ions in an ammonium bicarbonate EDTA-NaF solution, can solubilize Fe and Al bound P (Kamprath & Watson 1980). Also carbonate (CO₃⁻²) in the solution can replace adsorbed P. This consequently makes the solution more ideal for highly weathered soils contrast to the sandy soil used for this experiment. Thus calibrating using this solution might cause artificially high soil test P values, based on non-universal P pools.

Despite lack of significance to K uptake results, there was a parallel increase in K uptake with higher K levels recommended by NePeKe, contrary to the inverse relations which were observed when N and P were recommended in higher quantities by NcPcKc approach. Potassium optimum levels for the conventional method are based on NH₄OAc extractable K which reflects intensity parameter. For Q/I relations intensity parameter is derived from the activity ratio of K/(Ca + Mg). Significance of the latter approach is based on the ternary exchange between K-Ca-Mg especially in agricultural soils where these ions are dominating soil matrix (Sparks et al. 1990; Romheld & Kirkby 2010). Ohno and Grunes (1985); Welte and Werner (1963); and Jakobsen (1992) conclusively demonstrated that either K, Ca or Mg deficiencies are not exclusively dependent on the soil solution concentration. Interactions between the ions also play a crucial role, and this relationship is commonly antagonistic in nature, hence quantifying these ions by accounting for these interactions is mechanistically justified. Soil surface prefer divalent cations over monovalent cations, however this preference is not fixed, it is dynamic depending on the ratio of K:Ca:Mg, or even Na in sodic soils and Al in acidic soils (Agbenin & Yakubu 2006). The solution concentration is inversely correlated with the preference for a respective ion, so that when soils show higher preference for that particular ion its buffering capacity will be higher, and ultimately the effectiveness of fertilizer in increasing its concentration in solution will be lower. The preference as commonly indexed by Gapon, or Vanselow selectivity coefficients, and these are quantified by the same principle applied in this study to calculate KBC.

This is in contrast to the traditional extraction methods, which overlooks these relations. The lack of any form of buffer coefficient for K as currently applied in various soil testing institution compromise any possibility of accuracy in the method. On a technical standpoint it is only buffer coefficient which has a capability of quantifying the rate of change in solution concentration per amount of fertilizer applied. Not accounting for K buffer capacity is not only evident in South Africa, even similar axiomatic assumptions of standard values in relating external applications with solution concentration is evident in the United State; in Ohio States it has been reported by Vitosh et al. (1995), and in South Dakota it has been reported by Gerwing and Gelderman (2005).

The inverse correlation between nutrients and total carbon observed in this study can be ascribed to a well-studied concept in ecological chemistry i.e., carbon/nutrient balance theory (CNB)(Bryant et al. 1983). According to the theory, fertilization reduces production of carbon based metabolites, with special reference to phenolics and terpenes. Although these metabolites were not measured in this study, previous studies that have been conducted by Cronin and Lodge (2003), Mohd et al. (2010) have demonstrated a positive correlation between these compounds with total carbon. (Mohd et al. (2010)) observed that 82% variation in the concentration of these compounds can be explain by total carbon. The CNB theory postulates about biomass production; stipulating that there is a negative correlation between carbon based compounds with biomass production. This claim is in accord with the correlation observed in Figure 2, given we accept the Mohd et al. (2010)correlations to hold true in this instance.

This theory provides a unifying insight with regards to the conduciveness of the nutrient environment as a whole rather as a particular nutrient. Similar to the conclusion reached by Bazzaz and Reekie (1987), that carbon allocation reflect the allocation of resources in particular those limiting resources (NPK). It was hypothesize therefore that perhaps total carbon might provide that net effect due to the variables of the experiment. This net effect is reflective of optimality or lack thereof, of the treatments, based on optimal physiological response of crops to the fertilizer treatment strategies, as a whole rather for individual nutrients. So that if this supplementary rudimentary hypothesis is true, fertilization strategy as a whole should be assessed among other parameters on the basis of its effect on carbon content. Since carbon content on this study showed an inverse relation with biomass and nutrient content we further propose that fertilization strategy preeminence must be parallel with this drop on tissue carbon under non-carbon limiting environments. Although this is hypothesis it might hold true given previous ecological studies which have shown carbon content to be an important predictor of ecological productivity.

In addition to the previously observed support from crop response and nutrient uptake for the experimental fertilizer strategy proposed here, for both studies Ne and NePeKe; we further propose that the aforementioned theory is in favor of the eminence of this strategy. There are 6 independent observations made on this study to assess both Ne and NePeKe. The 2 separate observations were made on maize harvested after 5 weeks, under Ne and NePeKe, the other 4 constitutes maize harvested after 8 weeks and potato harvested after 8 weeks, with similar treatment structure of Ne and NePeKe compared to Nc and NcPcKc. In all of the observation made total tissue C was lowest when fertilizer recommendations were made by the experimental approach presented here (Table 4 and 6). The slight exception to this claim was observed on maize harvested after 5 weeks where tissue C was almost equal between NePeKe and NcPcKc with values of 37.8 and 37.9 % for NePeKe and NcPcKc respectively (Table 6).

Conclusions

On this study subtracting mineralizable nitrogen from conventional nitrogen recommendations did not have negative impact on growth of maize and potato under glasshouse study; it showed positive effects as parameterized by reduced fertilizer rates,

improved nutrient uptake and growth of both crops. If this is true under field conditions it has a potential of economic savings on nitrogen fertilizer. The Experimental approach employed in this study showed a potential, despite lower N and P rates the performance of both crops was not inferior compared to its conventional counterpart. The accuracy of extraction based fertilizer recommendations is highly unconvincing based on this study.

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CHAPTER 5

FIELD EVALUATION OF EXTRACTION BASED FERTILIZER RECOMMENDATION I

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Abstract

Use of extractants to index available P (phosphorus) or K (potassium) lacks mechanistical justification. Mineralizable N (nitrogen) is an important source of N which must also be accounted for, when making N recommendations. A field trial was established in two different sites using maize and potatoes as test crop for assessing the mechanistic validity of extraction based strategies on recommending N, P and K. Extraction based recommended higher rates of K and N, and these were not concurrently accompanied by improved growth or nutrient uptake. It was also found that extraction based intensities did not correlate with applied fertilizer, with R^2 ranging between 0.005 – 0.011, compared to R^2 of Q/I (quantity/intensity) intensity parameter which was 0.98 for both P and K. Similar results were obtained with regards to the correlation of extraction based intensity parameters to nutrient uptake, and total biomass of both crops. Q/I intensity parameter showed great linearity which was independent of sites. It was concluded that Q/I intensity parameters are more reliable compared to extraction based derived intensity.

Introduction

It is now becoming more apparent that use of extractants or chelating agents to quantify amount of bioavailable P (phosphorus) or K (potassium) as pioneered by Bray and Kurtz (1945), Mehlich (1953), Olsen et al. (1954), Mehlich (1984) is not sufficient (Evangelou et al. 1994; Jackson et al. 1997; Ogaard et al. 2002). There is an irrefutable positive correlation between P or K application with their relative intensity and crop yield. Disproportionateness therefore is a failure of comprehensively quantifying intensities, rather asymmetries between fertilizer with intensity or yield. The principal object of developing soil test – crop response calibrations is to extrapolate beyond the original sites, with margins of operation specified. Asymmetric relations between external applications – soil test – yield dynamics due to insufficiency of current approaches in quantifying intensity renders extrapolation nothing more than a guesstimate (Jordan-Meille et al. 2012).

An ideal intensity parameter should be independent of soil properties, and rather a consistent parameter reflective of the nutrient levels. Such a parameter should have a consistent performance across different soils and would limit the need for empirical adjustments made from soil to soil adjusting critical levels. For example in our local testing station critical P levels are adjusted according to clay content due to non-uniform performance of the extracting solution over different soils (Manson et al. 2011). Secondly: Intensity parameter must be specific, so that if the object is to index labile P interferences from other pools of P are minimal.

In order to realize these rigorous intensity parameters, buffer coefficients would have to be considered and become a pivotal part of recommending fertilizer. On a technical standpoint it is only buffer capacity which indicates the changes in intensity per amount of externally applied nutrient (Fox & Kamprath 1970; Hue & Fox 2010). Thus incorporating this parameter might make it possible to develop an intensity parameter which is independent of soil properties. Currently there are few attempts which have been made to parameterize this factor. Consider Equation 1 used in Ohio adopted from Vitosh et al. (1995) for P recommendations, and Equation 2 used in South Africa (Kwa-Zulu Natal) from Manson et al. (2011) for K recommendations;

$$lb\ acre^{-1}P_2O_5\ to\ apply\ =\ [(target\ soil\ test\ -\ Soil\ test)\ imes\ 5] + targeted\ yielded\ (1)$$

 $K\ to\ apply\ kg/ha = (Target\ soil\ test\ (mg\ l^{-1})\ -\ soil\ test\ (mg\ l^{-1})\ imes\ 2.5$

They all have an assumption of standard change in soil test per amount of externally applied nutrient. Manson et al. (2011) assumed that for every 2.5 kg/ha of K applied there will be a standard 1 unit increase in all soils, in Ohio they assume this factor to be 5. The ability of soil tests to resist changes due to depletion or application (buffer capacity), can be derived from sorption curves. For P, solution concentrations at equilibrium in relation to sorbed P over a wide a range of externally applied P provide a sufficient estimate for P buffer capacity (PBC) (Dodor & Oya 2000; Gichangi et al. 2008; Hue & Fox 2010). Also Beckett (1964), also has suggested that Q/I relations (quantity/intensity) can be developed

for potassium, and parameters which are derived from the relations are more comprehensive than currently used indices (Evangelou et al. 1994; Schindler et al. 2006)

Nitrogen recommendations are not free of controversy, nitrogen mineralization is one of the most important factor that is considered to have a potential of improving nitrogen recommendations (Rice & Havlin 1994). There are emerging suggestions that over applying N relative to crop needs might reduce soil N, and these suggestions have been illustrated by (Ramirez et al. 2010) on short term basis. Such short term observation appear to be consistent with N dynamics observed on Morrow and Rothamsted plots (>50 year old field trials) (Mulvaney et al. 2009). Such poses conundrums and threatens the sustainability since more N uptake originates from soil than the fertilizer (Schindler & Knighton 1999). Since actual effective quantities of externally applied N are relative to the mineralizable pool, estimating and integrating this pool in N fertilizer managements is crucial.

The objectives of this study were to compare P and K quantity/intensity (Q/I) fertilizer based recommendations with extraction based fertilizer recommendations (EBFR), and to evaluate the impact of integrating nitrogen mineralization on N recommendations.

Materials and Methods

Maize (*Zea mays*) cultivar EST: 1902 (border row king) and potato (*Solanum tuberosum*) Mnandi certified cultivar seeds were used for the trial. Land preparation involved disking and rotovating the fields to achieve a fine seedbed. Ridging and weeding were done by hand-hoeing.

Sites Description And Soil Classification

Trials were conducted on two different sites; Ukulinga University of KwaZulu-Natal research farm (29°37'S; 30°16'E), and Wartburg in a homestead field (29°51'S; 30°68'E), during summer planting season of 2014/15 using two test crops maize (*Zea mays*) and potato (*Solanum tuberosum*). Both trials were rainfed. Soils at Ukulinga were classified to be Sepane soil form which belongs to Duplex soil group or Vertisols according to USDA

(Fey 2010), and according to WRB reference soil groups it is Luvisols. Wartburg soils were classified to be Griffin soil form which belongs to Oxidic soil groups or Oxisol according to USDA (Fey 2010), and according to WRB reference soil groups it belongs to Arenosols.

Soil Characterization And Fertilizer Recommendations

Before planting samples were collected using a grid approach of 10×10 m within 35×35 m on both sites, thus an area of 0.26 ha was marked, and within it samples were collected at every 100 m^2 . The samples collected were combined in composite samples; with only topsoil (0-15 cm) collected for analysis. Conventional recommendations (extraction based) were made by the Department of Agriculture Forestry and Fisheries Kwa Zulu-Natal, after P was extracted with ammonium bicarbonate-EDTA solution and K was extracted with NH₄OAc (pH = 7) (Ammonium acetate). Nitrogen mineralization potential of soil was determined by anaerobic incubations for 7 days as suggested by Waring and Bremmer (1964). Net mineralizable N was calculated by Equation 4 to be 24 and 30 kg/ha for site 1 and 2 respectively, and this value was subtracted from the initial recommendations made by the conventional method (Rice & Havlin 1994) and the actual amounts applied are given on Table 1.

$$N_{min} = N_o (1 - e^{-kt})$$
 (Eq.4)

Where K is a mineralization rate constant taken to be 0.054/week (Stanford & Smith 1972); No is potentially mineralizable N (mg kg⁻¹); t is time (7 days); N_{min} is net mineralized N (mg kg⁻¹/week).

Quantity/Intensity Based Fertilizer Recommendations

Quantity/intensity relations were developed by the batch equilibration technique as described by Fox and Kamprath (1970) and Beckett (1964) for P and K respectively. Soil solution ratio of 1:10 was used to develop P sorption isotherms. Graded P equilibrating

solutions were used, and these had concentration ranges of (1 - 140 mg/l). 0.01 M of CaCl was used as a background electrolyte. The contents were shaken for 16 hours and allowed to equilibrate for two hours, they were centrifuged and filtered. Phosphorus remaining at equilibrium was analyzed using molybdate-ascorbic acid method (Murphy & Riley 1962).

Table 1. Amount of nutrient applied as recommended by different fertilizer recommendation strategies

		Maize		Potato		
	Recommendation strategy					
	C†	E‡	C†	E‡		
		applied nutrient (kg/ha)				
		<u>Ukulinga (Site1)</u>				
Nitrogen	200	176	240	216		
Phosphorus	20	30	80	32		
Potassium	0	6	65	10		
		Wartburg (Site2)				
Nitrogen	200	170	240	210		
Phosphorus	20	123	80	124		
Potassium	140	62	490	146		

[†] Recommendations made by extraction based recommendation strategy. ‡ Recommendations made by Quantity intensity relations for P and K, and for N recommendations made after adjusting for mineralizable N. LAN was used for N applications, single superphosphate was used for P recommendations and 2:3:4 was used for K recommendations and N and P applications were adjusted accordingly considering amounts applied by 2:3:4.

Amount of P adsorbed was taken as a difference between the amount of P added and P remaining in soil solution. The sorption data was then fitted into linearized form of Langmuir equation, and phosphorus buffering capacity was taken as a slope of the function.

Similar approach was adopted for developing K Q/I relations, graded K solution with concentration ranges of 1-120 mg/l were used in soil to solution ratio of 1:10. The contents were shaken for 2 hours and allowed to equilibrate for 24 hours. After centrifugation and filtering, K, Ca, and Mg of the supernatant were measured with AAS, electrical conductivity was also measured. Activity ratio (ARe) was taken as a ratio of the activity of K to root square of the activity of (Ca + Mg). Activity coefficients for respective ions were calculated using Debye-Huckel equation. Ionic strength for this equation was calculated

using electrical conductivity (Griffin & Jurinak 1973), potassium buffering capacity was taken as a slope of the linear function of amount of K adsorbed and ARe.

External P requirements (kg/ha) were calculated based on Langmuir linearized equation targeting equilibrium concentration of 0.05 mg/l and 0.18mg/l for maize and potato respectively (Hue & Fox 2010). The K recommendations were applied to target ARe of 0.02 mol/l^{0.5} as suggested by Beckett (1964), the actual amounts applied are given in Table 1.

Experimental Designs

The experimental design was a completely randomized block design, using replicates as blocks, the experiment was replicated three times. Main plot were 11×23 m. Individual plots for maize plots were 1.5×2.7 m, with planting space of 0.3×0.3 between and within rows. Individual plots for potato were 3×3 m, within row spacing was 0.35 m and between rows was 0.75 m. Fertilization strategy i.e., extraction based conventional fertilization strategy (EBFR) vs Quantity/Intensity and N adjusted for potential mineralization experimental fertilization strategy (E) were the main factors of the experiments. The amount of fertilizer applied for both treatments are given on Table 2.

Data Collection

For potatoes the data was collected when 98% of plants had flowered, while for maize it was collected at tasseling stage. Five plants were assessed per plot. Growth parameters determined for both crops were chlorophyll content using spad meter and number of leaves.

To determine above ground biomass three plants were sampled approximately 2 cm from the base per plot, and oven dried at 70°C until constant mass was achieved and dry biomass was determined therefrom. For nutrient analysis; fourth fully folded potato leaf was sampled on approximately 5 plants, and second fully unfolded leaves were sampled for maize. These were oven dried as outlined for biomass. For nutrient analysis these were ground and screened in 500 µm mesh. Plant material was digested in the CEM microwave

digestor MARS 6 (CEM Corporation) using concentrated nitric acid. After digestion was complete, samples were prepared for analysis for K, Ca and Mg by AAS, and P was analyzed in an UV spectrometer using method of Murphy and Riley (1962), N was analyzed by Dumas combustion method on LECO (CNS analyzer). Determined elemental nutrients were multiplied with oven dry mass to give nutrient uptake per ha (as this is more representative compared to the nutrient concentration. Data collected from all trials were analysed using analysis of variance (ANOVA) with GenStat® (Version 14, VSN International, UK). Thereafter, least significant differences (LSD) were used to separate means at the 5% level of significance.

Results

Total rainfall recorded for site 1 was 415 mm, this was less than that of site 2 which was 585 mm. Most of the rainfall was received during December and February on both sites. Throughout the season except on November the rainfall was higher on site 2 (Figure 1). Maximum temperatures on both sites were almost equal, with the minimum temperatures higher on site 1 (Figure 1).

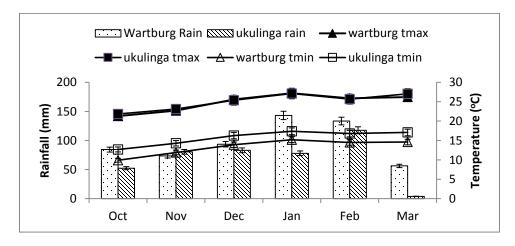


Figure 1. Rainfall and Temperature data between the two sites i.e., Ukulinga (site1) and Wartburg (site2), from October to March during 2014/15 growing season

Soil intensity parameters as described by extractable and exchangeable P and K respectively were highest at site 1 compared to site 2 (Table 2). Conventional intensity parameters of extractable P and exchangeable K were in agreement with intensity

parameters derived from Q/I curves and parameterized by ARe and 1/Qmax for K and P respectively. Site 2 soils had four times higher preference for K than Ca+Mg compared to site 1 soils, as parameterized by Gapon selectivity coefficient (Kg). Site 1 soils had the higher resistance to K changes from KBC (Table 2). Both soil had the same gravimetric field capacity of 26%.

Table 2. Selected properties of the soils used for field trials

Soil parameters	Site1	Site2
NH ₄ OAc K (cmol _c /kg)	0.85	0.17
ARe (moles/l) ^{0.5}	0.0018	0.0012
Δko (cmol _c /kg)	-0.04	-0.02
KBC (mmol kg ⁻¹ /mmol/l)	20.14	17.47
exchangeable acidity (cmol/l)	0.17	1.79
K Gapon selectivity coefficient	1.06	4.27
AMBIC extractable P (mg/l)	28.00	10.00
1/Qmax	0.0042	0.0013
Qmax (mg/kg)	238.10	769.23
$EC (dS m^{-1})$	1.21	0.62
P(mg/l)	28.00	10.00
Field capacity at -33 kPa (%)	26.00	26.00
pH (Water)	5.79	5.03
Bulk density (g ml ⁻¹)	1.13	0.92

Maize and Potato Growth Parameters Response to Fertilization Strategy

Chlorophyll content index and above ground biomass of both maize and potato was significantly affected by fertilization strategy (P < 0.05) (Table 3). Choice of site had a significant effect on most of the measured parameters.

Generally these parameters were high on site 1. Interactive significant effects between sites and fertilizer strategy were observed on potato CCI, biomass and number of leaves (Table 3). Growth parameters of crop fertilized according to EBFR were not statistically different to those fertilized using the Q/I approach (Table 4). The general trend was that growth parameters of maize were on average higher when the NPK was recommended with Q/I

relations (Table 4). This general trend was evident on potato growth parameters except on site 2.

Table 3. Statistical parameters to contrast the effect of fertilize recommendations strategy on growth of maize and potato

_	P value				$LSD_{p=0.05}$	_
			source (of variation		
	S†	F‡	S×F§	S†	F ‡	S×F§
			<u>Potato</u>			-
CCI	0.03	0.03	0.00	3.42	4.19	5.93
Biomass	0.28	0.00	0.01	7.83	9.60	13.57
no of leaves	0.02	0.35	0.04	0.76	0.93	1.32
			<u>Maize</u>			
CCI	0.03	0.03	0.21	6.09	7.45	10.54
Biomass	0.88	0.03	0.69	57.00	69.80	98.70
no of leaves	<.001	0.24	0.26	0.81	0.99	1.41

[†] Two sites used for the experiment. ‡ Fertilization strategy. § Interaction between site and fertilization strategy. ¶ Chlorophyll content index.

Table 4. Effect of fertilizer recommendation strategy on growth parameters of potato and maize

_	Site1			Site2		
			Crop re	sponse		
	C†	E‡	O§	C†	E‡	O§
		<u> </u>	<u>'otato</u>			
CCI¶	45.4	44.03	39.6	39.67	45	32.83
Biomass (g)	54.13	43.77	19.33	42.73	47.2	39.43
number of leaves‡	6.22	5.44	6.22	7.11	7.67	5.89
		<u>N</u>	<u>Maize</u>			
CCI¶	51.13	59.9	45.7	50.1	46.03	39.6
Biomass (g)	473.9	538.8	455.3	495	540	421.3
number of leaves	12.33	12.83	12.83	9.33	10.17	8.67

[†] Extraction based recommendation strategy. ‡ Quantity/Intensity recommendation strategy. § Control treatments with no fertilizer applied. ¶ Chlorophyll content index. ‡ number of leaves average of 5 plants

Effect of Fertilization Recommendation Strategy on the Uptake of Selected Macro-Nutrients by Maize and Potato

Fertilizer approach had no significant effect (P > 0.05) on the uptake of macro nutrients by maize (Table 5 and 6). Uptake of primary macronutrients by potatoes was significantly affected by the fertilizer strategy (Table 5), and P uptake was highly significantly affected by fertilizer strategy (P < 0.001). On site 1 the general trend on potatoes was that N, P and K uptake was higher when nutrients were applied using the EBFR (Table 6), the reverse of this general trend was observed on maize planted on site 2. There were no significant differences that were observed between the means of the two strategies. There was a significant interaction effect between site and fertilizer recommendation strategy on the uptake of N and P by potatoes (Table 5).

Table 5. Statistical parameters to contrast the effect of fertilizer recommendations strategy on uptake of nutrients by maize and potato

	P value			LS	LSD _{p=0.05} (kg/ha)		
			Source of	fvariation	variation		
	S†	F‡	S×F§	S†	F‡	$S \times F \S$	
			Potato				
Nitrogen	0.26	0.003	0.047	52.2	64	90.5	
Phosphorus	0.35	<.001	0.001	2.317	2.838	4.013	
Potassium	0.1	0.023	0.12	51.9	63.6	89.9	
Calcium	0.012	0.013	0.016	31.46	38.53	54.48	
Magnesium	0.022	0.006	0.011	5.09	6.24	8.82	
			<u>Maize</u>				
Nitrogen	0.48	0.12	0.54	29.19	35.75	50.56	
Phosphorus	0.15	0.38	0.54	2.741	3.357	4.747	
Potassium	0.025	0.92	0.7	20.95	25.66	36.29	
Calcium	0.17	0.83	0.13	8.22	10.06	14.23	
Magnesium	0.022	0.006	0.011	5.09	6.24	8.82	

[†] Two sites used for the experiment. ‡ Fertilization strategy. § Interaction between site and fertilization strategy.

Table 6. Effect of NPK fertilization strategy on the uptake of macronutrients by maize and potato

		Site1			Site2		
		1	Nutrient up	take (kg/ha)	(kg/ha)		
	C†	E‡	O§	C†	E ‡	O§	
			<u>Potato</u>				
Nitrogen	281.8	241.1	82.7	232.5	260.5	198.3	
Phosphorus	20.07	14.63	6.64	12.08	14.39	11.74	
Potassium	262.5	197.7	104.2	153.7	157	126.8	
Calcium	172.5	143.7	60.3	65.6	107	75.1	
Magnesium	13.18	17.37	17.72	21.29	27.1	34.51	
			<u>Maize</u>				
Nitrogen	106.9	131.2	99.1	137.7	134.6	94.4	
Phosphorus	7.697	10.609	8.046	11.63	11.233	9.365	
Potassium	40.86	49.16	54.29	74.41	75.66	67.83	
Calcium	33.33	40.98	42.13	38.81	34.03	27.23	
Magnesium	34.51	27.1	13.18	17.72	21.29	17.37	

[†] Conventional recommendation strategy. ‡ Quantity/Intensity recommendation strategy. § Control treatments with no fertilizer applied.

Relationships Between External Applications With Intensity Parameters

The correlation coefficient (R^2) value was 0.35 between EBFR P intensity and Q/I P intensity (Figure 2). Appreciable correlation was evident between the two K intensity parameters with R^2 of 0.64.

More than 90% of the variation in Q/I intensity parameter could be explained by the amount of fertilizer applied. This is contrary to 0.6% variations in EBFR P intensity which could be explained by amount of fertilizer applied (Figure 2). Similar results between external application and target concentrations were observed with K, Q/I intensity parameter had R^2 of 0.97 with external application. Only 1.1% of variations in EBFR intensity parameter could be explained by external applications (Figure 2).

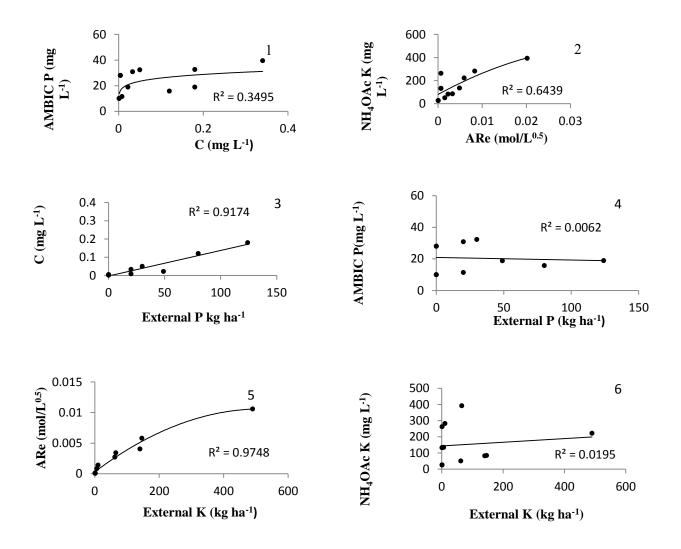


Figure 2. Relationships between 1) Phosphorus experimental intensity parameter C (mg/l) and Phosphorus conventional intensity parameter, AMBIC P (mg/l); 2) Potassium experimental intensity parameter, ARe (mol/l^{0.5}) and potassium conventional intensity parameter NH₄OAc (mg/l); 3, 4, 5 and 6 it's the relationship between external application of nutrients by fertilizer and respective intensity parameters given on the Y-axis

Relationships Between P and K Uptake with Intensity Parameters

Uptake of P and K by both potato and maize could be explained better by Q/I recommendation approach (Figure 3). Phosphorus Q/I intensity parameter was able to explain 85% and 62% variation in the P uptake by potato and maize respectively. Contrary

to the 18% and 2% of P uptake variations could be explained by EBFR intensity parameter for potato and maize respectively.

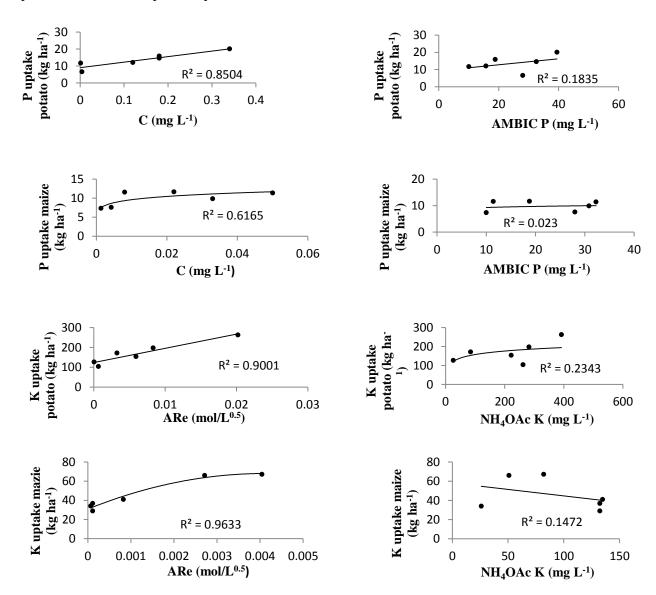


Figure 3. Relationships between phosphorus and potassium uptake by maize and potato with target intensity parameters where NH₄OAc K and AMBIC P refers to the conventional extraction based intensity parameters for potassium and phosphorus respectively. C and ARe refers to experimental intensity parameters for phosphorus and potassium respectively. Each point represents a mean of three points

Intensity parameter derived from Q/I relations could explain more than 90% of the variations in the uptake of K by both maize and potato (Figure 3), with values of 90% and 96% for potato and maize respectively. NH₄OAc extractable K could explain 23% of the variation in K uptake by potatoes and 14% on K in uptake of maize.

There was a linear relationship between uptake of P by potatoes and Q/I intensity parameter. Maize ability to uptake P displayed order of diminishing returns above 0.18 mg/l (Figure 3). Due to poor correlation in EBFR P with uptake no relations could be determined (Figure 3). Linear relations were observed between K uptake by potatoes and intensity parameters. Logarithmic relations were observed between intensity and K uptake in maize, with K uptake reduction evident beyond 0.002 mol/l^{0.5} (Figure 3).

Relationships Between Biomass and Intensity Parameters

Both maize and potato above ground biomass could be explained by Q/I relations than EBFR for both P and K(Figure 4). More than 65% of the variations in both maize and potato biomass could be explained by P Q/I intensity parameter. Correlation coefficient between EBFR P with potato above ground biomass was 0.03, and 0.10 with maize above ground biomass (Figure 4). Potassium Q/I intensity parameter correlated better with above ground biomass of either potatoes or maize, with values of 0.52 and 0.96 for potato and maize respectively (Figure 4). There was no evidence of correlation between above ground biomass of either maize or potato with NH₄OAc extractable K, with R^2 value of 0.02 and 0.05 for potato and maize respectively.

It appears that above 0.2 mg/l of soil solution at equilibrium is sufficient as characterized by the reduced response on both maize and potato above ground biomass beyond these P levels. The positive response between above ground biomass and K intensity parameter for potato occur from 0-0.015 mol/l^{0.5}, above which the response is reduced per unit increase in the intensity. Maize biomass response is linear between 0 and 0.002 mol/l^{0.5}, and above that the response is decreasing (Figure 3).

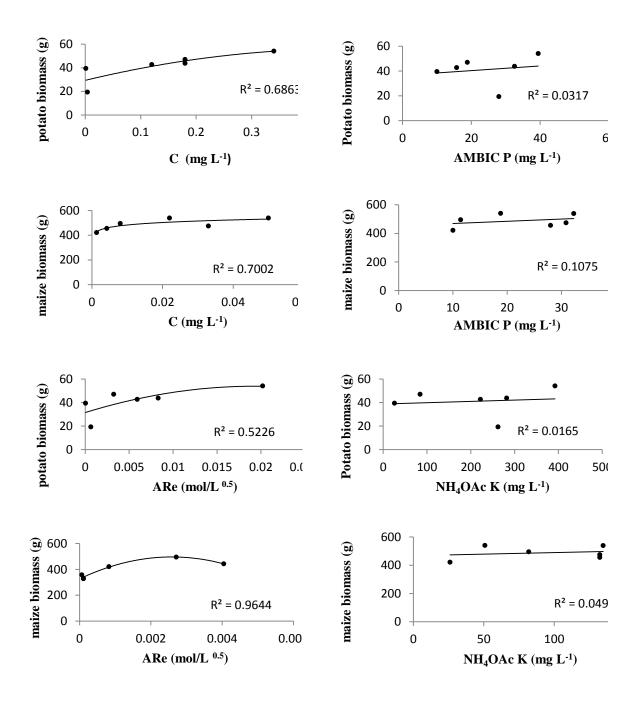


Figure 4. Relationships between maize and potato above-ground biomass with calculated target intensity parameters, where NH₄OAc K and AMBIC P refers to the conventional extraction based intensity parameters for potassium and phosphorus respectively. C and ARe refers to experimental intensity parameters for phosphorus and potassium respectively. Each point represents a mean of three point.

Discussion

Given that mean separation reveals that no growth parameter responded significantly to recommendations made by either method except CCI content of potato at Wartburg which was significantly higher than the control (Table 3 and 4).

Amount of N uptake by both crops was not significantly impacted by integrating N mineralization index. This implies that perhaps mineralizable N actually compensate for N withheld on its account. Higher N uptake by maize at Ukulinga and potatoes at Wartburg when N application were adjusted for potential mineralizable N, might be due to the propositions made by Mulvaney et al. (2009), that N fertilizer reduces soil N. This happens due to the accelerated N mineralization of N, which can either be lost through leaching or consumed luxuriously so that over the long soil N might be reduced. Since Schindler and Knighton (1999) using marked N demonstrated that plants primarily derive their N source from soil rather than fertilizer, reduction of this pool might ultimately compromise N uptake as observed on these fields.

Potassium uptake at Ukulinga was independent of K fertilizer, due to the initial high K concentration. Further the low K preference of 1.02 on these soils emphasis the possible saturation of the sites by K, thus there is considerable possibility of replenishing K in soil solution, and further K levels were high in soil solution as shown by intensity, these two factors might explain lack of response from K fertilizer. However K application plays a crucial role in moderating Ca and Mg levels in exchange sites, ultimately soil solutions. So that if K is applied it replaces other cations in exchange sites and increases their availability in solution (Agbenin & Yakubu 2006). This might explain the improved Ca uptake by potato on both sites with K applications, and by maize at Wartburg (Table 6). It is worth noting that Mg uptake by potato on both sites was lower on treated plots compared to control, this might be due to the well documented antagonistic interaction between K and Mg so that when K uptake increases the Mg uptake is reduced (Jakobsen 1992).

Intensity Parameter Relationships with External Applications

Intent of external application of fertilizer is to increase the intensity parameter, as this is the nutrient pool available for plant uptake. Any function that explains intensity changes should be independent of site and empirically correlated with the fertilizer application and use of buffer capacity or requirement factors to explain the change of intensity with the application of fertilizer, provide a standardizing parameter between different sites. The failure of AMBIC extracted P to concurrently change with external applied P as parameterized by low coefficient of determination of 0.35 compared to 0.92 for Q/I intensity parameter (Figure 2) undermines the whole validity of soil test – crop response, as it implies that intensity parameter is independent of fertilizer application which is fundamentally not true. This poor correlation between applied P and AMBIC P is further observed in NH₄OAc extractable K and externally applied K (Figure 2). This implies that these extraction based methods cannot be trusted to develop calibrations that would explain intensity with changes in external application. Asymmetrical relations therefore suggest that these parameters and the way at which they are currently utilized are not sufficient to explain such dynamics.

Intensity parameters derived from Q/I relations had coefficients of determination of > 0.9 with externally applied P or K. This further confirms the notion that Q/I derived intensity parameters are more robust compared to extraction derived intensity parameters (Fox & Kamprath 1970; Becket 1971; Jalali 2007a; Sharma et al. 2012). Improved robustness can be attributed to inclusion of buffer capacities, and comprehensively presented intensity dynamics of particular ions. Compared to the extraction based intensity parameter which appear to be non-related or randomly affected by externally applied P or K as implied by correlations obtained from extraction based and intensity parameter (Figure 1). The proposition that buffer coefficients of respective fields are standardizing parameters is perhaps supported by the appreciable correlation between the two intensity parameter of extraction and Q/I in Figure 2, especially for K. Thus, implying that asymmetrical relations obtained between external application and intensity parameters is due to a third parameter which was not accounted for, perhaps a capacity (buffering capacity) factor.

Intensity Parameter Relationships With Nutrient Uptake

Nutrient uptake by a crop is dependent on soil intensity, so that nutrient uptake changes proportional to intensity parameter so that if intensity increases nutrient uptake increases (within critical levels). Improved relationships between Q/I intensity parameters and nutrient uptake, as compared to relationships between extractable nutrients and uptake illustrate the earlier made proposition of the incomprehensive and unreliable intensity parameters derived from extraction based strategies. Relations between nutrient uptake and intensity parameters are fundamental relations relying on no assumption. As such as the amount of nutrient required by a particular crop for optimum growth is a constant independent of site. The rate by which the intensity parameter is influenced is a constant with no exceptional deviations from the symmetries of the relations. Deviations observed therefore on Figure 2 place an emphasis on the urgent need to reconsider currently used fertilizer recommendations approach.

Intensity Parameter Relationships with Biomass

Assimilated nutrients are partitioned accordingly; consequently optimizing physiological functions of crops hence improve growth. This statement relies on no assumptions or exceptions. Growth will be improved proportionally with the availability of nutrient until optimal growth is reached, similarly the growth will be reduced proportionally if the nutrients are limiting. The proportional improvements observed in Figure 3 for both maize and potatoes verify the consistency of Q/I intensity parameters compared to their conventional counterparts. Poor correlation between dry biomass and intensity implies the inadequacy of levels of P and K as accomplished by extractions. Optimal ARe of 0.02 mol/I^{0.5} and equilibrium P concentration of 0.2 mg/l are in agreement with the critical levels that have been suggested for these soil tests by (Beckett 1964) and (Fox & Kamprath 1970) for K and P respectively.

Conclusions

Integrating N mineralization index from the N recommendation does not compromise crop growth or nutrient uptake. Use of Q/I intensity parameters give more consistent results compared to extraction derived intensity parameters. Extraction based intensity cannot be explained by the variations in fertilizer levels, which is in violation of the fundamentals of soil testing. Q/I intensity relations have a better correlation with external applications, therefore more reliable to explain changes brought about by fertilizer applications. Q/I intensity correlates better with nutrient uptake, therefore is more reliable in determining the optimum levels i.e., calibrating. Q/I intensity can explain better the variations in crop growth, therefore is more reliable in calibrating the optimum levels of nutrients to bring about optimal growth. Extraction based intensity correlates neither with nutrient uptake nor with the growth, therefore, the use in determining critical levels for optimal plant growth are open to criticism.

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CHAPTER 6

FIELD EVALUATION OF EXTRACTION BASED FERTILIZER RECOMMENDATION II

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Abstract: There is an urgent need for accurate and mechanistically justified methods of recommending nitrogen, phosphorus and potassium. A study was established, with the objective of comparing between the yield response of maize and potatoes under two different field conditions as affected by NPK recommendations. Phosphorus and potassium for conventional recommendations were extracted with ammonium bicarbonate - EDTA and ammonium acetate (pH = 7) respectively, and nitrogen recommendations were made based on yield targets. For alternative approach, P and K were characterized based on Quantity and intensity relations using batch equilibration technique. Nitrogen recommendations for an alternative approach were made after adjusting for mineralizable N by subtracting its value from N rates recommended by a conventional approach. Nitrogen and potassium rates recommended by a conventional approach were higher and these were not concurrent with nutrient removal. Phosphorus rates recommended by an alternative approach were higher and these recommendations were concurrent with P levels of maize grains and potato tubers. It was concluded that the alternative approach of recommending NPK is not just theoretical justified, its performance under field conditions support its superiority compared to conventional approach.

Key words: Fertilizer recommendations, Nitrogen mineralization, Quantity intensity, soil test – crop response.

Introduction

Use of synthetic fertilizer played an important role during green-revolution between 1930's to late 60's, and it's use is expected to play a crucial role in ensuring food security considering the projected population increase in this century. Despite this importance, the methods of deriving fertilizer recommendations (from calibrations to the actual rates believed optimal) remains inadequate and poorly linked to the process guiding the indexing and recommendations of mineral nutrients in soil (Vanotti & Bundy 1994; Jordan-Meille et al. 2012).

Accurate fertilizer recommendations depends on accounting for the dynamics between quantity and intensity factors (Lindsay 1979; Jalali 2007b; Hue & Fox 2010). This relationship also enables for the quantification of capacity factor; and capacity factor is the only parameter which can mechanistically inform about the rate of change of intensity per amount of applied nutrient. It is worth noting, that intensity parameter is an important parameter in agro-ecosystems, since plants derived their nutritional needs directly from it. Also fertilizer applications are made with the intent of influencing intensity parameter, of which the degree of influence is left to empirical relations without the quantification of capacity factor. This relationship has been ignored mainly in favor of more financially feasible soil tests for P and K, the extraction based tests as popularized by Bray and Kurtz (1945), Mehlich (1953), Olsen et al. (1954), and Mehlich (1984), and these methods have recently been reviewed by Abdu (2006). It has been recently highlighted by Jordan-Meille et al. (2012) that there is a lack of mechanistic knowledge on extraction based approaches, also theoretical background is extremely limited and scientific rational is almost nonexistent, their worth is exclusively on their empirical yet poor relationships with crop response.

Considerable attention has also been given on improving nitrogen recommendation by integrating potential mineralizable N (Havlin et al. 1993; Picone et al. 2001; Sharifi et al. 2006), and other soil tests such as presidedress nitrogen test (Rozas et al. 1999). Although these indices are at a developmental stage they provide a significant leap forward compared to yield target N recommendations. Inherent errors of such an approach will not be given much attention, to name but few examples; residual N not accounted for, mineralizable N overlooked, uniformity assumption between calibration sites and sites that N is recommended for, overall this approach has absolutely no mechanistical basis.

Fertilizer recommendation challenges are not only limited on developing comprehensive soil test indices. There is also a need of evaluating crop response parameters which mechanistically and concurrently justify changes in fertilizer application rates, hence, soil tests changes. Such parameters could be of importance, considering that yield-fertilizer functions are currently ubiquitous; yet, there is little mechanistic justification for this

relationship except from a covariate perspective. Yield rather, is a subjective parameter of crop response, influenced by several other factors of which soil fertility status is one of those parameters. In the absence of objective crop parameters, and poorly presented intensity parameters; it has become a norm to approach fertilizer optimal rate as to be within certain ranges, rather discrete rate (within a homogenous field and environmental conditions).

The objective of this study was to compare the effect of fertilization strategy on maize and potato yield. It was hypothesized that integrating nitrogen mineralization on N recommendations will not negatively impact yields. Also, recommending P and K based on Q/I relations will outperform extraction based fertilizer recommendations.

Materials and Methods

Sites Description and Soil Classification (Same as Chapter 5)

Trials were conducted on two different sites; Ukulinga University of KwaZulu-Natal research farm (29°37'S; 30°16'E), and Wartburg in a homestead field (29°51'S; 30°68'E), during summer planting season of 2014/15 using two test crops (maize and potato). Both trials were rainfed. Soils at Ukulinga were classified to be Sepane soil form and belong to Duplex soil group or Vertisols according to USDA (Fey 2010), according to WRB reference soil groups it belongs to Pedocutanic-cumulic-hydromorphic. Soils at Wartburg were classified to be Griffin soil form which belongs to Oxidic soil groups or Oxisol according to USDA (Fey 2010), according to WRB reference soil groups it belongs to Arenosols.

Soil Characterization And Fertilizer Recommendations (Same as Chapter 5)

Before planting soil samples were collected using grid approach of 10 × 10 m within 35 × 35 m on both sites. The collected samples were combined to form a composite sample; only topsoil (0-30cm) was collected for analysis. Conventional recommendations (extraction based) were made by the Department of Agriculture Forestry and Fisheries Kwa

Zulu-Natal, after P was extracted with ammonium bicarbonate-EDTA solution and K was extracted with NH₄OAc (pH = 7). Nitrogen mineralization potential of soil was determined by anaerobic incubations as suggested by Waring and Bremmer (1964). Net mineralizable N was calculated by Equation 4 to be 24 and 30 kg of N ha⁻¹ for site 1 and 2 respectively, and this value was subtracted from the initial recommendations made by conventional method (Rice & Havlin 1994) and the actual amounts applied are given on Table 1.

$$N_{\min} = N_o (1 - e^{-kt})$$
 (Eq.4)

Where K is a mineralization rate constant taken to be 0.054 week⁻¹ (Stanford & Smith 1972); No is a potentially mineralizable N (mg kg⁻¹); t is time (7days); N_{min} is net mineralized N (mg kg⁻¹/week).

Table 1. Amount of nutrient applied as recommended by different fertilizer recommendation strategies

Recommendation strategy C† E‡ C† E‡ applied nutrient (kg ha ⁻¹)	
applied nutrient (kg ha ⁻¹) <u>Ukulinga (Site1)</u> Nitrogen 200 176 240 216 Phosphorus 20 30 80 32	
<u>Ukulinga (Site1)</u> Nitrogen 200 176 240 216 Phosphorus 20 30 80 32	
Nitrogen 200 176 240 216 Phosphorus 20 30 80 32	
Phosphorus 20 30 80 32	
Phosphorus 20 30 80 32	
-	
Wartburg (Site2)	
Nitrogen 200 170 240 210	
Phosphorus 20 123 80 124	
Potassium 140 62 490 146	

[†] Recommendations made by extraction based recommendation strategy; ‡ Recommendations made by Quantity intensity relations for P and K, and for N recommendations made after adjusting for mineralizable N.

Quantity/Intensity based recommendations were based on sorption isotherms. These were developed by the batch equilibration technique as described by Fox and Kamprath (1970) and Beckett (1964) for P and K respectively with some of the parameters given on Table 3. External P requirements (kg ha⁻¹) were calculated based on Langmuir linearized equation targeting equilibrium concentration of 0.05 mg L⁻¹ and 0.18mg L⁻¹ for maize and potato respectively (Hue & Fox 2010). The K recommendations were applied to target intensity parameter of 0.02 mol/L^{0.5} as suggested by Beckett (1964), the actual amounts applied are given on Table 1.

Experimental Designs (Same as Chapter 5)

The experimental design was a completely randomized block design, using replicates to block. The experiment was replicated three times. Main plot were 11×23 m. Individual plots for maize plots were 1.5×2.7 m, with planting space of 0.3×0.3 between and within rows. Individual plots for potato were 3×3 m, within row spacing was 0.35 m and between rows was 0.75 m. Fertilization strategy i.e., extraction based conventional fertilization strategy (EBFR) vs Quantity/Intensity and N adjusted for potential mineralization fertilization strategy (Q/I) were the main factors of the experiments.

Harvesting and Nutrient Analysis

Potatoes at Wartburg (Site1, henceforward) were harvested on the 10th of March 2015, and at Ukulinga (Site 2, henceforward) were harvested on the 17th of March 2015. While maize was harvested on the 13th and 22nd of March in 2015 in site1 and 2 respectively. Harvesting was carried out by choosing 6 plants within plots (excluding border rows). For maize, cobs were counted, weighed and trashed. Yield was calculated at a standard moisture percentage of 12.5, after moisture determination with grain moisture meter.

Potato harvest was carried out by selecting 6 plants and tubers per plant were harvested in different bags. Number of tubers per plant were noted, mass of tubers was also noted and used later to calculate yield, grading was done as outlined in Table 2. Commercial yield on site 1 was calculated by excluding the baby and small class, it is worth noting that this was

not possible on site 2 since most of the tubers fell within the aforementioned categories that were excluded in calculating commercial yield on site 1.

Table 2. minimum and maximum mass used to establish a class for potato tubers (Department of Agriculture Republic of South Africa, 2010)

Class	Minimum mass (g)	Maximum mass (g)
Baby	5	50.5
Small	50.6	100.5
Medium	100.6	170.5
Large medium	170.6	250.5
Large	250.6	>250.6

Approximately 150 g of grains per plot were grinded on a ball miller and screened in 500 µm mesh, the maize meal obtained therefrom was used for nutrient analysis. For potato approximately 8 tubers were selected and chopped in to small pieces, these were frozen dried and moisture percentage was noted after freeze drying. Frozen dried pieces were grinded using pestle and mortar, the powder obtained was fine enough thus no screening was considered necessary, and this was used for nutrient analysis. Maize meal and potato powder was then digested in the CEM microwave digestor MARS 6 (CEM Corporation) using concentrated nitric acid. After digestion was complete, samples were prepared for analysis for K, Ca and Mg by AAS, and P was analyzed in an UV spectrometer using method of Murphy and Riley (1962), N was analyzed by Dumas combustion method on LECO (CNS analyzer). Determined elemental nutrients were multiplied with yield to give nutrient removal per ha (as this is more representative compared to the nutrient concentration. Data collected from all trials were analysed using analysis of variance (ANOVA) with GenStat® (Version 14, VSN International, UK). Thereafter, least significant differences (LSD) were used to separate means at the 5% level of significance.

Results

Weather Data

Total rainfall recorded for site 1 was 415 mm, this was less than that of site 2 which was 585 mm. Most of the rainfall was received during December and February on both sites. Maximum temperatures on both sites were almost equal, with the minimum temperatures higher on site 1 (Figure 1)

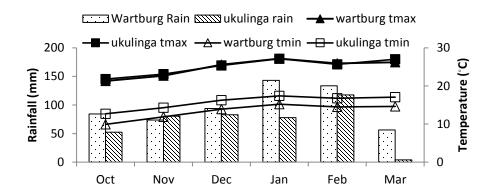


Figure 1. Rainfall and Temperature data between the two sites i.e., Ukulinga (site1) and Wartburg (site2), from October to March during 2014/15 growing season

Intensity parameters as described by extractable and exchangeable P and K respectively were highest on Site 1 compared to Site 2 (Table 3). Conventional intensity parameters of extractable P and exchangeable K were in agreement with intensity parameters derived from Q/I curves and parameterized by ARo and 1/Qmax for K and P respectively. Site 2 soils had four times higher preference for K than Ca+Mg compared to Site 1 soils (Gapon selectivity coefficient).

Table 3. Selected properties of the soils used for field trials

Soil parameters	Site1	Site2
NH ₄ OAc K (cmol _c /kg)	0.85	0.17
ARo (moles L^{-1}) ^{0.5}	0.0022	0.0012
Δ ko (cmol _c kg ⁻¹)	-0.04	-0.02
KBC (mmol kg ⁻¹ /mmol L ⁻¹)	20.14	17.47
exchangeable acidity (cmol L ⁻¹)	0.17	1.79
K Gapon selectivity coefficient	1.06	4.27
AMBIC extractable P (mg L ⁻¹)	28.00	10.00
1/Qmax (mg L ⁻¹)	0.0042	0.0013
Qmax (mg kg ⁻¹)	238.10	769.23
EC (Ms Cm ⁻¹)	1.21	0.62
Field capacity at -33 kPa (%)	26.00	26.00

Effect of Fertilizer application strategy on Potato Tuber Yield Grade

On Site 1 less than 50% of all tubers were graded as babies (<50.5 g), whereas on Site 2 more than 95% were babies (Figure 2).

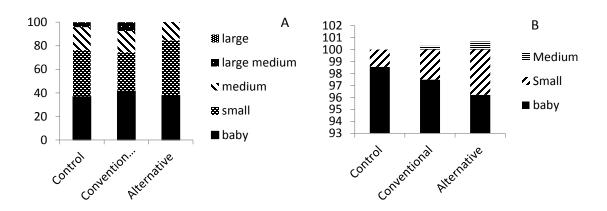


Figure 2. Potato grade as affected by fertilizer recommendation strategies (A) from site 1 (B) from site 2. Control refers to treatment where no NPK was applied, conventional refers to $N_c P_c K_c$ and alternative refers to $N_e P_e K_e$. Grading was done by % of number of tubers.

The number of small (<100.5 g) potatoes was higher when NPK was recommended by an alternative strategy. Also largest portion of medium grade potatoes was obtained when NPK was recommended by an alternative strategy. On Site 2 control treatment produced no medium grade potatoes, and conventional approach produced fewer medium grade potatoes compared to the alternative strategy. On Site 1 the portion of potatoes that was made up by large-medium grade was considerably high when NPK was recommended by conventional approach; nonetheless, no potatoes were graded to be large on this treatment contrary to the alternative strategy which had few potatoes which were graded to be large (Figure 1).

Effect of Fertilizer application strategy on maize yield and components

Choice of site had significant effect on maize yield components with P <0.01 (Table 4 and 5). Fertilizer application strategy significantly affected maize total biomass and cob mass. The only significant interaction that was obtained between site and fertilizer was with the total biomass (Table 4). Mean separation at 5% significant level showed that NPK recommended using an alternative strategy resulted in significantly higher total biomass of maize, compared to conventional strategy on Site 1 (Table 5).

Table 4. Statistical parameters to contrast the effect of fertilize recommendations strategy on yield components of maize

		Contrast			LSD	
	Source of			Variation		
	S†	F‡	S×F§	S†	F‡	S×F§
maize yield	**	ns	ns	2.552	3.126	4.421
maize total biomass	**	*	*	91.3	111.8	158.1
number of cobs	**	ns	ns	0.2516	0.3081	0.4358
Cob mass	**	**	ns	214.8	263	372
cob length	**	ns	ns	1.638	2.007	2.838
Harvest index	ns	ns	ns	0.085	0.10	0.15

[†] two sites used for the experiment; ‡ Fertilization strategy; § interaction between site and fertilization strategy; * P < 0.05; ** P < 0.01; ns, not significant.

Yield of maize was almost two times higher on Site 2 than site 1, with control treatments of Site 1 higher than either fertilizer treatments on Site 2. Nonetheless, the average maize yield on both sites was higher than the national average of 4.06 t ha⁻¹ (NedBank 2013). There were few significant differences between fertilizer recommendations strategies major difference were between different sites. On average harvest index on Site 1 was the highest when NPK was recommended by a conventional approach with a value of 0.34 followed by treatments where NPK was recommended by an alternative strategy with a value of 0.30, and control treatments had the lowest harvest index with a value of 0.29. Alternative fertilizer recommendation strategy resulted in an almost 2 times higher harvest index on Site 2, with value 0.41 and both conventional recommendation strategy and control resulted in 0.25 harvest index (Table 5).

Table 5. Effect of fertilization strategy on yield components of maize

	Site 1uku					
•	Maize Yield Co			omponents††		
•	C†	E‡	O§	C†	Ε‡	O§
Yield (t ha ⁻¹)	12.71b	15.3b	13.34b	6.37a	7.43a	6.36a
Total biomass $\P(g)$	833.9b	1064.3c	768.8b	605a	447.7a	475.1a
number of cobs plant ⁻¹	1.6bc	2c	1.467ab	1.067a	1a	1.067a
Cob mass (g)	1763cd	2112d	1402bc	1019ab	1073ab	871a
cob length (cm)	19.93a	20.6a	20.33a	18.67a	19.73a	18.73a
Harvest Index	0.34a	0.30a	0.29a	0.25a	0.41a	0.25a

[†] extraction based recommendation strategy; ‡ Quantity/Intensity recommendation strategy; § control treatments with no fertilizer applied; †† means in a row followed by the same letter are not significantly different; ¶ dry matter value is derived from an average of five plants.

On both sites yield was significantly affected by fertilization strategy (Table 6). As outlined for Figure 2, more than 95% of tubers on Site 2 were graded as baby potatoes, hence, it was not possible to determine marketable yield on this site. Potato yields were

Effect of Fertilizer application strategy on Potato Yield and Components

almost two times higher on Site 1 than on Site 2 (Table 7). The average yields obtained on Site 2 were almost half of the potato yield national average of 41.25 t ha⁻¹ (ABSA-Agribusiness 2011). Marketable yield was significantly higher when NPK was recommended by an alternative strategy with a yield value of 34.94 t ha⁻¹, and this was significantly higher than the marketable yield of conventional NPK recommendation of 28.98 t ha⁻¹, of which was significantly higher than that of control.

Table 6. Statistical parameters to contrast the effect of fertilizer recommendations strategy on potato yield components

	Yield	average number of tubers (plant ⁻¹)	moisture	marketable yield
		<u>UKULINGA (SITE1)</u>		
Contrast	*	ns	ns	**
$LSD_{p=0.05}$	10.83	4.12	1.52	5.04
		WARTBURG SITE2		
Contrast	*	ns	ns	
$LSD_{p=0.05}$	7.25	4.13	1.385	

^{*} P < 0.05; ** P < 0.01; ns, not significant; average number of tubers represents a mean of 5 plants. Note: Due to enormous differences between potato yield from the two sites we decided to statistically analyze the data separately.

Table 7. Effect of fertilization strategy on yield components of maize

	Site1			Site2			
•	Potato Yield Components††						
·	C†	E‡	O§	C†	E‡	O§	
Yield (t ha ⁻¹)	48.69b	57.27b	37.41a	19.74ab	21.45b	12.5a	
number tubers plant ⁻¹ ¶	17.53a	15.13a	12.2a	9.2a	10.07a	12.27a	
Moisture (%)	84.02a	83.72a	83.35a	85.5a	84.61a	85.13a	
marketable yield (t ha ⁻¹)‡‡	28.98b	34.94c	22.8a				

[†] extraction based recommendation strategy; ‡ Quantity/Intensity recommendation strategy; § control treatments with no fertilizer applied; †† means in a row followed by the same letter are not significantly different; ‡ number of tubers value is derived from an average of five plants; ‡‡ commercial yield considers those tubers in size which are above 50g.

Fertilization strategy had no significant effect on the nutrient removal by maize grains on Site 1 (Table 8). Choice of site had a significant effect on the removal of nutrients. Nitrogen and potassium removal was highly significantly affected by the choice of site (P < 0.01). All three primary macro nutrients removal by potato tubers were significantly affected by fertilizer recommendation strategy on Site 2 (Table 9).

Table 8. Statistical parameters to contrast the effect of fertilizer recommendations on nutrient removal by maize grains

	Contrast			LSD _{p=0.05}			
_	Source of Variation						
_	Site1				Site2		
_	S†	F‡	S×F§	S†	F‡	S×F§	
N removal (kg ha ⁻¹)	**	ns	ns	3.93	4.82	6.81	
P removal (kg ha ⁻¹)	*	ns	ns	6.62	8.11	11.47	
K removal (kg ha ⁻¹)	**	ns	ns	38.65	47.33	66.94	
Carbon content (%)	ns	ns	ns	2.38	2.92	4.14	

[†] two sites used for the experiment; ‡ Fertilization strategy; § interaction between site and fertilization strategy; * P < 0.05; ** P < 0.01; ns, not significant.

On average, the alternative NPK fertilizer recommendation strategy resulted on improved primary macro nutrient removal my maize grains on Site 2, except for potassium (Table 10). Nutrient removal by potato tubers on Site 2 was the highest when NPK was recommended by an alternative strategy (Table 10). On Site 1 both N and P was lower when NPK was recommended by the alternative strategy. Phosphorus removal by tubers on Site 2 was significantly higher when NPK recommendations were made by an alternative strategy compared to conventional NPK recommendation approach, P removed by tubers on Site 2 when NPK was recommended by conventional approach was not significantly different from the control at P = 0.05 (Table 10).

Table 9. Statistical parameters to contrast the effect of fertilizer recommendations strategy on nutrient removal of potato tubers

N removal	P removal	K removal	Carbon (%)					
kg ha ⁻¹								
<u>UKULINGA (SITE1)</u>								
*	ns	*	ns					
27.48	35.79	167.4	1.47					
Wartburg (SITE2)								
*	**	*	ns					
14.28	7.79	105.9	2.26					
	27.48	* ns 27.48 35.79 ** Wartburg **	* ns * 27.48 35.79 167.4 Wartburg (SITE2) * * *					

^{*} P < 0.05; ** P < 0.01; ns, not significant

Table 10. Effect of fertilization strategy on nutrient removal my maize grains or potato tubers

	site1 uku				site2 wrt			
•	nutrient removal by harvestable organs (kg ha ⁻¹)††							
•	C†	E‡	O§	C†	E ‡	O§		
	maize nutrient removal							
N removal	21.95b	26.22b	21.54b	8.69a	11.11a	7.72a		
P removal	11.57a	13.90a	15.20a	3.88a	8.28a	3.57a		
K removal	69.69abc	85.3bc	88.91c	17.05abc	15.33ab	11.33a		
Carbon content (%)	35.97a	35.67a	37.79a	35.36a	34.06a	37.52a		
potato nutrient removal								
N removal	98.85b	98.14b	53.04a	42.79b	46.62b	25.32a		
P removal	61.16a	56.41a	32.05a	15.18a	25.16b	8.30a		
K removal	703.5b	807.8b	492.6a	311.5b	317.7b	182.3a		
Carbon content (%)	35.73a	36.41a	37.06a	35.33a	35.22a	36.03a		

[†] two sites used for the experiment; ‡ Fertilization strategy; § interaction between site and fertilization strategy; * P < 0.05; ** P < 0.01; ns, not significant.

Potato Selected Relationships

We herein evaluated a parameter that have a consistence relationship with all three macro nutrients of subject in this study. Carbon content had a high inverse correlation with all three macro nutrients (Figure 3), the r² of this inverse relationship ranged from 0.78 to 0.91 for K and N respectively and 50 % of variation of tuber P concentration could be explained by tuber carbon content (Figure 3).

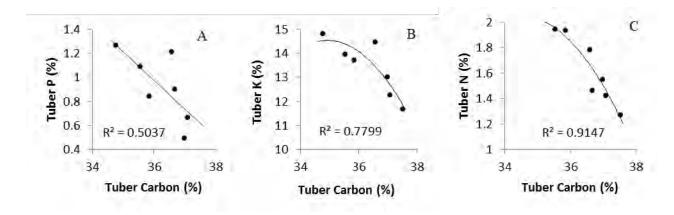


Figure 3. Relationships between potato tuber total carbon content with (A) Tuber total P content (B) Tuber total K content and (C) Tuber N content.

Maize Selected Relationships

There was an appreciable and consistent relation between maize grain total carbon content with P and K concentration, the r^2 values were 0.96 and 0.75 for K and P respectively (Figure 4). Both P and K had an inverse relationship with total carbon content of maize grains. Total carbon had a similar inverse relationship with harvest index of maize (Figure 4), with r^2 of 0.62. Grain N content showed a positive correlation with cob mass, with a correlation coefficient value of 0.72 (Figure 4).

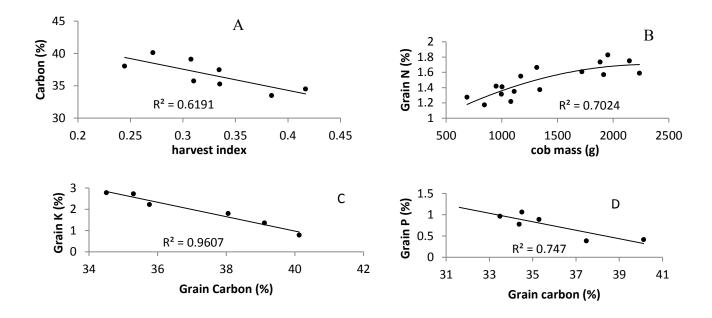


Figure 4. Relationships between (A) maize grain total carbon and harvest index from site 2 (B) maize grain total nitrogen and cob mass (average of five cobs) from site 1 and 2 (C) maize grain total potassium and maize grain total carbon from site 2 (D) maize grain total phosphorus and maize grain total carbon from site2.

Discussion

A Comparative Overview of the TWO NPK Recommendation Strategies

Lower N rates recommended by an alternative approach were by default. Since, mineralizable N was subtracted from the conventional N recommendations, assuming; that this pool is overlooked when recommending N. Holford (1980), suggested that the P extracting solution performance is not independent of buffering capacity, thus the extracting solutions have inconsistence performance when indexing intensity parameter. Kamprath and Watson (1980), showed that OH in bicarbonate solution can solubilize metal bound P, and the inconsistences in P extracting solutions have recently been reviewed by Abdu (2006). Metal bound P is not readily available thus does not represents a true

intensity parameter; an overestimation of P levels might inevitable. So that if this is true, lower recommendations made by a conventional approach might be based on erroneous indexing of intensity parameters. This is in contrast to Q/I relations, which mimic changes in soil solution as influenced by external applications.

Potassium availability is not solely determined by K concentration in soil solution, this is so because K exchange with Ca and Mg and other cations (Sparks 1987b; Agbenin & Yakubu 2006; Romheld & Kirkby 2010; Samadi 2012). This implies that quantifying K in relation to Ca and Mg is more theoretically justified than use of K concentrations in isolation. Also conventional approach lacks any form of buffer parameter, thus there is no parameter which actually explains or used to relate external application to solution concentration. Given these fundamental differences on the two approaches used on this study, the different rates recommended were not unexpected. The plausible reason for higher rates that were made by conventional approach might be due to the lack of consideration of buffer capacity, and K preference as mainly indexed by Gapon and Vanselow equations. Selectivity coefficients are determined by the same principle as the one used to calculate K buffering capacity.

The true worth of a fertilizer recommendation approach should be beyond theoretical analysis and technical justifications; it must be assessed on the field. There are several studies which have done comparison on Q/I indices and extraction approach indices, for phosphorus (Holford 1980; Anderson & Wu 2001; Hue & Fox 2010), similar comparative studies for potassium have been done (Sinclair 1982; Ninh et al. 2009; Hosseinpur & Tadayon 2013).

On Nitrogen Recommendations

Lesser N rates recommended by an alternative approach in this experiment did not compromise yields as would have been so if the recommended rates were not sufficient to meet N crops requirements. We therefore, propose that the higher rates recommended by a conventional approach were unwarranted and perhaps wasteful.

Integrated N mineralization perhaps actually compensated for N withheld on its account. We support this proposition by N removed by maize grains and potato tubers. According to Masclaux-Daubresse et al. (2010) 50-90% of N content in grains is remobilized from the leaves, thus the N content of grains is a function of N uptake. On both sites the N removed by grains was not different between the two approaches. Yet, the rates recommended by an alternative approach were higher. It is worth noting that on both sites the N removal was on average higher, when N recommendations were made after adjusting for mineralizable N (Table 10).

The difference on N grain content when N was recommended after integrating mineralizable N and conventional N recommendation was more than 10 times higher than the difference between conventional and control on site 1. Such reduction on N uptake might be explained by the proposition made by Mulvaney et al. (2009) and Ramirez et al. (2010) based on long and short term basis respectively, that N fertilizer might reduce soil N. The same was true with regards to N recommendations for potatoes. The argument can be extend so it is applicable to above biomass for maize on potatoes, based on Masclaux-Daubresse et al. (2010) propositions that, whether a plant uses C3 or C4 photosynthesis system the principles of nutrient remobilization with specific reference to N, are the same.

On Potassium Recommendations

Potassium removal by maize grains did not significantly respond to either recommendation strategy on either site. This was more pronounced on site 1, however this lack of response on site 1 was no surprise. Because the initial high K concentration as indexed by intensity parameters might have masked the effect of fertilizer treatments on this sites. There was no difference in K removed by both crops; this suggests that enormously higher rates recommended by the conventional methods were unwarranted and wasteful.

On Phosphorus Recommendations

Contrary to the N and K recommendations made by the alternative approach, Q/I based recommendations mostly recommended higher P rates. Perhaps higher rates recommended by an alternative approach were warranted given their significant impact on nutrient removal (Table 10). Amount of P removed by maize on both sites was higher on average when NPK was recommended using Q/I relations. To appreciate the difference that was between the conventional and Q/I relations, it is worth noting that the difference between conventional and control which was 0.41 and 0.97 kg ha⁻¹ on site 1 and 2 respectively, and the difference between the conventional approach and Q/I relations was 4.27 and 2.42 kg of P ha⁻¹ on site 1 and 2 respectively (Table 10). These results perhaps suggest that the recommendations made by Q/I relations for P were justified.

The justified P application rates recommended by the Q/I relations, could be further supported by Liebig's law of the minimum. Which might be applicable in this case given that N and K rates recommended by the conventional approach were higher, thus, these nutrients were not limiting. The amount of P recommended by the conventional were lower, thus, if there was a limiting nutrient within this approach might have been P. Given that the potatoes were of a better grade when NPK recommendations were made by Q/I relations it can perhaps be deducted that the compromising factor was P recommendations (Figure 2). This proposal can be further extended to maize parameter such as total above ground biomass of maize and marketable yield of potatoes (Table 5 and 7), given that these parameters were significantly improved when NPK was recommended by the alternative approach, thus implying that there was a limiting factor within the conventional approach.

On NPK Recommendations

These results perhaps suggest that the alternative approach of integrating N mineralization on N recommendations, and recommending P and K using Q/I approach are more valid.

Physiological response in particular yields although they might be popular in calibrating fertilizer recommendations, and as such a popular variate used to assess fertilizer effectiveness. Yield responses remain hugely subjective and affected by various other variables. Thus, their exclusive use as variates that informs about the conduciveness or lack thereof of fertilizer treatments must be interpreted with caution. This can be further supported by the physiological and yield response with total carbon variation for maize and potatoes (Figure 3, 4 and Table 10). On empirical basis, we found that total carbon content of either grains or tubers consistently and inversely correlated with all three primary macronutrients, and similar results were obtained on Chapter 4.

Such consistent response might perhaps be due to the net effect of fertilizer treatments, rather an influence of an individual. If it is so, it can be used as a unifying variate which its variation is dependent on the conduciveness of fertilizer treatment as a whole rather as a product of single nutrient variation. It is worth mentioning that when calibrating soil test, yields are currently utilized to serve this purpose. Nonetheless, yields are subjective variates and theories about its formation are hardly based on soil fertility status. This is contrary to total carbon, since carbon/nutrient theory as suggested by Bryant et al. (1983), provide theoretical basis with regards to using carbon as a variate which its variation is dependent on the fertility status. According to the theory, improvement in fertility status as parameterized by increase nutrient levels causes the drop in carbon based metabolites, with special reference to terpenes and phenolics. Although these carbon based metabolites were not measured in this study, previous studies by Cronin and Lodge (2003) and Mohd et al. (2010) have showed that there is a positive correlation between these metabolites with total carbon with r² value of 0.82 (Mohd et al. 2010).

So that if this theory is valid, total carbon can be used along other variates to assess the validity of fertilizer recommendation approach. Given that on this present study we obtained inverse relationship between total carbon and nutrients, the preeminence of fertilizer recommendation must be concurrent with this drop in total carbon. Given that maize grain total carbon was lower when NPK was recommended with the alternative approach, and potato total carbon on site 2 was low as well when recommendations were

made by alternative, it can therefore conclude based on this and aforementioned arguments that the alternative approach proposed on this study is superior to the conventional approach of recommending NPK. We acknowledge the weakness of this study as shown by extreme differences in the yields of the two sites for both crops; we attribute this difference to low pH on site 2, hence exchangeable acidity. It is however worth noting that this is one of very few studies which assess the recommendation of nitrogen, phosphorus and potassium in combination. It is traditional that these nutrients are assessed on individual basis, with the rest provided as basil cover.

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CHAPTER 7

General Discussion and Conclusions

Use of inorganic fertilizer is a necessity in modern agriculture, and the pressure on this necessary resource is not expected to ease. Synthetic fertilizer contributes significantly on net input cost, hence sustainability of farming. Fertilizer recommendations can only be derived from soil test data. Use of extractants as a tool of soil testing represents major challenges i.e., 1) theoretical challenges; such as the insufficient description of intensity parameters, and overlooking fundamental soil reaction such as cation exchange and anion adsorption. 2) Technical challenges; such as relating external applications with the soil test values, such relations are necessary in computing the actual application rates based on a current soil test. 3) Practical challenges; poor relationships between crop response and soil tests. These challenges are not mutually exclusive, they are all interrelated. correlations between crop yield and parameters, and fertilizer application rates are fundamental relationships. By extension positive correlations between soil test indices are supposed to, and this has not always been the case with soil test indices derived from extraction based. There is also a need of improving N recommendations. The main aim of this study was to evaluate conventional fertilizer recommendation strategies. This was done by comparing conventional recommendations to alternative approach of recommending N, P and K. Alternative approach for N was achieved by integrating mineralizable N, and for P and K it was derived from Q/I relations. It was hypothesized that alternative approach was more mechanistically justified than the conventional approach.

Crop Response to alternative N recommendations

By default, N rates recommended by the alternative approach were lower compared to the rates recommended by the conventional approach. There were 14 different experimental units on which this assessment was made, these experimental units only considers N uptake and N removal by harvestable organs. These experimental units can be summarized as follows: pot trial where N was the only variable on two crops (maize and potato), and maize harvested after 5 weeks and 8 weeks. The second pot trial with two harvest dates for maize, and N along with P and K were the variables, field observations on both crops on two different sites, this included N uptake during tasseling stage, and N removal by potato tubers or maize grains. In all the observations made there is no instance where N uptake was significantly higher under conventional recommendations as per higher recommendation rates.

The lack of significant response could be interpreted in two ways, 1) since there was an amount of N fertilizer applied even when recommendations were made by an alternative approach, these rates were still sufficiently to not significantly reduce nutrient uptake. 2) Since the fundamental assumption of adjusting for mineralizable N is that the amount subtracted from original yield target rates will be compensated for by mineralized N, so that the 2nd interpretation may be that the N withheld on account of mineralizable N, was actually compensated for by mineralized N. To this end interpretation 2 is applicable in this instance. Of 14 observation made on this study the trend was that, 6 of them N uptake was higher when N recommendations were made by an alternative approach, and 2 the N uptake was equal between the two approaches. Therefore mineralizable N can actually compensate for N withheld on its account. The reason for 6 observations where N uptake was higher when N was recommended by an alternative approach is unknown and unclear. We can hypothesize, nonetheless, that N fertilizer might have reduced soil N as proposed by Mulvaney et al. (2009), and since soil N contributes significantly to N needs of plant, this might have ultimately reduced N uptake (Schindler & Knighton 1999).

Crop Response to Alternative P recommendation and K Recommendations

Chapter 5 of this thesis conclusively demonstrated that extraction based intensity, is insufficient in explaining P or K uptake by either potatoes or maize, and this in violation of the entire basis of soil test objective. Coefficient of determination (R^2), between extraction based intensity and P uptake by maize and potato was 0.18 and 0.02 respectively. These value were extremely low compared to R^2 of Q/I intensity, which were 0.62 and 0.85 for maize and potato respectively, and the same trend appeared to be true between K intensities and K uptake by crops. Implying that the variation of P or K uptake is independent of extraction based intensities. This interpretation seemed valid based on crop response, on pot trials, extraction based recommended higher P and K rates, and these higher rates were not concurrent with the nutrient uptake, perhaps suggesting that these higher rates were unjustified. This might be because of the inconsistence performance and lack of specificity of the extractant used. Chapter 2 showed that there is a relationship between Q/I parameters and easily measured soil parameters perhaps these relationships can be exploited so as to predict these comprehensive soil parameters which seem to comprehensively account for changes in nutrient uptake.

Overall Performance of Alternative NPK Recommendation

Both yields of maize and potatoes on average were higher when NPK was recommended by an alternative approach. It is therefore concluded that this approach is more mechanistically justified. For P and K this might be because of consideration given to fundamental chemistry that affects the availability of respective nutrients. We acknowledge the limitations of using yield as an ultimate assessor, in this thesis we proposed that total carbon could be used as an ultimate assessor of NPK recommendation program, we justify the adoption of this parameter on the basis of carbon/nutrient theory. We also showed that both under field and controlled environment that total carbon correlates well with all three

nutrients, either in plant tissue or harvestable organ. The consistence performance might prove useful in future assessments, although it needs further investigation.

There is a potential of routinely determining P and K Q/I parameters by multiple linear regression equations. Extraction based intensity for P and K need some revision, as they appear none related either to external applications or crop response, therefore, in violation of fundaments soil test objective. On this study Q/I parameters proved to be useful indices in explaining the variances in crop response. There is a room for improvement on N recommendations through integrating mineralizable N.

Recommendations for Future Work

Our objective was to justify the need to change the currently used fertilizer approach, and we herein proposed an alternative and we justified it theoretically and experimentally, nonetheless there is still a lot of work to be done on this subject:

- It is necessary to investigate whether these alternative parameters proposed in this study can be routinely determined by the use of M/NIR or soil inference system. This would be important to justify any further work done on this subject.
- Activity ratios of K need a refinement to account for exchangeable acidity, in order to be considered truly mechanistic.
- In order to truly to consider P recommendations made by Q/I relations mechanistic; investigations on implications of P sorption hysteresis on fertilizer recommendation is needed.
- consideration of timing and placement of fertilizer needs to be considered in future works