

**LAND USE EFFECTS ON CHARACTERISTICS AND MINERALIZATION OF
NITROGEN AND PHOSPHORUS DURING INCUBATION OF HUMIC TOPSOILS
FROM SELECTED SITES IN KWAZULU-NATAL, SOUTH AFRICA**

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DECLARATION

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ABSTRACT

Humic soils are highly weathered and leached and contain a high content of carbon (C) (>1.8%) in the humic A horizon, and are commonly used for production of vegetables, sugarcane, maize, forestry and pasture. There is little information on effects of land use change on the characteristics of the humic topsoils and their potential to supply nitrogen (N) and phosphorus (P) through mineralization. Therefore, this study was conducted to investigate the effects of land use and soil depth on characteristics and N and P mineralization of selected humic topsoils. The soils were collected from 0-10 and 10-20 cm depths of humic soils under natural forest and sugarcane at Eshowe, wattle plantation and sugarcane at Eston, and pasture and maize at both Karkloof and Cedara in KwaZulu-Natal, South Africa. The soils were analysed for texture, pH, exchangeable acidity and bases, extractable aluminium (Al) and iron (Fe), total C and N content and extractable P. A phosphorus sorption study was conducted for each sample and Langmuir parameters determined. An incubation experiment was conducted to monitor N and P mineralization at 25 °C, with destructive sampling at 0, 7, 14, 28, 42, 63 and 84 days. Sequential extractions of inorganic P fractions were performed at the end of incubation. Topsoils from Karkloof and Cedara had a clay texture with >50% clay and <33% sand, while those from Eston and Eshowe were sandy clay loams with <33% clay and >50% sand. Arable soils had higher exchangeable Mg and K, and pH and lower exchangeable acidity, than non-arable ones at all sites. Exchangeable Ca was higher in arable when compared to non-arable ones only for soils from Karkloof. Exchangeable Na was not affected by land use or depth. Arable humic topsoils had lower total C and N compared to non-arable ones at all the sites. Land use did not affect S_{max} of soils from Eston, Eshowe or Karkloof at 0-10 cm and 10-20 cm depth. The non-arable soil at Cedara had higher S_{max} at both 0-10 cm and 10-20 cm than arable. All soils had high to very high P sorption, with S_{max} of about 2 500 mg/kg for Eston, about 2 000 mg/kg for Eshowe, just under 800 mg/kg for Cedara and 1 000 mg/kg for Karkloof. Soil

pH decreased during incubation, with arable having higher pH than non-arable soils at Eston throughout incubation. For the first 14 days of incubation, non-arable soils at Eshowe had higher pH than arable soils. The arable soils from Cedara and Karkloof had higher pH values than non-arable throughout the incubation. Extractable P declined during incubation, for all depths and land uses with gradual increase after 28 days, increasing more rapidly for the 0-10 cm arable soil from Eston. Incubation increased the Al-P, Fe-P and reductant-P fractions. Extractable P was higher on arable soils than non-arable soils. Ammonium-N was higher in the non-arable than arable soils, throughout the incubation, for soils from the 0-10 cm depth from Eston and Eshowe. Ammonium-N decreased with time for both depths and all land uses from about 50 mg/kg to less than 10 mg/kg within the first 14 days. Arable soils released more nitrate-N than non-arable soils during incubation except the soils from Eshowe. Nitrate-N increased after 14 to 28 days with some of the soils reaching ≥ 70 mg/kg. The findings of this study showed that converting humic soils to arable soils increases pH and plant available N but decreases extractable P, total carbon and nitrogen, through enhanced decomposition of the organic matter. The changes in physico-chemical properties of humic topsoils as a result of change to arable cropping could contribute significantly to soil fertility but may have long term negative effects on soil organic C.

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CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background

The high permeability and low bulk density resulting in easy workability and high water holding capacity of humic A horizon, make humic soils important for the production of arable crops such as maize, sugarcane and vegetables, as well as for forestry in South Africa. The humic A horizon which is characterized by high organic carbon (>1.8%) and low exchangeable bases <4 cmol(+) per kg clay for every one percent organic carbon present, distinguishes humic soils from other soils (Soil Classification Working Group, 2018). The strong weathering and leaching explains the low base status and cation exchange capacity (CEC), pH and the high pH buffering capacity.

The conversion of humic soils from non-arable to arable land uses could be of significant value in terms of making nutrients available from decomposition of the high organic matter and mineralization of nutrients. These may need to be considered when making fertilizer recommendations especially for nitrogen (N) and phosphorus (P). Potential N mineralization from humic soils has been estimated to be up to 400 kg N/ha annually and pome fruit plants have been reported to show vigorous growth even without N application (Fey, 2010). While the mineralized N could be beneficial, the long-term decomposition may result in significant reduction in soil organic matter, negatively affecting the favourable physical properties of these soils, as a result of tillage and other management practices in the arable soils. Land use change on most soils, from their natural systems to pasture and cropping and subsequent tillage practices, has resulted in significant decrease in soil organic matter, total porosity and soil aggregate stability (Kizilkaya and Dengiz, 2010). In addition to potential benefits of increased N availability, management practices such as lime application, fertilizer application and residue

removal, may alter the physico-chemical properties of humic A horizons. Lime application to acidic soils has been shown to reduce acidity, increase soil pH and soil available P, with the increase depending on the rate of lime application (Osundwa *et al.*, 2013). In addition to pH increase and P availability, Anikwe *et al.* (2016) reported an increase in base saturation with lime addition and that was even more so when lime was added together with gypsum. The use of fertilizers in soils to support crop production has been reported to increase available macro and micro nutrients for plant uptake (Ayeni *et al.*, 2012). Studies have been conducted to investigate the effects of crop harvest and residue removal on soil properties and on nutrient dynamics of agricultural soils. The applicability of such studies has not been well tested on humic soils, yet they form a large part of the agro-ecosystem (Fey, 2010).

Trivelin *et al.* (2013) investigated the loss of nutrients especially N during the pre-harvest burn of sugarcane and residue removal from the soil and found very significant losses due to these practices. Mandal *et al.* (2004) suggested that a yield of 4 t/ha wheat crop could remove more than 300 kg N/ha, 30 kg P/ha and 300 kg K/ha from the soil and also estimated that about 80% of N, 25% of P and 21% of K was lost from burning wheat residues. While many studies have been done on effects of land use and management on soil quality (McGrath *et al.*, 2001), there is a paucity of such studies on humic soils. The comparison of physico-chemical properties of humic soils under arable agriculture with those that are non-arable, will show effects of arable cropping on these properties. These potential effects may vary as a result of differences in site and management factors. Incubation studies give an impression on processes taking place in soils in the short-term. For example, incubation studies are essential to understand short-term availability of N and P in humic soils. Understanding the effects of land use on N and P release patterns of humic A horizons, could be essential when making fertilizer recommendations for these soils.

While N may be increased by decomposition of organic matter and mineralization, the same effects may be limited for P through fixation as inorganic P (Pi) compounds are largely associated with amorphous and crystalline forms of iron (Fe), aluminium (Al) and calcium (Ca) (Negassa and Leinweber, 2009). This could result in complications in understanding the patterns of P mineralization during decomposition of organic matter from humic soils. Phosphorus sorption in humic soil was viewed as a tool in understanding P release patterns. The potential increase in acidity during the decomposition of the organic matter from these soils could also affect the different P fractions.

Although a variety of studies have focussed on soil nutrient dynamics in South Africa, few have investigated humic soils. This study was therefore conducted to address some broad questions concerning N and P relations in humic soils.

1.2 Research questions

- a) Are there any land use effects on the common characteristics of the 0-20 cm layer of humic soils?
- b) Do land use and sampling depth affect P-sorption capacity of humic soils?
- c) Do land use and depth of sampling affect N and P mineralization during incubation and distribution of P fractions in humic soils?

1.3 Objectives

The specific objectives of this study were to determine effects of land use and depth of sampling on:

- a) Selected properties of surface layers of humic soils.
- b) P-sorption capacity of surface layers of selected humic soils.
- c) N and P mineralization during incubation and P fractions of selected humic soils.

CHAPTER TWO

NITROGEN AND PHOSPHORUS MINERALIZATION IN HUMIC SOILS: A REVIEW

2.1 Introduction

Mineralization of nutrients from organic materials in soils is one of the crucial processes that contribute to plant growth (Cooper *et al.*, 1987). Decomposition of the organic matter results in microbial conversion of organic forms of nutrients to ionic or inorganic forms, which are plant available (Du Preez *et al.*, 2011). This conversion is very important in the supply of N and P, which can only be taken up as ammonium (NH_4^+) or nitrate (NO_3^-) (Chen *et al.*, 2016) and orthophosphate (H_2PO_4^-) or (HPO_4^{2-}) (Sharpley *et al.*, 1994). Mineralization of organic nutrients is the main source of nutrients such as P in natural systems, especially in highly weathered soils that are low in P (Vincent *et al.*, 2010). Decomposition of organic matter and mineralization of elements are governed by the biophysico-chemical properties of the soil.

The P retention capacity of soils is an important parameter for understanding soil fertility, as well as for defining the environmental fate of P (Graetz and Nair, 1995). Highly weathered and leached soils, including humic soils, are dominated by 1:1 layer silicate minerals, and oxyhydroxides of Al and Fe in the clay fraction, and have a high affinity to adsorb P. The adsorption behaviour of these soils tends to be rapid initially and becomes period specific adsorption thereafter (Sposito, 1989). The high P adsorption capacity of highly weathered soils may result in low levels of available P for uptake by plants.

The aim of this chapter is to review work that has been done on N and P mineralization with the emphasis on highly weathered soils (including humic soils) under different land uses and the effect of those land uses on mineralization and soil properties.

2.2 Distribution of humic soils in South Africa

Humic soils are among the most important agricultural and forest soils in South Africa. They are found on old land surfaces, with high rainfall and cool temperatures on gentle to moderate elevations (Fey, 2010). They occur in places with moist, cold or cool climates of KwaZulu-Natal, Mpumalanga and the Pondoland coast in the Eastern Cape (Fey, 2010). Figure 2.1 shows the distribution of humic soils in South Africa. Humic soil distribution like any other is governed by the combination of soil forming factors. The climatic regions of rainfall greater than 850 mm per annum have more likelihood of having humic soil forming (Soil Classification Working Group, 2018). The vegetation type such as moist subtropical forest or short grassland have been suggested as some indicators of the presence of humic soils (Fey, 2010; Soil Classification Working Group, 2018).

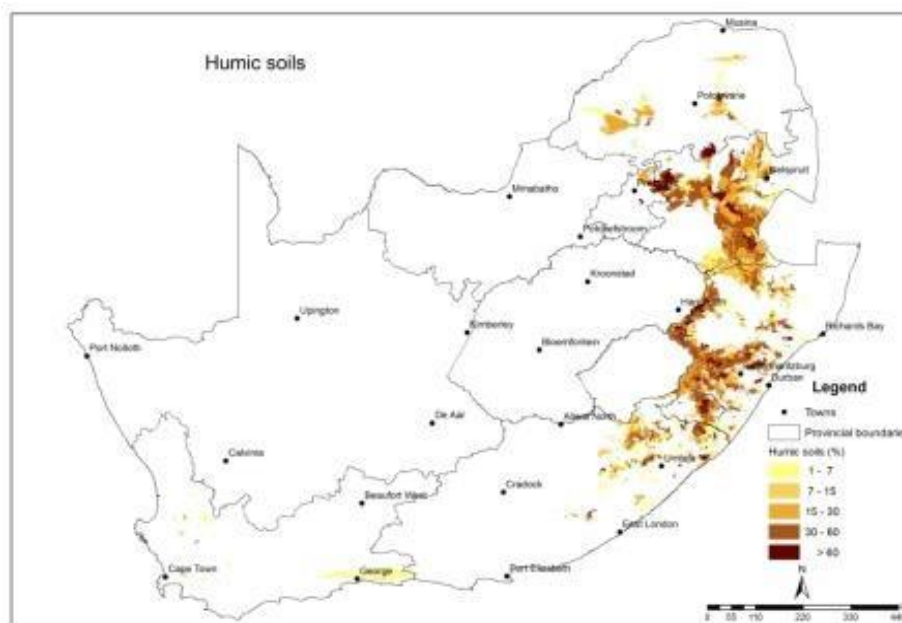


Figure 2.1 The distribution of humic soils in South Africa (Fey, 2010).

Humic soils have been classified into different forms, mainly based on variation in characteristics of materials underlying the humic A horizon, giving the following soil forms: Inanda (thick Red Apedal), Kranskop (Yellow Brown Apedal over Red Apedal), Magwa (thick

Yellow Brown Apedal), Sweetwater (thick Neocutanic), Nomanci (Lithic), Dartmoor (Yellow Brown Apedal over Gelyic), Eland (Yellow Brown Apedal over Soft Plinthic), Longtom (Yellow Brown Apedal over Lithic), Highmoor (Red Apedal over Gelyic), Netherley (Red Apedal over Soft Plinthic), Gangala (Red Apedal over Lithic), Umvoti (Neocutanic over Soft Plinthic), Henley (Neocutanic over Lithic) and Graskop (Hard Rock) (Soil Classification Working Group, 2018), with the closest international translations of Umbrisols, Ferralsols, Acrisols, Luvisols, Lixisols, and Cambisols (Fey, 2010; FAO, 2014). The characteristics of the humic A horizons distinguish them from other soils. They an accumulation of large amounts (>1.8% carbon) of humified organic matter, being well-drained and having low base status (Soil Classification Working Group, 2018). The notably high amount of organic carbon (C) content in humic soils affects many of the soil properties and yet the humic soils have been poorly studied. The effects of land use change to cultivation, on physicochemical properties, have been particularly poorly studied on these soils, and yet their importance for agriculture is clear.

2.3 Importance of humic soils

Humic soils are reported to accommodate a diversity of land uses, including natural forests, grasslands, improved pastures and commercial production of maize, sugarcane, vegetables and orchards (Fey, 2010). The particular physiochemical properties of the humic topsoil, low bulk density resulting in easy workability and high water holding capacity, make these soils important in many regards. These morphological features such as texture of humic soils are different from those of other dark coloured soils such as melanic and vertic soils. Low base status in these soils is because of the extent of weathering, which has been moderate to strong compare to that of other soils (Soil Classification Working Group, 2018). The relatively moist and cold/cool climates that the humic horizon has developed under has also influenced the morphological features that occur. Figure 2.2 shows some examples of humic soil forms.

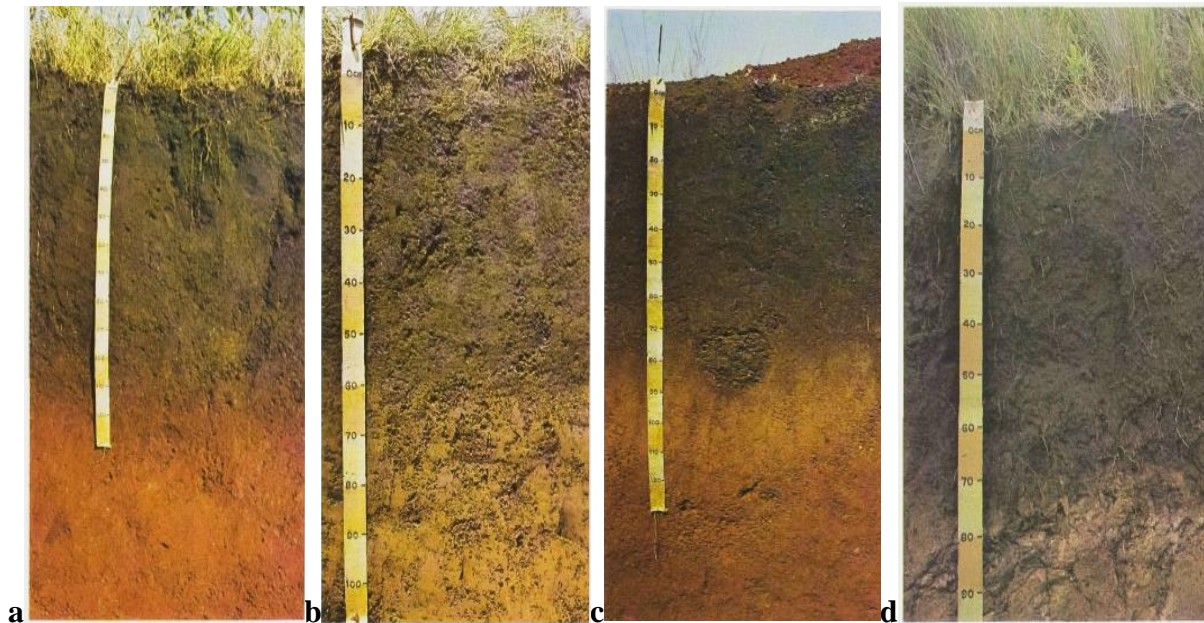


Figure 2.2: Some humic soil forms: (a) Inanda, (b) Magwa, (c) Kranskop and (d) Nomanci (Soil Classification Working Group, 1991).

In addition to favourable physical properties, the agricultural importance of these soils could also be a result of the contribution of mineralization in making nutrients more available. It has been estimated that a 5% annual mineralization in a 30 cm thick humic A, with 2% C and a C/N ratio of 10, could release up to five times the annual amount of N applied on young pome fruit trees (Fey, 2010). Such mineralization of N could be accompanied by significant mineralization of P. The occurrence of humic soils on old land surfaces with moist, cold or cool climates in KwaZulu-Natal, Mpumalanga and the Pondoland coast in the Eastern Cape (Fey, 2010), make the contribution of the possible N and P mineralization hugely important.

2.4 Effects of land use change to arable cropping on chemical properties of acidic soils

Increasing human population has been identified as one of the major reasons for land use change to meet increasing food demand (Solomon *et al.*, 2000). These changes in land use have resulted in soil quality degradation coupled with nutrient depletion in some cases (Du Preez *et al.*, 2011). Lal (1996) investigated different cropping system treatments (i.e alley cropping,

mucuna fallow and ley farming) on soil chemical quality and reported a decrease in pH, soil organic C, total N and basic cations with time regardless of the cropping system. However, Adugna and Abegaz (2016) suggested that there could be some positive effects from land use change if the integrated approach to land management was to be used through minimum tillage, crop rotation, cover crops, manures and compost. Islam and Weil (2000) studied the effect of land use on soil pH, soil organic C and total N amongst other parameters, using well-stocked *Shorea robusta* natural forest, land reforested with *Acacia*, grassland and arable land on a silt loam soil. The authors reported that pH values of the soils varied significantly from 4.9 to 5.6 with natural forest and reforested being more acidic than those of the grassland and arable land. The acidic nature was explained by the pre-weathered parent materials, amphoteric nature of aluminium in the tropical soils, and the extreme leaching of basic cations. The higher pH values were attributed to ash from biomass burning on the grasslands that could have returned basic cations into soil to increase pH. The lower levels of organic C (7.4 g/kg) and total N (0.81g/kg) in arable soils compared to non-arable (12.8 g/kg OC, 1.25 g/kg N) were explained by the lower C inputs that were due to less biomass C return on harvested land and greater C losses from aggregate disruption and increased aeration during tillage, as well as crop residue management through burning. A similar study was conducted by Emiru and Gebrekidan (2013) using Alfisols with natural forest, shrub, grass and arable cropping. It was found that the pH varied from 4.6 to 6.6, the forest having the highest pH and grassland having the lowest. The pH variation was explained by basic cations leaching and depletion in crop harvest and continuous overgrazing on grassland, in turn increases the activity of Al^{3+} and H^+ in the soil solutions, thus decreases soil pH and in that way increases soil acidity. The use of ammonium based fertilizers like di-ammonium phosphate on grassland and arable land was also considered as a reason for the lower pH, as these fertilizers increase acidity upon nitrification (oxidation) by soil microorganisms. The highest soil organic matter contents (7.7 %) and total N (0.39%) were in

the surface soils of forest land while least amounts (4.2% C) and (0.24% N) were in arable soils .Unlike in previous studies, where crop residues were burnt, cereal crop residues were returned back into the soil but these inputs proved to be low to match the amounts of organic matter input in forest. The tillage effects and rapid mineralization of organic matter contributed to the organic matter losses. Available P content varied from 2.1 mg/kg in soils under the shrub lands to 42.8 mg/kg in forest soil. Available P in arable soils reported to be 3.8 mg/kg which was higher than in the shrub land and grassland due to animal manures being added and slow release of P from di-ammonium phosphate. Majaliwa *et al.* (2010) reported the same effects of land use change from natural forest (6.48% C, 0.26% N) to tea (7.20% C, 0.31% N) and woodlot (*Eucalyptus grandis*) (4.97% C, 0.24% N) on soil pH, organic matter, total N and available P of Lixic Ferralsols. In addition, the changes in exchangeable calcium (Ca) and magnesium (Mg) were also observed by the same authors, where tea plantation had the lowest concentrations of these bases. This corresponded with the soil pH 3.5 under tea plantation, which was more acidic as compared to forest and woodlot. Areas with high chance of soil erosion as result of land use change have been suggested to allow the base-poor surface soil to be eroded away and exposed fairly less weathered subsoil. Over time, the newly exposed surface could present the characteristics of an increase in pH and exchangeable Ca and Mg. This was observed by Navarrete and Tsutsuki (2008) when investigating the effect of different land use on soil properties on Ultisol under secondary forest, mahogany plantation, rainforest coffee plantation and grassland. However, this did not improve soil C and N as they decreased with the change in land use with the lowest on grassland and rainforest, available P remained low at about 1.8 to 3.7 mg/kg. These were explained by the long extensive arable cropping history before the establishment of the permanent grassland and rainforest which were about 14 years old at the time of the study. In contrast to these studies, Getachew *et al.* (2012) found no effect of land use on soil pH, soil organic C, total N and available P in Andosols under

natural forest (4.38% C, 0.68% N), arable land (3.92% C, 0.60% N), grassland (4.68% C, 0.53% N) and *Eucalyptus saligna* plantation (4.94% C, 0.58% N). These unique findings were explained by the high resilience of the soil used to change in chemical properties induced by change in land use and management. The resilience to change of Andosol was explained by the presence of allophanic and soil minerals pumice from volcanic activities, which are more resistant to change, also the Al and humified organic matter complexes were responsible for chemical stability of these soils (Getachew *et al.*, 2012). Considering that humic soils as Andosols have low pH, high concentrations of Fe and Al oxides, and high organic matter suggest that they could behave the same way to a limited extent because humic soils do not have any influence that could relate to volcanic activities. Therefore, humic soils could behave like the rest of the other soil although the changes could not be expected to be rapidly due to Al and humified organic matter complexes.

2.5 Effects of land use on organic matter decomposition and mineralization

Land use change results in changes in the organic matter composition in both the short and long terms. For example, converting arable land to permanent grassland results in the heavy density fraction of the macro organic matter increasing because soil organic matter accumulated earlier is less susceptible to be lost as the soil disturbance is minimal under grassland compared to arable (Accoe *et al.*, 2004). Different land uses could have their own effects on mineralization and sometimes the same land use could show differences solely because the plant species and site characteristics are different. Usman *et al.* (2000) showed that plant species could influence N mineralization and uptake in forest soils. Their findings indicated that nitrate-N was the dominant form of mineral N taken up by plants in *Quercus ilex* (oak) forest, while both nitrate-N and ammonium-N were equally taken up in *Pinus sylvestris* L. (chir pine) forest. Olsson *et al.* (2012) reported that soil C and N pools were significantly

larger under spruce than under *Betula pendula* (birch), with C mineralization rate being higher in birch and spruce humus than in pine humus. The net N mineralization rate and annual field net N mineralization were estimated to be very low ($<4 \text{ kg N ha}^{-1} \text{ year}^{-1}$) with no tree species differences. The reason for this finding is mainly that each different tree species is often associated with different soil characteristics. Saetre *et al.* (1999) demonstrated effect of tree species when studying the mineralization in forest soil under spruce and birch trees, and found that C mineralization was 15% higher under birch than spruce. This suggested that leaf litter from birch trees increased the pool of available substrate for soil microbes. Factors such as temperature, soil pH and organic matter were the main drivers of the changes that were observed. Chapin *et al.* (2003) observed higher N mineralization in the fen than in the bog when studying peatlands nutrients mineralization with a close to zero P mineralization. Furthermore, fertilizer application increased cumulative N and P mineralization with no liming effect shown in the bog, in the fen only liming effects were significantly. These differences suggested that peatlands nutrient cycles are controlled by different factors. Chen *et al.* (2016) investigated N mineralization responses to P addition on red soils with long term P deficiency. The authors reported the increase in nitrification due to increase in some enzymatic activities. The other important factor that influences the extent of mineralization of nutrients is the soil management from one land use to the next. Gill *et al.* (1995) studied the net mineralization under grassland on a silty clay loam soil, which had previously on fertilizer and drainage management, and found the highest annual net N mineralization on drained and N fertilized soil and the lowest on undrained and unfertilized soil.

Cooper *et al.* (1987) found that land use affected total P and dissolved reactive P in the order pasture > pine > natural forest but this order was reversed for nitrate-N with no effect found for ammonium-N. Land uses such as pasture and cropping as well as other activities, including

grazing and cattle manure additions, could impact on mineralization directly or indirectly (Mathews *et al.*, 1994, Braos *et al.*, 2015).

Available P in highly weathered soils is typically low and naturally depends on organic P mineralization (Maranguit *et al.*, 2017). Land use change and management could influence P pools, as reported by Negassa and Leinweber (2009), who reviewed literature on the effects of land use and management on soil P fractions as extracted by the Hedley *et al.* (1982) sequential P fractionation procedure. They found that, in a natural ecosystem, P concentration and distribution was similar in all soils but soils subjected to different land uses and management systems had shifts in the P concentration and distribution. Cropping with more P application, than recommended, increased the labile and moderately labile inorganic P (Pi) fractions. However, the decline of these fractions was more pronounced under cropping without P applications.

Maranguit *et al.* (2017) observed that land use and management had effects on both inorganic and organic P in that fertilization increased inorganic P in the short term and organic P decreased due to reduction of soil organic matter in intensive rubber (*Hevea brasiliensis*) and oil palm plantations (*Elaeis guineensis*) compared to rubber agroforest (*Alstonia spp.*, *Artocarpus spp.*, *Fabaceae sp.*, *Macaranga spp.*, *Porterandia sp.*, and *Hevea sp.*). Velásquez *et al.* (2016) also observed that fertilization resulted in higher P concentrations in arable soil when compared with grassland soil, and the NaOH-extractable organic P (Po) (moderately labile P pool) fraction was higher than the inorganic pool (NaOH-Pi), while the HCl (residual P) and NaHCO₃ (labile P pool) extractable fractions were not affected. In the arable soil, labile P was lower than in the grassland soil.

Furthermore, Solomon *et al.* (2002) concluded that stable P pools tend not only to be a sink but also contribute to the plant-available P following the progressive depletion of the labile P fractions. Oberson *et al.* (2001) reported that changing from native savannah to agricultural

land use systems affected the balance between inorganic and organic P fractions on Oxisols, mainly because the higher P fertilizer applications significantly increase the available inorganic P contents with a lesser effect on the organic P pool sizes. Sharpley and Smith (1985) demonstrated that cultivation had no effect on the relative distribution of P within inorganic and organic pools on calcareous soils whereas it increased the non-occluded pools and decreased the occluded pools on non-calcareous soils. This was because the pool of plant available, loosely-bound inorganic P is maintained at a relatively constant level by fertilizer, crop residue, and manure addition and organic P mineralization. If this pool surpasses crop needs, it will be depleted by sorption. While many studies have been done on effects of land use on mineralization of N and P in soils, there is limited information on humic soils. Based on the reviewed literature in this section, it is evident that land use management such fertilizer and lime applications affect the mineralization of N and P. Humic soils are generally used for forestry, grassland, pasture and cultivation (maize, sugarcane, vegetables), some of these are supported by both fertilizer and lime application for their production. Therefore, the decomposition and mineralization of N and P on humic soils would be expected to behave the same way as one on the reviewed literature, which changes from one land use to the next guided by each individual land use activities.

2.6 Effects of soil physico-chemical properties on nitrogen and phosphorus mineralization

2.6.1 Soil pH

One of the most important properties governing organic matter decomposition and elemental mineralization in soil is pH, which has been shown to be critical in the availability of P and other nutrients.

Rangeley and Knowles (1988) demonstrated that nitrification only occurred after the liming of peat from pH 3.5 to 6.6 with the inoculation of *Nitrosomonas*. It was also shown that at the original pH, cells from the added inoculation did not survive. This demonstrates the effects that pH could have on the products of mineralization, this is more so because it affects the microbial community and structure that regulates decomposition and mineralization processes (Wyngaard *et al.*, 2016). The effect of pH on microbial community and subsequent C mineralization was also demonstrated by Rousk *et al.* (2009). The authors reported a five times decrease in bacterial growth and five times increase in fungal growth at lower pH, and that change in composition decreased the total C mineralization. Wilhelmi and Rothe (1990) reported an increase in C mineralization by measure of CO₂ emission at weakly acidic to neutral pH values as compared to strong acidic pH when studying the mineralization of the organic layer of the spruce (*Picea abies L.*) forest floor. It was also reported by same authors that pH values less than 2.4 inhibited C mineralization. Depending on the pH, the P mineralized from organic forms could remain in solution, immobilized in cells of microorganisms, precipitate with Ca, Al and Fe, or be fixed by oxides of Al and Fe.

Antoniadis *et al.* (2016) reported that high basic pH results in precipitation of insoluble Ca-P species and direct retention of P electrostatically, through the exchange of HCO₃⁻ for H₂PO₄⁻ especially in soils with a high clay percentage. Acidic pH results in P forming complexes with Al and Fe ions and fixation on oxides of Al and Fe in the soils due to their positive pH-dependent charge (Schulten and Schnitzer, 1998). The suggested pH values (less than 2.4), which could hinder the decomposition and mineralization by prohibiting microbial activity, are lower than that of humic soils generally. Seemingly, the decomposition of organic matter and N and P mineralization could take place in humic soils but with some limitations in P mineralization if the pH is left uncontrolled.

2.6.2 Temperature and soil moisture content

Temperature is one of the most important factors in many biochemical reactions in soils because it regulates many microbial activities. The effects of temperature have been studied even at the extremes. Moni *et al.* (2015) found that low (below freezing) temperature limits mineralization, and as temperature rises and results in thawing, a small pool of fast cycling organic matter decomposes resulting in a mineralization flush. Carbutt *et al.* (2013) experimented with mineralization assays to test the effect of temperature on the soil N budget, at the Drakensberg Alpine Centre ('mountain site') in a sandy loam soil, and found that only 1% of the total N was mineralized to inorganic N at 12°C but when temperature increased to 30°C about 37% of the N was mineralized. Soil water content and the availability of that water to microbes are also important in enhancing the microbial activity (Usman *et al.*, 2000). McIntyre *et al.* (2009) investigated the effect of moisture on mineralization of C and N and found that large pulses of water (including floods) resulted in full soil saturation and slower release of mineralization products compared to small pulses which stimulated a rapid cycle of C and N mineralization. It was suggested that when water-filled pore space was greater than 40% and less than 70%, mineralization of elements increased.

The temperature and moisture content relationship in mineralization was also studied by Wilhelmi and Rothe (1990) who observed optimum C mineralization at 20°C to 35°C temperature range with water content ranging from 40% to 60% under laboratory conditions. Knoepp and Swank (2002) studied temperature-moisture interactions on N mineralization in forest soil representing Inceptisol and Ultisol orders at different elevations (739 m, 865 m and 1 001 m elevation) to capture different temperature and moisture conditions, and simulated those field conditions in the laboratory. The temperature and temperature-moisture interaction effects were reported to be significant on net soil N mineralization with the higher rates at higher temperature and increased moisture represented by summer season conditions. Wang *et*

al. (2006) did not observe any changes in N mineralization at temperature less than 5°C but mineralization only increased at 15°C to 35°C with improved moisture for grazing grassland. Increased N mineralization rate by at least three times, where both temperature and moisture were improved, was also observed by Marrs *et al.* (1988) in tropical rain forest soils. The same authors also observed the decrease in soil N mineralization and nitrification with increasing altitudes (100 m, 1 000 m and 2 600 m) under field conditions, and there were changes in mineralization rates where both temperature and moisture were increased but not where only temperature was increased. In contrast, Morecroft *et al.* (1992) reported no change in N mineralization with altitude when investigating altitudinal and seasonal trends in soil N mineralization rate. This was despite the altitudinal drop in temperature. The emphasis was that, at high altitude there were freezing temperatures in winter, which resulted in readily decomposed N containing compounds not to be broken, while at low altitudes, this resulted in an altitudinal rise in the substrate availability for mineralization. Stottlemeyer and Toczydlowski (1999) reported that the quality of substrate under improved temperature and moisture conditions increased the net mineralization in forest soil under birch and spruce. The increase in moisture alone resulted in nitrate immobilization, this accentuated the importance of temperature-moisture interactions and the effect of balancing the two for the optimal rate of mineralization and optimal mineralization product output. The temperatures and rainfalls at the places where humic soils occur are of cool temperature and high rainfall nature. These could give the ideal temperature-moisture interactions that support the microbial activity. Practically, in the field these interactions might vary from time to time thus giving the limited decomposition and mineralization products cumulatively.

2.6.3 Organic materials and soil organic matter

Soil organic matter composition and microbial community structure are central to the mineralization processes (Moni *et al.* 2015), but these could themselves prevail as a function

of a wide range of factors such as soil type and site, the source and age of the C and soil management activities. Accoe *et al.* (2004) reported that gross N mineralization and nitrification increase with the age of grasslands. The C/N ratio is an important biochemical property governing decomposition of organic matter, and mineralization of N. The suggested optimum C/N for mineralization is below 20 (Qiu *et al.*, 2008). Based on a variety of literature the threshold for N mineralization ranges from 20:1 to 30:1, with higher ratios resulting in N immobilization. The addition of organic materials such as plant residues, manures and composts into soil may increase the mineralization of N as they themselves supply N. These organic materials bring their different chemical and structural make-up into the soil.

Masunga *et al.* (2016) found that soils amended with *Trifolium spp* (clover) released 240 mg N/g soil, which was more than twice the amount released from soils amended with manure or composts (76–100 mg N/g soil) during a 97-day incubation. Microbial biomass C content was also higher in clover-amended soil than in the soils amended with manure or compost. Mafongoya *et al.* (2000) investigated the C, N and P mineralization from leaves of different browse tree species and from manure of goats that were fed on those leaves. The C mineralization had a positive relationship with the initial N content of the organic material (leaves or manure), P released had a positive relation with initial P content of the organic inputs, while N mineralized showed no relationship with initial N. These differences were also explained by C/N as leaves had high ratio than the manure from the same leaves. Organic amendments such as cattle manure has been shown to increase the proportion of potential mineralizable N and P in soils after long term applications (Whalen *et al.*, 2001).

2.7 Conclusions

Changing land use from natural ecosystems to arable cropping decreases pH, soil organic C, total N, available P and basic cations, these are corrected to desired ranges for specific land use with the addition of organic amendments, lime and fertilizers. Mineralization is reduced by

strong acidic conditions and is increased with improved temperature-moisture interactions. Lime and fertilizer applications subsequent to land use change influence the rate and direction of N mineralization-immobilization. Phosphate fertilizers increase inorganic P fractions especially with frequent P application. Both labile and moderately labile P fractions are decreased with the land use change from natural ecosystems to arable.

However, there is very limited information effects of land use change to arable cropping on soil pH, acidity, bases, soil C and N, P availability sorption, N and P mineralization and distribution of P fractions, in humic soils, and yet their actual significance in agriculture could be significant. Climatic conditions under which humic soils are formed, and their chemical properties, suggested they influence mineralization rate of nutrients. Therefore, the need for more work on these soils is pertinent.

CHAPTER THREE

EFFECT OF LAND USE ON SELECTED PROPERTIES OF HUMIC TOPSOILS

3.1 Introduction

Understanding the characteristics of agricultural soils is essential for their proper management. This understanding is particularly important for studies on the decomposition of organic materials and mineralization of nutrients that are affected by soil physico-chemical characteristics such as pH, texture and nutrients. In addition to natural differences among soils, due to variations in climate, living matter, parent material (weathered mineral or organic matter), topography, together acting over time (Brady and Weil, 2002), differences in land use and management also affect soil properties. Land uses such as permanent grasslands and forests have proven to result in higher carbon (C) stocks when compared to arable cropping (Accoe *et al.*, 2004). The differences are mainly the effect of tillage in arable land, which exposes aggregate protected organic matter to decomposition (Piñeiro *et al.*, 2010). In forestry, the higher stocks could be accompanied by a higher pH that varies from one tree species to another (Dijkstra *et al.*, 2001). Current global socio-economic demands for food, feed, fibre and biofuel, driven by population growth, have increased the need for changes in land-use and intensification of cultivation (Maranguit *et al.*, 2017). Some humic soils that were under long-term wattle plantations have been converted to sugarcane, while others have been converted from natural grasslands to maize production or improved pasture production. These changes in land use and associated management practices may have affected the characteristics of the humic soils.

Changing soil use from a natural ecosystem to an agricultural system significantly reduces soil quality (Briedis *et al.*, 2018). Some of the effects include decreasing soil pH and total C and nitrogen (N) values, with a continuous need to supplement nutrients such as calcium (Ca) and magnesium (Mg) (Mathews *et al.*, 1994). Some of the activities on individual land uses could

have irreversible consequences for soil parameters over time (Buol, 1995). The land use effects on properties of humic soils are not clearly understood considering that these soils have high concentration of C and extremely low pH and basic cations. It is important to understand the effects of land use on humic soils especially on parameters such as soil pH, exchangeable bases, other ions such as aluminium (Al) and iron (Fe), soil organic C and N and extractable phosphorus (P).

The objective of this study was to determine the effect of land use on (a) selected physico-chemical properties, and (b) phosphorus sorption characteristics of selected humic topsoils. These characteristics were investigated using the Langmuir model to obtain information on the P sorption maximum, and a constant k which relates to the P bonding energy (Nair *et al.*, 1984).

3.2 Materials and methods

3.2.1 Study sites

The soils used in this study were sampled from Eston, Eshowe, Karkloof and Cedara, which varied in parent material and climate, in the KwaZulu-Natal Province, South Africa (Figure 3.1). These areas were selected to represent a variety of land uses, which were compared for each individual site.

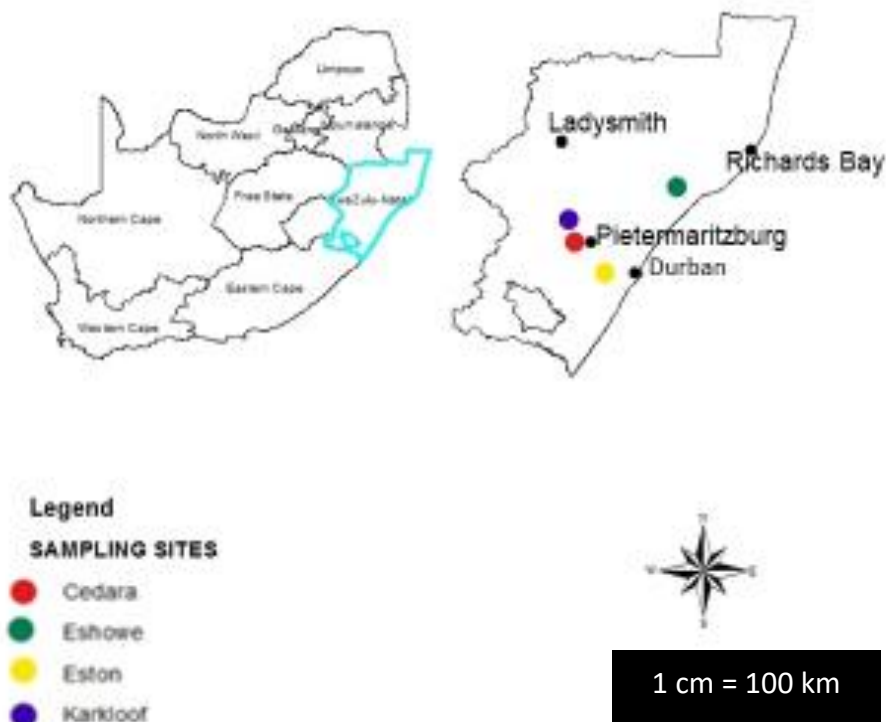


Figure 3.1: Location of study areas in KwaZulu-Natal, South Africa.

3.2.1.1 Eston

This was a commercial farm located at $29^{\circ} 33.376' S$ and $30^{\circ} 15.107' E$ with an elevation of 784 m.a.s.l. and an annual rainfall of 805 mm. The soils were Magwa form (humic A, thick Yellow-Brown Apedal horizon,) (Soil Classification Working Group, 2018) formed from weathering Natal Group sandstone. The humic A horizon was over 100 cm thick. Land uses were sugarcane (*Saccharum officinarum*) alongside wattle plantation (*Acacia mearnsii*). The production of sugarcane had been sustained over a period of more than 20 years by adding 10 t/ha of chicken litter before planting, with dolomitic lime and phosphorus applied as guided by soil tests. No amendments had been applied to the wattle. Both land uses were rain fed.

3.2.1.2 Eshowe

Soils from Eshowe were collected from a commercial farm located at $28^{\circ} 52.478' S$ and $31^{\circ} 25.077' E$ with an elevation of 540 m.a.s.l. and received 1 113 mm/annum rainfall. The soil form was Magwa (Soil Classification Working Group, 2018) with an Nsuzo Group sandstone

parent material and the humic A horizon was over 100 cm thick. Sugarcane was grown, alongside indigenous forest. The sugarcane was fertilized annually with an application of 130 kg N/ha, 20 kg P/ha and 140 kg K/ha. Calcitic lime had been applied at replanting once every 10 years. Both land uses were rain fed.

3.2.1.3 Karkloof

The soils from Karkloof were sampled from a commercial dairy farm located at 29° 37.275' S and 30° 28.15 3' E at an elevation of 1 596 m.a.s.l. The area receives 1 400 mm/annum of rainfall. The humic soils were formed from dolerite, and were classified as Inanda form (humic A, thick Red apedal horizon) (Soil Classification Working Group, 2018). The humic A horizon was about 40 cm thick. The land uses were improved pasture (ryegrass, *Lolium perenne* with clover, *Trifolium* spp) and maize (*Zea mays*) production. Maize had been grown for over 10 years with application of N (urea) and P fertilizers guided by the soil test together with calcitic lime (1 t/ha) with no irrigation. Pasture had been grown under no-till for more than 10 years with application of NPK fertilizers with irrigation using centre pivot system.

3.2.1.4 Cedara

The soils from Cedara were sampled on a farm located at 29° 33.376' S and 30° 15.107' E with an elevation of 1 054 m.a.s.l. and 900 mm/annum of rainfall. The humic soils were formed from dolerite, and were classified as Inanda form (Soil Classification Working Group, 2018), with a humic A horizon about 30 cm thick. The land uses were pasture (*Eragrostis* spp) and maize production. Maize had been grown on the soil for at least 10 years before sampling, with fertilizers applied every year at 120 kg N/ha, 20 kg P/ha and 40 kg K/ha and calcitic lime applied once every three years based on the acid saturation. Pasture had been cultivated for 16 years under no-till with 300 kg N/ha, 10 kg P/ha and 200 kg K/ha application every year with no lime application. Both land uses were rain fed.

3.2.2 Soil sampling and soil preparation

At each study site, a pit per each land use was sampled, two replicate samples were collected with augers. The sampling was done at 0-10 and 10-20 cm depths. Samples from each depth per land use were bulked into one sample. The soils were air dried for three days, crushed with a mortar and pestle to pass through a 2 mm sieve and then stored in jars prior to analysis. An example of pits that were sampled from two of the sites is shown in Figures 3.2 and 3.3.



Figure 3.2: Inanda soil form sampled at the Karkloof site under maize.



Figure 3.3: Magwa soil form sampled at Eshowe site under sugarcane.

3.2.3 Soil analysis

3.2.3.1 Soil texture

Particle size distribution (sand: 2.0-0.05 mm; silt: 0.05-0.002 mm; and clay: <0.002 mm fractions) of the soils was determined in triplicate using the pipette method as described by Gee and Bauder (1986). The full method is given in Appendix 3.1.

3.2.3.2 pH and exchangeable acidity

Soil pH was determined by suspending 10 g soil in 25 mL of distilled water, allowing the suspension to stand for 30 minutes with occasional stirring using a glass rod, followed by measurement with a Hanna pH Micro-Processor Meter (Model 211).

Exchangeable acidity was measured by suspending 10 g air dry soil in 25 mL of 1M KCl. The suspension was shaken for 4 minutes on a horizontal shaker at 180 cycles/minute and allowed to stand for 30 minutes, followed by filtering through a Whatman No.1 filter paper. The soil was leached with another five portions of 25 mL of 1M KCl solution to give a volume of 150 mL, before titration with 0.1M NaOH to the permanent pink endpoint with phenolphthalein indicator (Benton, 1999). Both pH and acidity measurements were determined in triplicate.

3.2.3.3 Exchangeable bases and extractable aluminium and iron

Calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), and aluminium (Al) were extracted using the Mehlich 3 method as outlined by Wolf and Beegle (2009) and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Varian 720-ES). The full method is given in Appendix 3.2.

3.2.3.4 Total carbon, nitrogen and extractable phosphorus

Total C and N were analysed on 0.2 g soil samples using an automatic analyzer Leco TruMac CNS/NS Determinators (LECO Corporation, 2012). Phosphorus was extracted by the AMBIC-2 method (Van der Merwe *et al.*, 1984) and determined using the molybdenum blue method (Murphy and Riley, 1962). The full method is given in Appendix 3.3

3.2.4 Phosphorus sorption study

Phosphorus adsorption was studied by following a procedure proposed by Nair *et al.* (1984). Air-dry soil samples (1.0 g), in 50 mL centrifuge tubes, were equilibrated with 25 mL solutions containing 0, 20, 40, 60, 80, 120, 160 and 200 mg P/L as KH_2PO_4 , with 0.01 M CaCl_2 as the background electrolyte. For soils from Cedara, additional equilibrating solutions containing 5, 10, and 30 mg P/L were included because the first sorption maximum was observed at concentrations below the 60 mg P/L equilibrating solution. Three drops of toluene were added to each tube to inhibit microbial activity. The tubes were shaken on a horizontal shaker at 180

cycles/minute, at 25 ± 1 °C for 24 h, allowed to settle for an hour and filtered through a Whatman No.1 filter paper. The P in the equilibrium solution was determined using the molybdenum blue method (Murphy and Riley, 1962), with a spectrophotometer UV-5500(PC) at a wavelength of 880 nm. The sorption experiment was carried out in duplicate. Data for sorbed P were plotted against equilibrium solution P and fitted to the Langmuir isotherm (Equations 3.1 and 3.2).

The Langmuir adsorption equation is: $S = \frac{S_{max}kC}{1+kC}$Equation 3.1

The linearized Langmuir adsorption equation is: $\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}}$Equation 3.2

Where: S = amount of P retained in mg/kg; C = equilibration concentration of P, in mg/L after 24 h; S_{max} = P sorption maximum in mg/kg, and k = a constant related to the bonding energy, in L/mg P.

3.2.5 Statistical analysis

An analysis of variance (ANOVA) was performed across all soils for each site for assessment of interactions of soil depth and land use on each measured soil parameter using GenStat 18th edition (VSN International, 2015). The land uses were different across sites, with arable being sugarcane at Eshowe and Eston, while Cedara and Karkloof had maize. For the non-arable Cedara had *Eragrostis* pasture, Karkloof had ryegrass pasture, Eston had wattle forestry while Eshowe had natural forest. As such the land uses were compared separately for each site. The least significant difference (LSD) at 5% level was used to separate the means and multiple comparisons were performed using Tukey analysis. The results of the P sorption were expressed as means and standard errors of the means.

3.3 Results

3.3.1 Particle size distribution

Effects of soil depth and land use were not statistically significant on sand, silt and clay contents at any of the sites. At both the Eston and Eshowe sites the soils were sandy clay loam while those from Cedara and Karkloof were clay (Table 3.1).

Table 3.1: Particle size distribution at 0-10 and 10-20 cm depths under different land uses at the four sampled sites

Particle size fraction (%)	Sugarcane /Maize		Forest /Pasture		LSD
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	
<i>Eston</i>					
Clay	26.3	27.0	30.7	29.3	8.29
Silt	17.7	11.7	11.6	10.0	8.79
Sand	56.0	61.3	57.7	60.7	11.6
<i>Eshowe</i>					
Clay	27.7	25.0	30.3	33.3	12.5
Silt	13.4	14.7	16.2	14.7	11.6
Sand	58.9	60.3	53.5	52.0	22.6
<i>Cedara</i>					
Clay	54.7	56.7	51.3	54.0	5.08
Silt	16.7	14.4	17.7	12.7	5.13
Sand	28.6	28.9	31.0	33.3	4.41
<i>Karkloof</i>					
Clay	51.0	50.7	49.0	53.7	4.70
Silt	22.3	16.7	21.3	19.0	5.84
Sand	26.7	32.6	29.7	27.3	4.17

3.3.2 pH and exchangeable acidity and bases

Soil pH was significantly higher at both depths of the arable than the non-arable soils from Eston and the 0-10 cm depth had significantly higher pH than the 10-20 cm depth under the arable land use. The non-arable soil from Eshowe had significantly higher pH at 0-10 cm than arable soil at both depths. The arable soil at Cedara had significantly higher pH than the non-

arable at both depths. At the 0-10 cm depth, the arable soil had a significantly higher pH than the nonarable one for Karkloof (Table 3.2).

Exchangeable acidity was significantly higher in the non-arable than arable soils from Eston, with arable soil having significantly higher exchangeable acidity at 10-20 cm than at 0-10 cm while the reverse was the case for the non-arable soil. The soils at Eshowe had a significantly higher exchangeable acidity at 10-20 cm than at 0-10 cm on both land uses. The non-arable soil at Cedara had a significantly higher exchangeable acidity than the arable soil, with non-arable soil having significantly higher exchangeable acidity at 0-10 cm than at 10-20 cm. The non-arable soil from Karkloof had a significantly higher exchangeable acidity than arable soil, with non-arable soil having significantly higher exchangeable acidity at 0-10 than at 10-20 cm while under arable the reverse was the case (Table 3.2).

There were no significant differences in exchangeable Ca as affected by land use and sampling depth for soils from Eston, Eshowe and Cedara. Exchangeable Ca was significantly higher in the arable soil than the non-arable soil from Karkloof (Table 3.2), although there were no differences between the depths on either soil. At Eston, the arable soil had a significantly higher exchangeable Mg than the non-arable soil in both 0-10 and 10-20 cm depths. At Eshowe, the non-arable soil had higher exchangeable Mg than the arable soil at both sampled depths. In the non-arable soil there was significantly higher exchangeable Mg at 0-10 cm than at 10-20 cm. At Cedara, there were no significant differences in exchangeable Mg between the soils. At the Karkloof site, exchangeable Mg was significantly higher at 0-10 cm on the arable soil than at 10-20 cm but this was reversed on the non-arable soil.

The arable soil at Eston had a significantly higher exchangeable K in the 0-10 cm depth than at 10-20 cm. Eshowe had significantly higher K at 0-10 than 10-20 cm, only for non-arable soil. Cedara had significantly higher K at 0-10 cm arable soil than 10-20 cm. At Karkloof, the 0-10 cm arable soil had higher exchangeable K than at 0-20 cm. (Table 3.2). Eston had

significantly higher Na at 0-10 cm non-arable than 10-20 cm. Exchangeable Na was significantly higher in the non-arable soil than the arable soil from Karkloof. There were significant differences on Na from Eshowe and Cedara (Table 3.2).

Table 3.2: Effect of land use and soil depth on pH, exchangeable acidity and bases in soils from the four sampled sites.

Soil property	Sugarcane /Maize		Forest /Pasture		LSD
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	
<i>Eston</i>					
pH (H ₂ O)	5.93 ^{c#}	5.29 ^b	4.66 ^a	4.79 ^a	0.189
Acidity*(cmolc/kg)	0.031 ^a	0.861 ^b	4.28 ^d	3.90 ^c	0.096
Ca (cmolc/kg)	1.67	3.35	1.87	0.433	2.061
Mg (cmolc/kg)	2.59 ^b	1.85 ^b	0.542 ^a	0.513 ^a	0.864
K (cmolc/kg)	0.842 ^b	0.422 ^a	0.313 ^a	0.271 ^a	0.384
Na (cmolc/kg)	0.160 ^{ab}	0.141 ^a	0.284 ^c	0.25 ^{bc}	0.102
<i>Eshowe</i>					
pH (H ₂ O)	5.12 ^a	4.75 ^a	5.91 ^b	5.16 ^a	0.475
Acidity (cmolc/kg)	0.944 ^b	1.21 ^c	0.191 ^a	1.27 ^c	0.047
Ca (cmolc/kg)	1.93	2.56	3.14	1.42	1.471
Mg (cmolc/kg)	0.454 ^a	0.433 ^a	4.84 ^c	1.42 ^b	0.422
K (cmolc/kg)	0.421 ^b	0.301 ^{ab}	0.582 ^c	0.26 ^a	0.101
Na (cmolc/kg)	0.203	0.171	0.402	0.34	0.153
<i>Cedara</i>					
pH (H ₂ O)	5.15 ^b	5.25 ^b	4.68 ^a	4.62 ^a	0.320
Acidity (cmolc/kg)	0.492 ^a	0.461 ^a	1.83 ^c	1.33 ^b	0.065
Ca (cmolc/kg)	3.21	2.81	1.87	3.35	1.166
Mg (cmolc/kg)	1.97	1.59	1.69	1.29	0.721
K (cmolc/kg)	0.503 ^c	0.222 ^a	0.412 ^{bc}	0.304 ^{ab}	0.129
Na (cmolc/kg)	0.171	0.194	0.162	0.182	0.049
<i>Karkloof</i>					
pH (H ₂ O)	5.69 ^b	5.63 ^b	5.36 ^a	5.72 ^b	0.129
Acidity (cmolc/kg)	0.073 ^a	0.161 ^b	0.333 ^d	0.242 ^c	0.043
Ca (cmolc/kg)	5.00 ^b	4.29 ^b	1.77 ^a	0.643 ^a	1.481
Mg (cmolc/kg)	2.90 ^b	1.67 ^a	2.38 ^{ab}	4.19 ^c	0.767
K (cmolc/kg)	1.05 ^b	0.453 ^a	0.233 ^a	0.481 ^a	0.198
Na (cmolc/kg)	0.182 ^{ab}	0.153 ^a	0.222 ^{bc}	0.222 ^c	0.027

#Means followed by the same letter in the same row are not significantly different at p<0.05.

*Exchangeable acidity

3.3.3 Extractable aluminium and iron.

Results of extractable Al in the soil were highly variable (large LSDs) and the concentration did not show any effects of land use and soil depth for soils from Eston, Eshowe and Karkloof. However, the concentrations were all higher than 2 000 mg/kg for all the soils studied. Cedara was the exception, with non-arable soil having significantly higher extractable Al than arable soil (Table 3.3). The non-arable soil at Eshowe had significantly higher extractable Fe in the 0-10 than at 10-20 cm depth. The 10-20 cm had a significantly higher Fe than the 0-10 cm depth of the arable soil from Cedara, but this was reversed for the non-arable soil. There were no significant differences in extractable Fe in the soils at Eston (315 - 430 mg/kg) and Karkloof (118 - 203 mg/kg).

Table 3.3: Effect of land use and soil depth on extractable aluminium (Al) and iron (Fe) in soils from the four sampled sites.

Soil property	Sugarcane/maize		Forest /Pasture		LSD
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	
<i>Eston</i>					
Extractable Al (mg/kg)	3 244	2 098	3 929	3 603	2 012
Extractable Fe (mg/kg)	332	430	339	315	203.3
<i>Eshowe</i>					
Extractable Al (mg/kg)	2 567	3 033	2 611	2 871	1 090
Extractable Fe (mg/kg)	158 ^{a#}	154 ^a	229 ^b	149 ^a	10.3
<i>Cedara</i>					
Extractable Al (mg/kg)	2 014 ^a	1 979 ^a	2 630 ^{ab}	3 036 ^b	1 007
Extractable Fe (mg/kg)	59.8 ^a	95.3 ^b	132 ^c	68.2 ^{ab}	27.91
<i>Karkloof</i>					
Extractable Al (mg/kg)	2 003	2 703	2 763	2 450	1 124
Extractable Fe (mg/kg)	134	118	154	203	118

#Means followed by same letter in the same row are not significantly different at $p < 0.05$.

3.3.4 Total carbon, nitrogen and extractable phosphorus.

Total C was significantly higher in the non-arable soil than in the arable soil at each depth for the soils from Eston (Table 3.4), while the 0-10 cm layer had significantly higher total C than the 10-20 cm under the non-arable (wattle plantation). For Eshowe soils, the 0-10 cm depth had significantly higher C than the 10-20 cm depth in the forest soil, while there were no significant differences in C between the depths in the arable soil (Table 3.4).

At the 0-10 cm depth of soils from Cedara, the non-arable soil had significantly higher C than arable soil (Table 3.4). Soils from Karkloof showed that non-arable had significantly higher C than arable for both depths, and that the 0-10 cm depth had higher C than 10-20 cm for both land uses (Table 3.4).

Total N at 0-10 cm was significantly higher in the non-arable than in the arable soil from all the soils (Eston, Eshowe, Cedara and Karkloof) (Table 3.4). In Eshowe soils, the 0-10 cm depth had significantly higher N than the 10-20 cm depth only in the non-arable soil (forest) (Table 3.4). The non-arable soil from Cedara had significantly higher N at 0-10 cm than the 10-20 cm depth soil (Table 3.4), while soils from Karkloof showed significantly higher total N at 0-10 cm than 10-20 cm depth under both land uses (Table 3.4).

The C/N in arable were significantly higher than in non-arable in the soils from Eston, Eshowe and Cedara with no significant land use differences for the Karkloof (Table 3.4). Eston arable soil had significant higher C/N on the 10-20 cm than 0-10 cm layer and no significant depth effects on Eshowe. The non-arable soil from Cedara had significantly higher C/N in the 10-20 cm than 0-10 cm layer, while soils from Karkloof showed significantly higher C/N at 10-20 cm depth than at 0-10 cm depth under both land uses (Table 3.4). Extractable P was not affected by land use at Eston but was significantly higher in the 0-10 cm than the 10-20 cm depth in the arable soil (Table 3.4). In the 10-20 cm depth of Eshowe soil, the arable had significantly higher

extractable P than the non-arable soil (Table 3.4). No significant land use differences were found for the soils from Cedara, while for the arable soil, the 0-10 cm depth had significantly higher P than at 10-20 cm. For soils from Karkloof the 10-20 cm depth had significantly higher P than the 0-10 cm of the arable soil (Table 3.4).

Table 3.4: Effect of land use and soil depth on total carbon (C), nitrogen (N) and extractable phosphorus (P) in soils from the four sampled sites

Soil property	Sugarcane /Maize		Forest /Pasture		LSD
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	
Eston					
Total C (%)	4.91 ^{ab#}	3.62 ^a	10.4 ^c	6.09 ^b	1.931
Total N (%)	0.242 ^a	0.113 ^a	0.761 ^b	0.484 ^a	0.187
C/N	20.3 ^b	32.0 ^c	13.7 ^a	12.6 ^a	5.927
Extractable P (mg/kg)	54.3 ^c	20.6 ^a	43.3 ^{bc}	30.3 ^{ab}	18.34
Eshowe					
Total C (%)	4.78 ^b	4.46 ^{ab}	6.53 ^c	4.33 ^a	0.530
Total N (%)	0.193 ^a	0.171 ^a	0.402 ^b	0.231 ^a	0.042
C/N	24.8 ^b	26.1 ^b	16.2 ^a	18.7 ^a	4.205
Extractable P (mg/kg)	22.6 ^a	42.5 ^b	23.0 ^a	22.6 ^a	14.74
Cedara					
Total C (%)	2.52 ^a	2.36 ^a	6.20 ^b	2.72 ^a	0.331
Total N (%)	0.101 ^{ab}	0.089 ^a	0.384 ^c	0.131 ^b	0.038
C/N	25.0 ^c	26.5 ^c	16.2 ^a	20.8 ^b	2.262
Extractable P (mg/kg)	29.79 ^b	16.46 ^a	31.88 ^b	28.59 ^b	12.06
Karkloof					
Total C (%)	5.83 ^b	3.42 ^a	10.5 ^c	7.38 ^b	1.861
Total N (%)	0.333 ^b	0.061 ^a	0.543 ^c	0.151 ^a	0.088
C/N	17.5 ^a	56.1 ^b	19.3 ^a	48.9 ^b	9.571
Extractable P (mg/kg)	38.6 ^a	72.1 ^b	51.5 ^{ab}	49.8 ^{ab}	23.87

#Means followed by same letter in the same row are not significantly different at $p < 0.05$.

3.3.5 Sorption isotherms

All the soils showed the L-type adsorption isotherms (Figure 3.4) (Hinz, 2001). When the first sorption maximum was reached an extended leg between sorption and equilibrium solution P was observed. The maximum P sorption (S_{\max}) on soils from Eston was about 2 500 mg/kg, Eshowe about 2 000 mg/kg, Cedara just under 500 mg/kg and Karkloof about 1 000 mg/kg (Figure 3.4). There were no significant differences in S_{\max} as a function of land use for both the 0-10 (Table 3.5) and 10-20 cm (Table 3.6) depths of soils from Eston, Eshowe and Karkloof. For Cedara, the pasture soil had a significantly higher S_{\max} than maize in both the 0-10 (Table 3.5) and 10-20 cm (Table 3.6) depths.

The k values were significantly higher for the soil under wattle than under sugarcane at Eston at both the 0-10 cm (Table 3.5) and 10-20 cm (Table 3.6) depths. For Eshowe, the soil from the 0-10 cm depth under sugarcane had a significantly higher k value than under forest (Table 3.5). The k values for soils under pasture were significantly higher, at Cedara and lower at Karkloof, when compared to soils under maize for both the 0-10 cm (Table 3.5) and 10-20 cm (Table 3.6) depths.

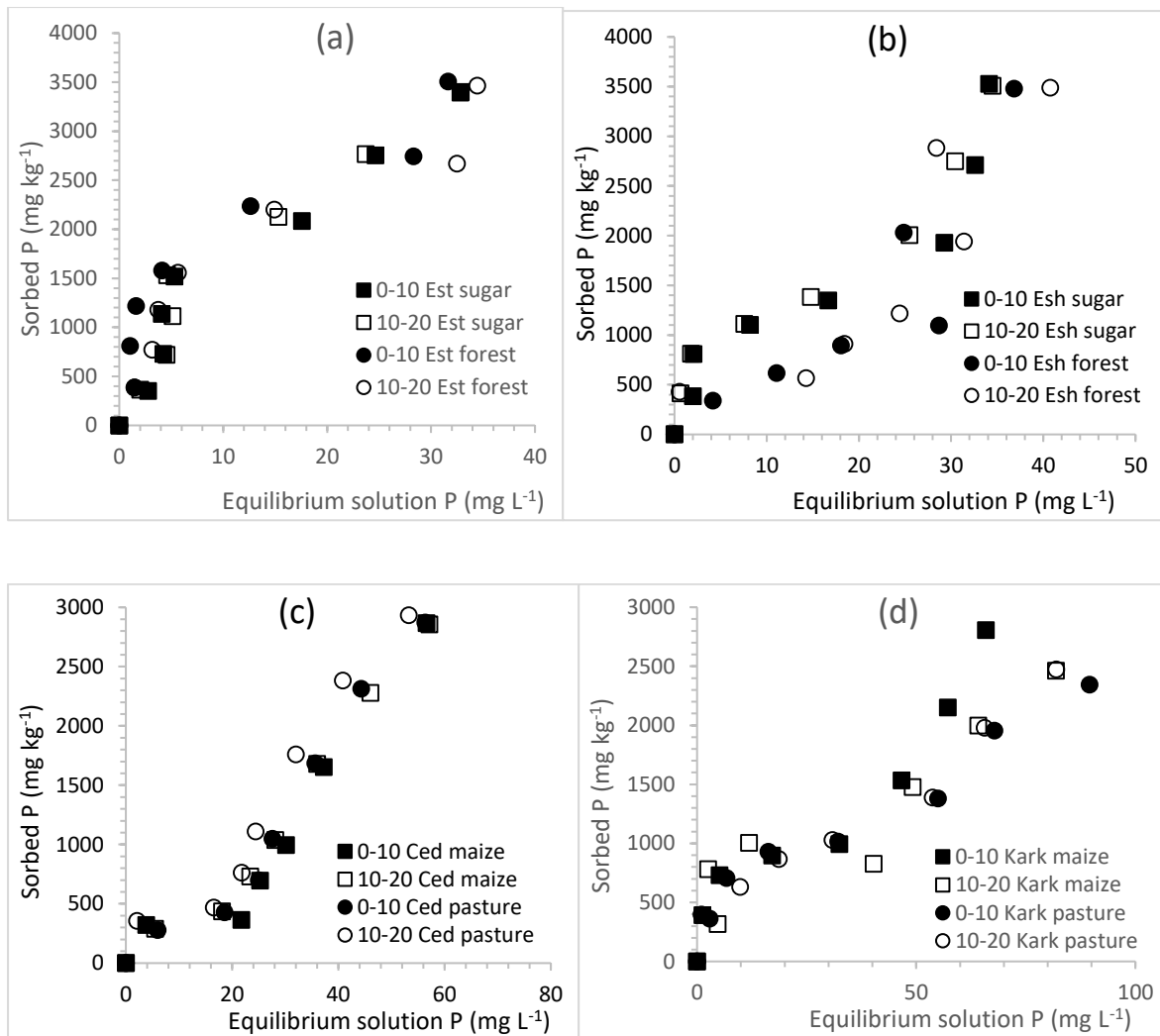


Figure 3.4: Phosphorus adsorption isotherms for soils from (a) Eston, (b) Eshowe, (c) Cedara and (d) Karkloof.

Table 3.5: Langmuir sorption isotherm parameters for the 0-10 cm depth of soils from the four sampled sites.

Site	Land use	S _{max} (mg/kg P)	k (L/kg P)	R ²
Eston	Sugarcane	2 369±285	0.070±0.031	0.886±0.134
	Forest	2 618±48.5	0.422±0.006	0.974±0.033
Eshowe	Sugarcane	1 921±432	0.218±0.012	0.936±0.005
	Forest	1 530±468	0.079±0.046	0.768±0.121
Cedara	Maize	610±12.3	0.202±0.003	0.621±0.028
	Pasture	889±24.3	0.445±0.088	0.662±0.062
Karkloof	Maize	1 054±3.15	0.442±0.010	0.876±0.173
	Pasture	1 246±220	0.141±0.009	0.963±0.042

Table 3.6: Langmuir sorption isotherm parameters for the 10-20 cm depth of soils from the four sampled sites.

Site	Land use	S _{max} (mg/kg P)	k (L/kg P)	R ²
Eston	Sugarcane	2 246±183	0.098±0.006	0.897±0.051
	Forest	2 314±211	0.114±0.013	0.885±0.005
Eshowe	Sugarcane	1 268±67.0	1.28±0.150	0.981±0.011
	Forest	1 193±81.5	1.50±0.628	0.855±0.102
Cedara	Maize	630±65.8	0.111±0.045	0.681±0.182
	Pasture	753±29.3	0.451±0.234	0.801±0.021
Karkloof	Maize	902±41.4	0.380±0.139	0.931±0.190
	Pasture	1 020±119	0.151±0.001	0.917±0.082

3.4 Discussion

The textural similarities at each site reflect the similar parent material that may have undergone the same degree of weathering presumably over similar time periods, under the same climatic conditions. This was expected given the proximity of the sampling sites to each other at each place. Also, the samples were only collected from the top 20 cm and there could be differences in texture at greater depths. The sandy clay loam texture of soils from Eston and Eshowe was because the soils were both formed from sandstone, although they were from different groups (Natal and Nsuzi group sandstone). On the other hand, the soils from Cedara and Karkloof were formed from dolerite and have clayey texture (Osok and Doyle, 2004). The higher exchangeable Ca, Mg and K in some of the arable soils could be explained by liming and K fertilizer application, while lower concentrations of these bases in the non-arable soils is because the soils are naturally highly weathered and leached (Ayeni *et al.*, 2012). Naturally, humic soils have low base status (Fey, 2010) and the use of soil amendments such lime, chicken manures and fertilizers could have influenced the amount of bases. The dolomitic lime used at Eston under sugarcane (arable) resulted in the exchangeable Mg to be higher in the top layer as compared to the soil under wattle (non-arable). The effects of liming were clearly observed through the higher pH and lower exchangeable acidity values in the arable soils compared to the non-arable soils from Eston, Cedara and Karkloof. These effects were not found for the Eshowe soils. Only Eshowe showed higher pH in non-arable than arable soils, suggesting that lower liming could have been applied when opened up for sugarcane. The low frequency of lime application (once every 10 years) could have led to insignificant effects on bases in contrast to Eston, where the lime application was at every planting. In addition, the higher acidity in the non-arable (wattle plantation) than the arable soil at Eston could have been a result of addition of acidic litter from the wattle trees. Forest trees exude organic acids through their roots, and some of the acidity could come from decomposition of acidic wattle litter and

leaching from leaf washing (Dijkstra *et al.*, 2001). During mineral weathering, acidity can be neutralized by exchange with base cations on the cation exchange sites. These ions can then increase the leaching of base cations from the surface soil (Sposito, 1989). The high extractable Al (>2 000 mg/kg) in all the soils show the effects of extreme weathering and leaching of bases and is also supported by the low pH nature of the soils. However, the lack of land use effects could be explained by the high variability of the results (large LSDs) even when the absolute amounts of Al and Fe look different. This then masked these effects with only Cedara as the exception, where non-arable soil had significantly higher extractable Al than arable soil.

The lower soil C and N, particularly in the 0-10 cm depth, of arable than non-arable soils at all the sites could be explained by lower organic matter inputs and tillage operations, which increased aeration and exposed protected organic matter through breaking down of soil aggregates. Mikha and Rice (2004) reported a decrease in macroaggregates and a decrease in aggregate protected labile C and N with a 10 year conventional tillage practice as compared to no-till for the same period. The organic C could have been lost under tillage as CO₂ emission, while mineralized N could have been leached as nitrate-N from the arable soils (Dossa *et al.*, 2009). Nitrification is known to result in increased acidity, which was supported by the results of pH and acidity in soils from Eshowe, where arable soils were more acidic.

The no-till system has been suggested as a way that could provide physical protection to the labile C fractions including strong organo-mineral associations in highly weathered soils (Paustian *et al.*, 2000, Briedis *et al.*, 2018). No till had been initiated at Cedara three years before the sampling for the study and this would likely be too short a period to measure increased C after many years of conventional tillage (Stevenson and Cole, 1999). However, the same effects were also found in the soils from Karkloof, which had been under no-till for a longer period. This suggests that even if no-till is being used for the maize, the effects of conventional tillage used before could be higher than the C build up during the more recent no-

till systems. A higher amount of total carbon in the non-arable soils at Eston and Eshowe than on the arable soils could be also attributed to the inputs that are presumably higher under trees combined with zero tillage resulting in slower decomposition (Martens *et al.*, 2003). Under sugarcane the opposite happens because, during tillage and burning before harvest, more organic matter is prone to decomposition whereas under forest there is no soil disturbance over a long period (Licht and Al-Kaisi, 2005). The high acidity in the non-arable soils, particularly under the wattle plantation at Eston, could also have lowered microbial activity and slowed decomposition of organic matter. The natural forest at Eshowe and the wattle plantation at Eston could be considered as closed ecosystems where the losses are assumed to be equal to gains in terms of nutrients (Walna *et al.*, 2005). The higher total C and N under forests and pastures were due to greater inputs which are in equilibrium with the losses from decomposition, compared to arable soils (Piñeiro *et al.*, 2010). Martens *et al.* (2003) compared soil organic C composition in a 130-year-old trial with crops, pasture and forest and found that forest and pasture retained more C compared with cropped land. In addition to protection in soil aggregates, soil organic matter could be protected from decomposition by formation of stable complexes with Fe and Al in the soil (Briedis *et al.*, 2018). The decomposition of soil organic matter could contribute to the N and P fertility of the soil in these soils.

The differences in extractable P between arable and non-arable soils could possibly be as a result of repeated application of fertilizers. This is coupled with liming to increase pH and lower acidity, which would otherwise counteract the effectiveness of P fertilizer applied. This view is supported by P amounts in the 0-10 cm depth at Eston with the corresponding pH and acidity values at the same depth. The differences in pH and acidity between arable and non-arable, which are much higher at Eston than the other sites, resulting in greater need of lime (1 to 10 t/ha) and P fertilizer application (Osundwa *et al.*, 2013). The greater P at 10-20 cm in places than 0-10 cm could be due to plant uptake differences between depths.

The Langmuir P isotherms show that the humic soils studied have high affinity for phosphorus. Using the scale of phosphate sorption by Juo (1981), which sorted the soils based on their S_{\max} into these groups; very low (<10), low (10-100), medium (101-500), high (501-1000) to very high (>1000); Eston and Eshowe soils have very high P sorption, Cedara soils have high P sorption and Karkloof soils have high to very high P sorption. The stepped isotherms showed that there were various mechanisms in operation with increasing P addition, with precipitation as Al and Fe phosphates possibly being one (Bunemann *et al.*, 2007). In acidic soils, Al and Fe oxide surfaces are suggested to be the primary fixers of inorganic P (Giardina *et al.*, 1995). This is because both crystalline and amorphous Fe and Al oxides have huge reactive surface areas and high anion exchange capacity (AEC) for the sorption/fixation of P. Decomposition of the organic matter could have resulted in conversion of organic N and P into mineral forms, and due to high Al and Fe contents in these soils, P sorption could be increased.

Based on S_{\max} measurements, Eston and Eshowe did not show any differences in sorption between land uses per site, even though the pH and acidity values differed significantly. The expectation was that the non-arable soils would sorb more P than arable soils because of the differences in acidity. The reason is not clear, but it could possibly be a result of organic acids from the tree litter, which could have competed for sorption sites with P at Eston and Eshowe. Organic acids contribute to the lowering of the pH and also compete with soil surfaces, plants and microbes for inorganic P in solution (Dijkstra *et al.*, 2001; de Campos *et al.*, 2016). Higher (S_{\max}) P sorption in the non-arable soil at Cedara is explained by its lower pH and higher acidity. The differences in k values with depth even when the S_{\max} are similar especially for Eshowe and Eston (forestry), suggest that the binding energy could vary from weaker to stronger within the soil even if the same maximum had to be achieved. However, the higher clay content of soils at Cedara and Karkloof than those from Eston and Eshowe did not explain

the differences in the measured parameters, which were affected more by the effect of land use on organic matter.

3.5 Conclusions

The effects of land use on soil properties appeared to vary between sites and soil depths on soil. The texture of the humic topsoils was not affected by land use. Changing humic soil from non-arable to arable use increased exchangeable Ca, Mg and K especially in the 0-10 cm depth topsoil layer. The pH was also increased in arable land use except for Cedara soils. Extractable Al and Fe were not affected by land use and depth at all sites except Cedara, where Fe in the 0-10 cm, and Al in the 10-20 cm depth, were lower in the arable than non-arable soil. The Al data reliability was, however, limited. Non-arable soils (under forest and pasture), which were not regularly tilled, had higher C and N contents than arable soils (under maize and sugarcane), particularly in the 0-10 cm depth. Land use change increased extractable P in Eshowe, with no clear land use effect on other sites. Arable soils had more P in the 0-10 cm depth than 10-20 cm at Eston and Cedara, while the 10-20 cm had more than 0-10 cm for soils from Eshowe and Karkloof. The humic soils had P sorption capacities ranging from high to very high. Considering that the parameters studied in this chapter may have effects on decomposition of the soil organic matter, mineralization and release patterns of N and P, and the fractions of P in humic soils need to be studied if their contributions to soil productivity are to be clearly understood.

CHAPTER FOUR

NITROGEN AND PHOSPHORUS RELEASE FROM SELECTED HUMIC SOILS UNDER DIFFERENT LAND USES

4.1 Introduction

The dynamics of soil organic matter are intimately linked to climate and agricultural productivity (Feng *et al.*, 2007). In addition to other soil properties, the high amount of organic matter in humic soils makes these soils important, although they must be fertilized and usually limed to achieve high productivity. Soil organic matter has been demonstrated to affect the physical and chemical soil properties such as soil structure (Boekel, 1963), porosity (Barral *et al.*, 1998), infiltration rate (Lado *et al.*, 2004), water holding capacity (Vengadaramana and Jashothan, 2012) and nutrient availability (Ellert and Bettany, 1995). Many studies have recently focussed on increasing soil organic carbon in view of climate change (Lehmann and Kleber, 2015). However, the goal of carbon (C) sequestration seems to contradict the need for soil productivity, which is increased when soil organic matter decomposes and releases energy and nutrients. Microbial decomposition of organic matter and mineralization increase available nutrients, such as nitrogen (N), phosphorus (P), and sulphur (S), for plant uptake (Schulten and Schnitzer, 1998). After N, P as H_2PO_4^- and HPO_4^{2-} forms (Bunemann *et al.*, 2007) is often the second most frequently limiting macronutrient for plant growth (Maranguit *et al.*, 2017) as it is key in many physiological and biochemical processes.

Nitrogen fertilizers are often applied based on crop demand, while fertilizers supplying P are applied based on soil tests, without considering or estimating the nutrients from mineralization. For example, commonly used soil P tests in general consider the available inorganic P (Pi) pool, without considering organic P (Po), which can represent up to 80% of total P (Pt) (Wyngaard *et al.*, 2016) and can be mineralized. This consideration may be particularly crucial

for soil with reactive organic matter. Such organic matter would be most likely to occur in young soils, as with time organic matter is lost (and thus reduces in amount unless refreshed) and only the more resistant (less reactive) fractions of the organic matter tend to remain (Six *et al.*, 2002). The position of humic soils in this regard is anomalous since they contain high organic matter and yet are old soils (Chapter 1). This raises the question ‘what is the reason for the high organic matter content of these soils’? Related to this is whether this organic matter is reactive or has age reduced its reactivity? One explanation given for the high organic matter content of humic soils is that, due to the low pH of the soils, the organic matter is complexed with Al (and perhaps Fe) (Fey, 2010). Such complexes are known to be highly resistant to decomposition and thus the amount of organic carbon has remained high despite the age of the soils (Sollins *et al.*, 1996). If correct then the amount of reactive organic matter in humic topsoils is likely to be represented by only a small fraction of the total C. The C/N was lower in the 0-10 than the 10-20 cm depth in places (Section 3.3.4) possibly as a result of frequent addition of fresh organic matter. The C/N was higher in the arable than non-arable soils except in the Karkloof. These differences in the C/N could have implications on decomposition and N mineralization of the selected humic soils.

The high organic matter in humic soils (>1.8% C), however, suggests that its ultimate decomposition may release substantial quantities of N, and perhaps P, which could significantly affect fertilizer recommendations. However, their relevance to fertilizer application may depend on time they were to occur against the lifetime of a crop. The low pH (Section 3.3.2) coupled with high concentrations of solution Al and Fe (Section 3.3.3) suggest that decomposition of organic matter may increase inorganic N and P and a possibility of solution of Al and Fe precipitating with the released P. The higher total C and N and the lower C/N ratio of the non-arable soils in the present study (Section 3.3.4) suggest a potential for N mineralization compared to arable soils with some exceptions of 10-20 cm layer of arable soil

from Eston and both land uses for Karkloof. These exceptions suggest the potential of immobilization with C/N between 32.0 and 56.1. In addition to the C/N ratio, acidity and high concentrations of extractable Al and Fe could also contribute to the processes of mineralisation of N and P. If decomposition of soil organic matter and expected N and P mineralization were to be established, it is important to know the amounts of N and P released that remain available within the lifetime of a crop. It is essential to understand the effect of land use on concentration of solution P in view of possible precipitation and fixation. The objective of this study was to determine the effects of land use on inorganic N and P concentrations during incubation of humic topsoils from different sites.

4.2 Materials and methods

4.2.1 Soils

The soils used for incubation study were from the 0-10 and 10-20 cm depths of all the sites and land uses as described in Chapter 3 but P fractionation was studied with soils from the 0-10 cm depth of both land uses from Eshowe and Karkloof.

4.2.2 Field capacity determination

The soil moisture at field capacity was determined using pressure plate apparatus at -10 kPa for clays and at -33 kPa for sandy clay loam soils (Cassel and Nielsen, 1986). Each soil sample was weighed, put on a small core ring fitted with filter material underneath, saturated with water for 24 hours. The soils from Eston and Eshowe were drained at -33 kPa while soils from Cedara and Karkloof were drained at -10 kPa for another 24 hours because of their textural differences as shown in the previous chapter. The drained samples were weighed, oven dried at 105°C for 24 hours, and then reweighed and moisture at field capacity was calculated.

4.2.3 Incubation experiment

The incubation study was carried out in a constant temperature room (25°C) for 84 days. The experiment was laid out in a completely randomized design, each soil sample replicated three times for each sampling period to allow for destructive sampling. Air dry soil mass (100 g) was weighed into each plastic container (500 mL) with four small holes drilled below the rim to allow for gaseous exchange. Moisture was adjusted to 80% field capacity and the container was closed with a tightly fitting lid. Throughout the incubation period, soil moisture was adjusted to the initial 80% field capacity by correction for weight loss in 2-3 days intervals. Destructive sampling was done after 0, 7, 14, 28, 42, 63 and 84 days of incubation, and the samples analysed for pH, ammonium-N, nitrate-N and extractable P.

4.2.4 Soil analysis

4.2.4.1 Soil pH

Soil pH was analysed in 1M KCl at a ratio of 1:2.5 (soil: solution) using a Metrohm Hershiau E396B pH meter (Thomas, 1996). A 10 g sample of soil was suspended in 25 mL of 1M KCl solution in a 50 mL plastic beaker. The suspension was stirred for a few seconds, and allowed to stand for about 30 minutes, before pH measurement. This analysis was done for all sampling periods.

4.2.4.2 Ammonium and nitrate nitrogen

Ammonium-N and nitrate-N were analysed up to the 63-day sampling period. A known mass (about 2 g) of moist soil sample was weighed into a 50-mL centrifuge tube and 20 mL of 2 M KCl solution added. The suspension was shaken on a horizontal shaker at 180 cycles/minute for 30 minutes, centrifuged at 7 000 rpm for 5 minutes, and filtered using Whatman No.1 filter paper. Ammonium-N and nitrate-N were determined using a Thermo Scientific Gallery Discrete Auto-analyser. Another 10 g moist sample was then oven dried overnight at 105 °C,

to determine moisture content, to correct the concentration of ammonium- and nitrate-N for moisture present (oven-dry basis).

4.2.4.3 Extractable phosphorus

Phosphorus was extracted by the AMBIC-2 method (Van der Merwe *et al.*, 1984) as described in Appendix 3.3. Moisture was corrected as for the N analyses above since samples were coming out from moist incubation. This analysis was done for all sampling periods.

4.2.5 Phosphorus fractionation

After studying the P release patterns (Section 4.2.4.3) at the four sites, 0-10 cm depth samples from the Eshowe (sugarcane and forest) and Karkloof (maize and pasture) sites were selected for fractionation of inorganic P. These soils fairly represented all the variations and trends from P release patterns that were observed during incubation. Only soil samples from the last sampling period (after 84 days of incubation) and the same soils without prior incubation were used for P fractionation, to determine effects of incubation on the fractions.

4.2.5.1 Inorganic phosphorus fractionation

Inorganic P fractions were separated by following the sequential extraction method as described by Kuo (1996) and given in Appendix 4.1. Soluble and loosely bound P was extracted by adding 50 mL of 1 M NH_4Cl to 1.0 g of air dry soil in a 100-mL centrifuge tube. The mixture was shaken on a horizontal shaker at 180 cycles/minute for 30 minutes and then centrifuged for 10 minutes at 7 000 rpm. The supernatant was filtered using Whatman No.1 filter paper into 50-mL volumetric flask and brought to volume with deionized water (extract A).

The residue was suspended in 50 mL of 0.5 M NH_4F (pH 8.2) and the suspension was shaken for 1 hour, and centrifuged for 10 minutes at 7 000 rpm to extract P from Al phosphates. The supernatant was filtered into a 100-mL volumetric flask (extract B). The soil sample was

washed twice with 25 mL portions of saturated NaCl and centrifuged for 5 minutes at 7 000 rpm. Both the washings were combined with extract B and brought to volume with deionized water.

The P from Fe phosphates was extracted from the soil residues with 50 mL of 0.1 M NaOH, with 17 hours of shaking, followed by centrifugation for 10 minutes at 7 000 rpm, and the supernatant was filtered into a 100-mL volumetric flask (extract C). The soil sample was washed twice with 25 mL portions of saturated NaCl and centrifuged for 5 minutes at 7 000 rpm. Both the washings were combined with extract C and brought to volume with deionized water.

Reductant-soluble P was extracted by addition of 40 mL of 0.3 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (sodium citrate) and 5 mL of 1 M NaHCO_3 to the residue. The suspension was then heated at 85°C in a water bath for 15 minutes, and 1.0 g of $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionite) was then added to the mixture that was heated for another 15 minutes. The content was then centrifuged for 10 minutes at 7 000 rpm, and the supernatant filtered into a 100-mL volumetric flask (extract D). The soil sample was washed twice with 25 mL portions of saturated NaCl and centrifuged for 5 minutes at 7 000 rpm. Both the washings were combined with extract D and brought to volume with deionized water. Extract D was then exposed to air to oxidize the excess $\text{Na}_2\text{S}_2\text{O}_4$ by transferring the extract to a beaker and leaving it uncovered overnight.

Phosphorus from Ca phosphates was extracted by adding 50 mL of 0.25 M H_2SO_4 to the soil residue and shaking on a horizontal shaker at 180 cycles/minute for 1 hour. The suspension was then centrifuged for 10 minutes at 7 000 rpm, and the supernatant filtered into a 100-mL volumetric flask (extract E). The soil sample was washed twice with 25 mL portions of saturated NaCl and centrifuged for 5 minutes at 7 000 rpm. Both the washings were combined with extract E and brought to volume with deionized water. Due to the absence of Ca

phosphates in these acidic humic soils, this fraction is assumed to be equivalent to residual P and is henceforth so referred to.

Analysis of inorganic phosphorus fractions

An aliquot (5 mL) from each of five extracts was transferred to separate 50-mL volumetric flasks. About 10 mL deionized water and five drops of p-nitrophenol indicator were added to volumetric flasks containing extracts C and E, pH was adjusted with 2 M HCl or 2 M NaOH until the indicator colour just changed. The indicator colour changed from yellow to colourless for extract C, and from colourless to yellow for extract E. To the volumetric flask containing extract B, 15 mL of 0.8 M H₃BO₃ was added. The P concentrations in the various solutions were determined colorimetrically using the molybdenum blue method (Murphy and Riley, 1962) with the absorbance read at 882 nm wavelength using a spectrophotometer UV-5500(PC). A set of P standards that contained the same volume of extracting solution as in the extracts were prepared.

The amount of P in each fraction was calculated with the following equation:

P concentration in given fraction (mg/kg) = [Conc. of P (mg/L) x Volume of extractant (L)] ÷ mass of soil (kg)

4.2.6 Statistical analysis

An analysis of variance (ANOVA) was performed across all soils for each site for assessment of interactions of soil depth and land use for each incubation time on pH, ammonium-N, nitrate-N and extractable P using GenStat 18th edition (VSN International, 2015). The least significant difference (LSD) at 5% level was used to separate the means. For each P fractionation, ANOVA was performed to assess the effect of land use on soil P fractions after 84 days of incubation.

4.3 Results

4.3.1 pH

The pH values of the Eston soils showed similar trends throughout the incubation (Figure 4.1). Arable soils had significantly higher pH values than non-arable. The arable soil from the 0-10 cm had significantly higher pH than the 10-20 cm depth for the whole incubation period, while there were no significant differences between depths under non-arable land use. The non-arable soil from the 0-10 cm depth had significantly higher pH than arable from Eshowe for the first 14 days, after which there were no significant differences between land uses and between depths (Figure 4.1). The arable soils from Cedara and Karkloof had higher pH values than non-arable ones throughout the incubation period though significance varied (Figure 4.2).

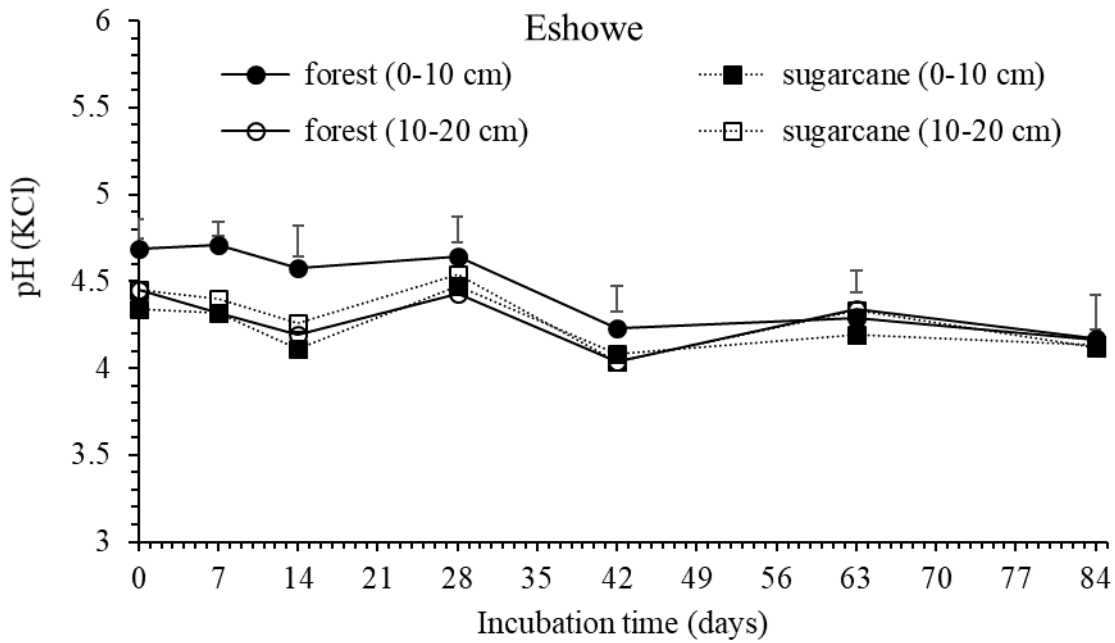
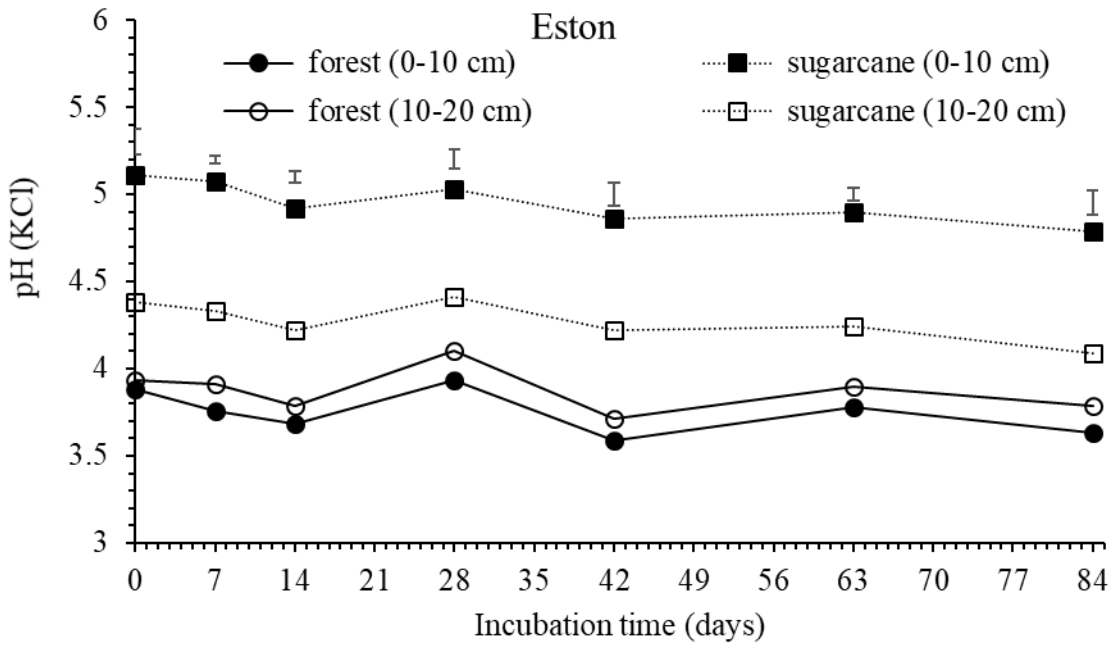


Figure 4.1: Changes in pH during incubation of soils from Eston and Eshowe. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

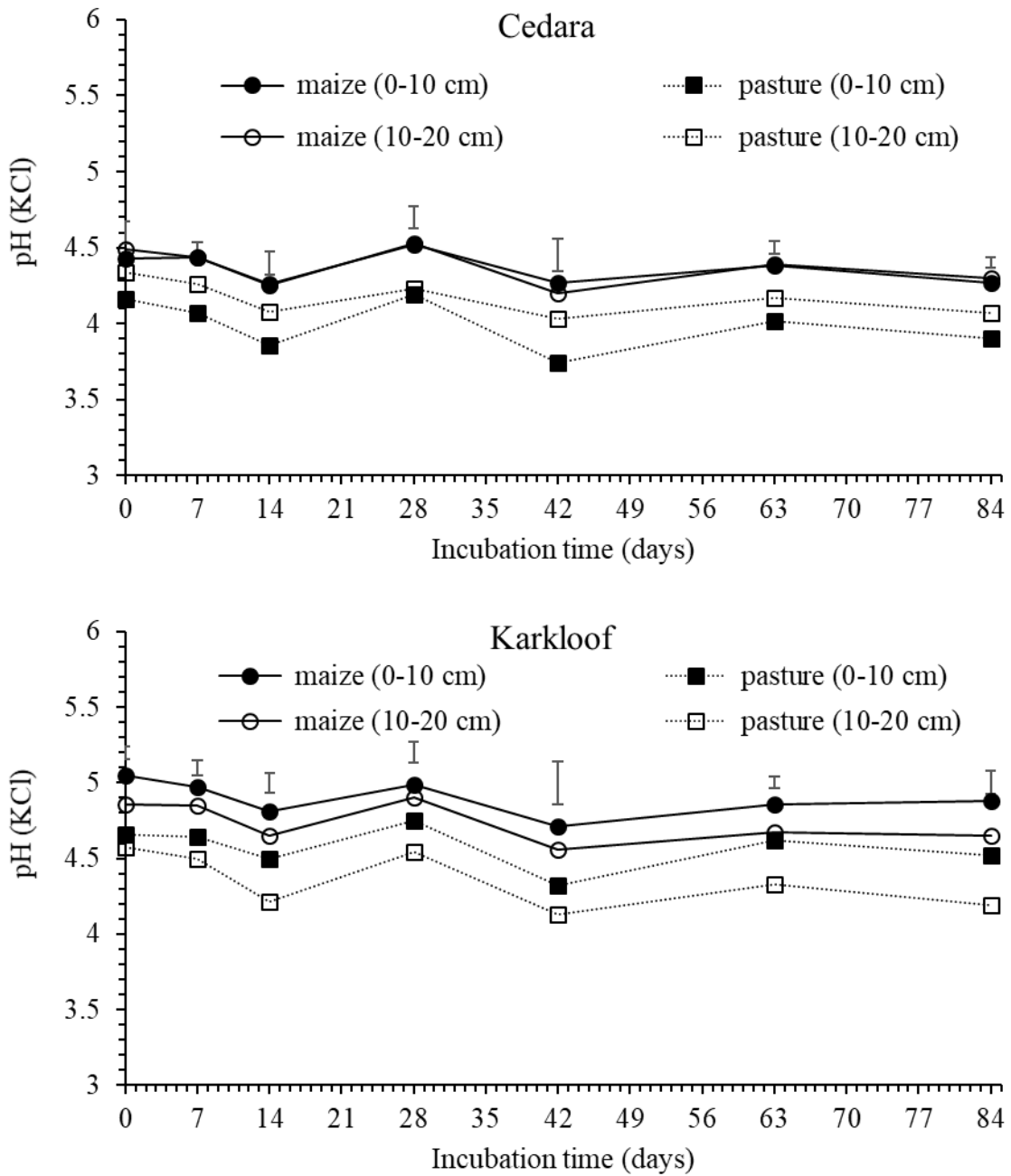


Figure 4.2: Changes in pH during incubation of soils from Karkloof and Cedara. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

4.3.2 *Ammonium nitrogen*

The patterns of ammonium-N released showed generally similar trends throughout the incubation period, with more ammonium-N at the beginning of the experiment, followed by a decrease, which was either gradual or rapid. In general, the Eston and Eshowe soils showed a gradual decline in ammonium-N throughout the incubation period (Figure 4.3). Ammonium-N was higher in the non-arable than arable soils, particularly for soils from the 0-10 cm depth, throughout the incubation period. The soils under both land uses from Karkloof and Cedara showed a rapid decline in the first 14 days without significant change thereafter (Figure 4.4). There were no differences in ammonium-N among the treatments throughout the incubation period except the concentrations in the 0-10 cm depth were higher within the first 7 days for non-arable soil from Cedara and lower after 14 days for Karkloof.

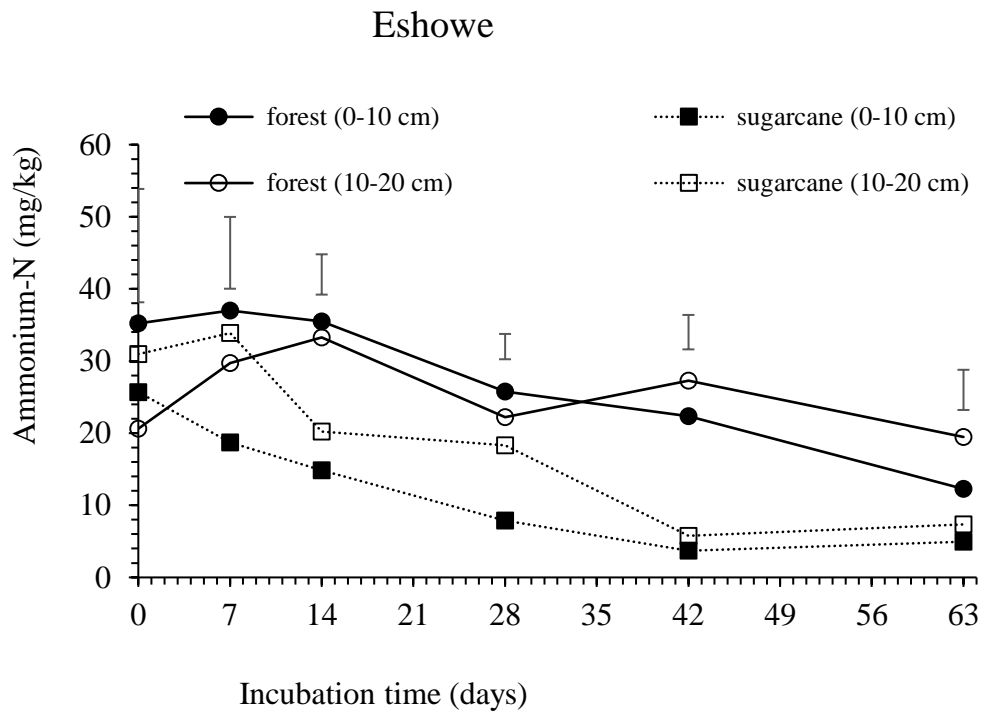
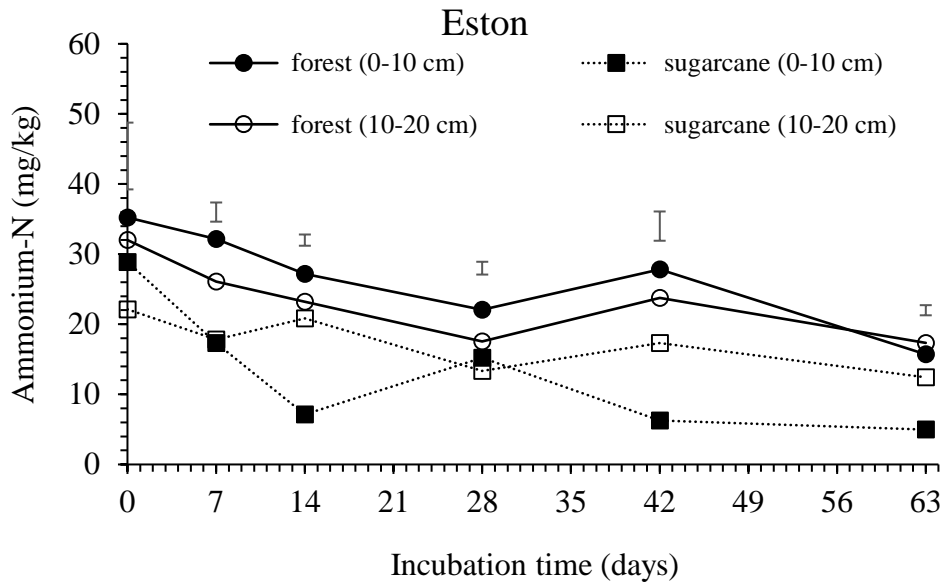


Figure 4.3: Ammonium-N released during incubation of soils from Eston and Eshowe.

Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

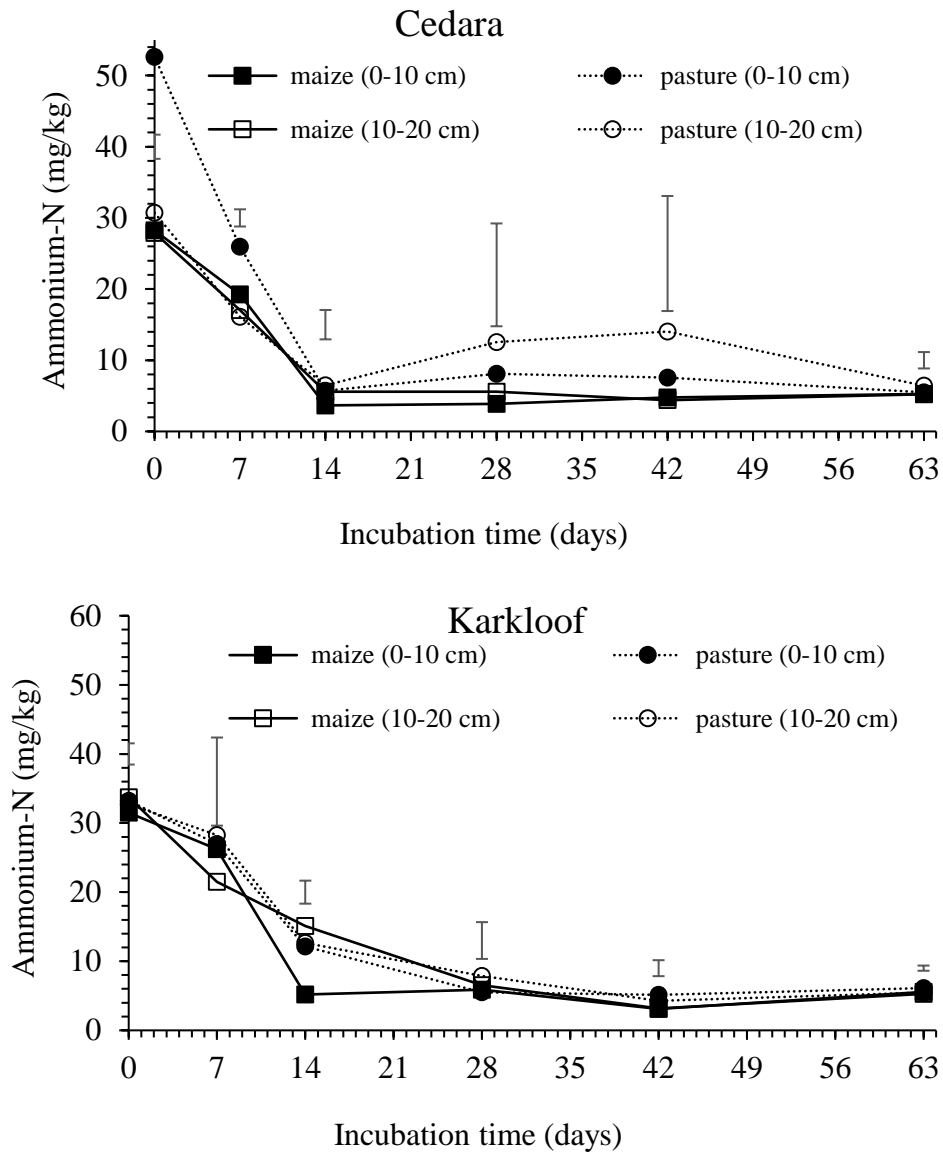


Figure 4.4: Ammonium-N released during incubation of soils from Cedara and Karkloof. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

4.3.3 Nitrate nitrogen

The nitrate-N released showed generally similar trends throughout the incubation period, with low nitrate-N at the beginning, followed by a gradual increase for soils from Eston, Eshowe (Figure 4.5) and Cedara, and sharper increases up to day 28 for soils from Karkloof, with no further changes thereafter (Figure 4.6). There were no significant differences between land uses and between depths throughout the incubation period except at day 14 for Eston and at day 28 for the other three sites. After 14 days, the 10-20 cm depth of the non-arable soil from Eston had significantly higher nitrate-N than the 0-10 cm non-arable and the 10-20 cm depth of arable. At 28 days, the 0-10 cm depth of the arable soil had significantly higher nitrate than the other three soils (depth x land use combinations) of Eshowe (Figure 4.5). At Cedara, the nitrate-N in the 10-20 cm depth of the non-arable soil was significantly higher than the rest of the soils at day 28 (Figure 4.6). At day 28 the Karkloof soils showed significantly higher nitrate-N in the 0-10 cm of the non-arable than the other three soils. At day 42, 10-20 cm samples under both arable and non-arable had significantly lower nitrate-N than the 0-10 cm depth of the non-arable from Karkloof (Figure 4.6). After 63 days of incubation the nitrate-N concentrations ranged 64-83 mg/kg for Eston, 42-74 mg/kg for Eshowe, 72-104 mg/kg for Cedara and 29-71 mg/kg for Karkloof.

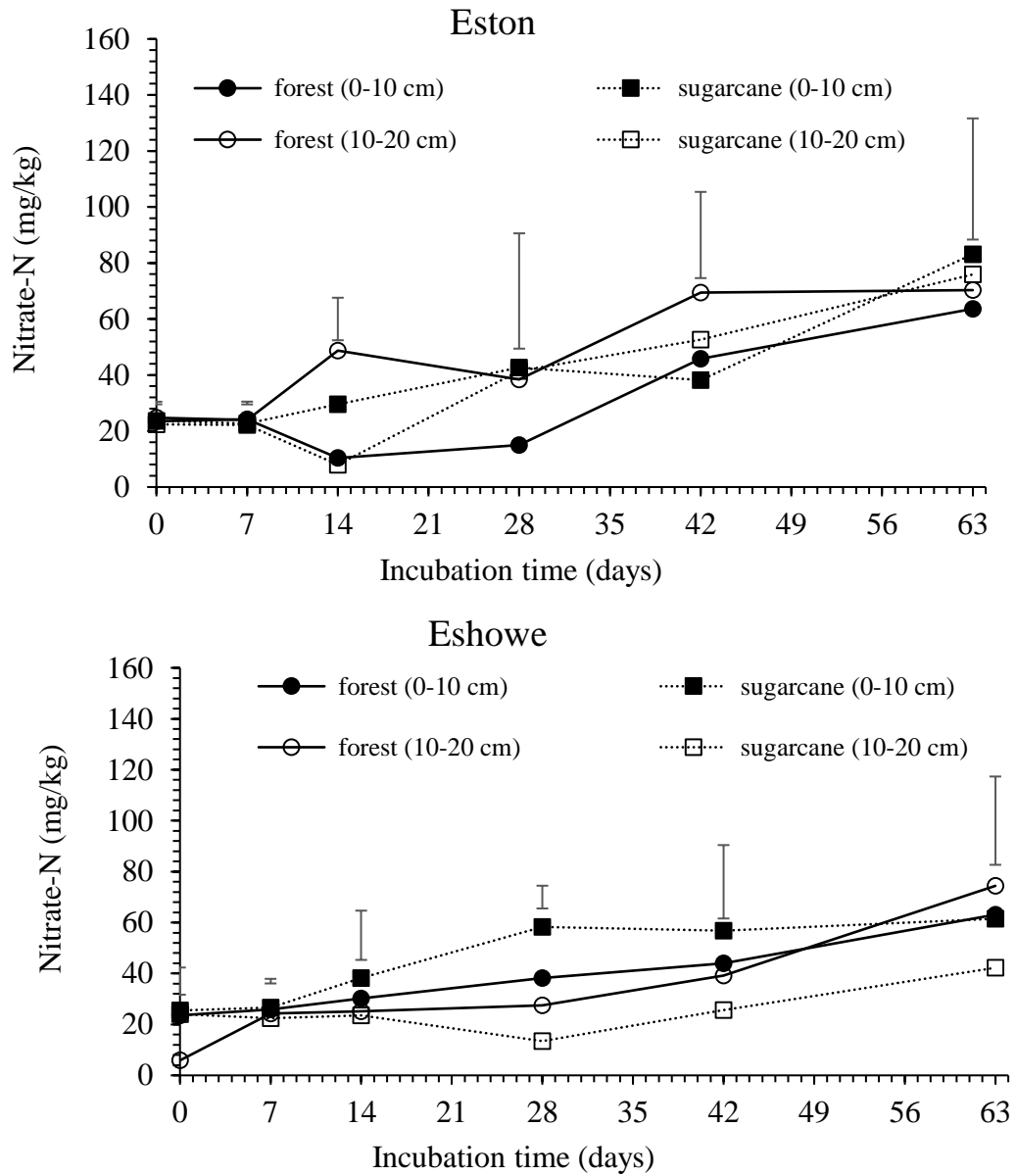


Figure 4.5: Nitrate-N released during incubation of soils from Eston and Eshowe. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

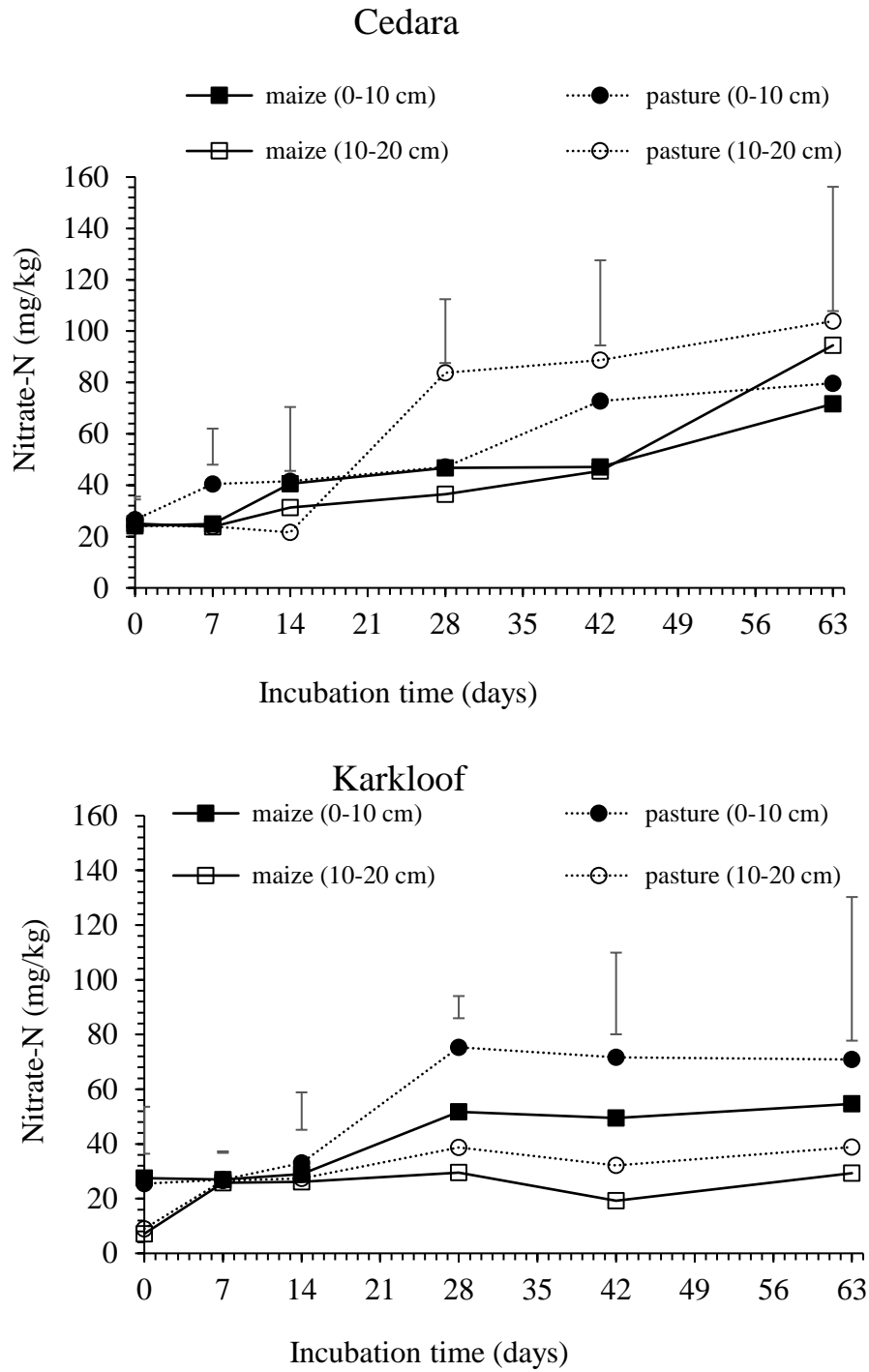


Figure 4.6: Nitrate-N released during incubation of soils from Cedara and Karkloof. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

4.3.4 Mineral nitrogen

The mineral-N released showed generally similar trends throughout the incubation period, with low mineral-N at the beginning, followed by a gradual increase for soils from Eston, Eshowe (Figure 4.7) and Cedara, and sharper increases up to day 28 for soils from Karkloof, with no further changes thereafter (Figure 4.8). There were significant differences between land uses and between depths at particular times during incubation period. At day 14 non-arable 10-20 cm of Eston had significantly higher mineral-N than the 0-10 cm and other two depths from arable land use, again at day 42 non-arable 10-20 cm had significantly higher than the 0-10 cm arable (Figure 4.7). For Eshowe at day 14 non-arable 0-10 cm had significantly higher mineral-N than both depths of arable land use, at day 28 non-arable 0-10 cm had significantly higher mineral-N than 0-10 cm non-arable and both depths from arable (Figure 4.7). At Cedara, the mineral-N in the 10-20 cm depth of the non-arable soil was significantly higher than the both depths of arable soil at day 28 (Figure 4.8). At day 28 the Karkloof soils showed significantly higher mineral-N in the 0-10 cm of the non-arable than in 10-20 cm depth of both non-arable and arable soils (Figure 4.8).

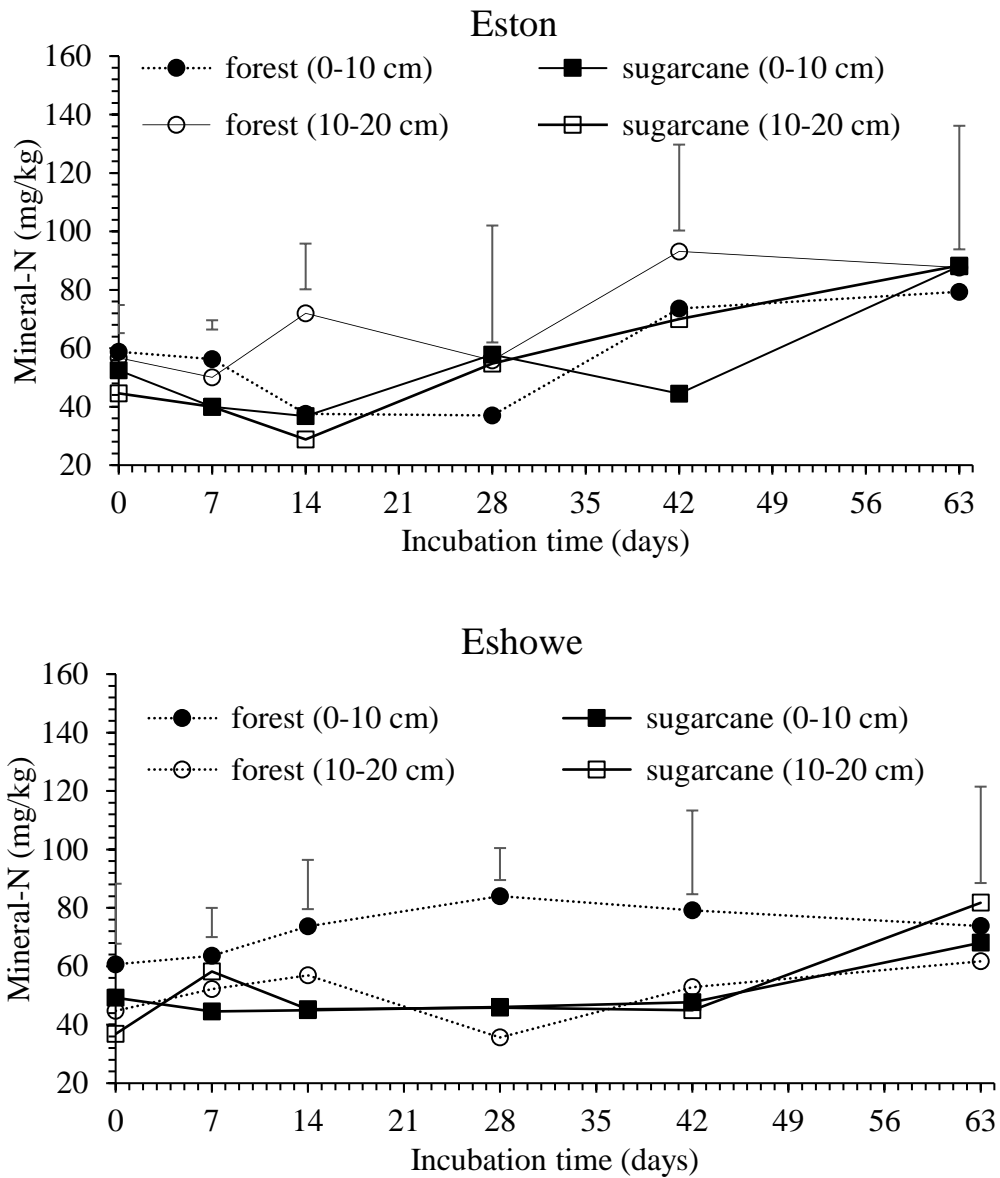


Figure 4.7: Mineral-N released during incubation of soils from Eston and Eshowe. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

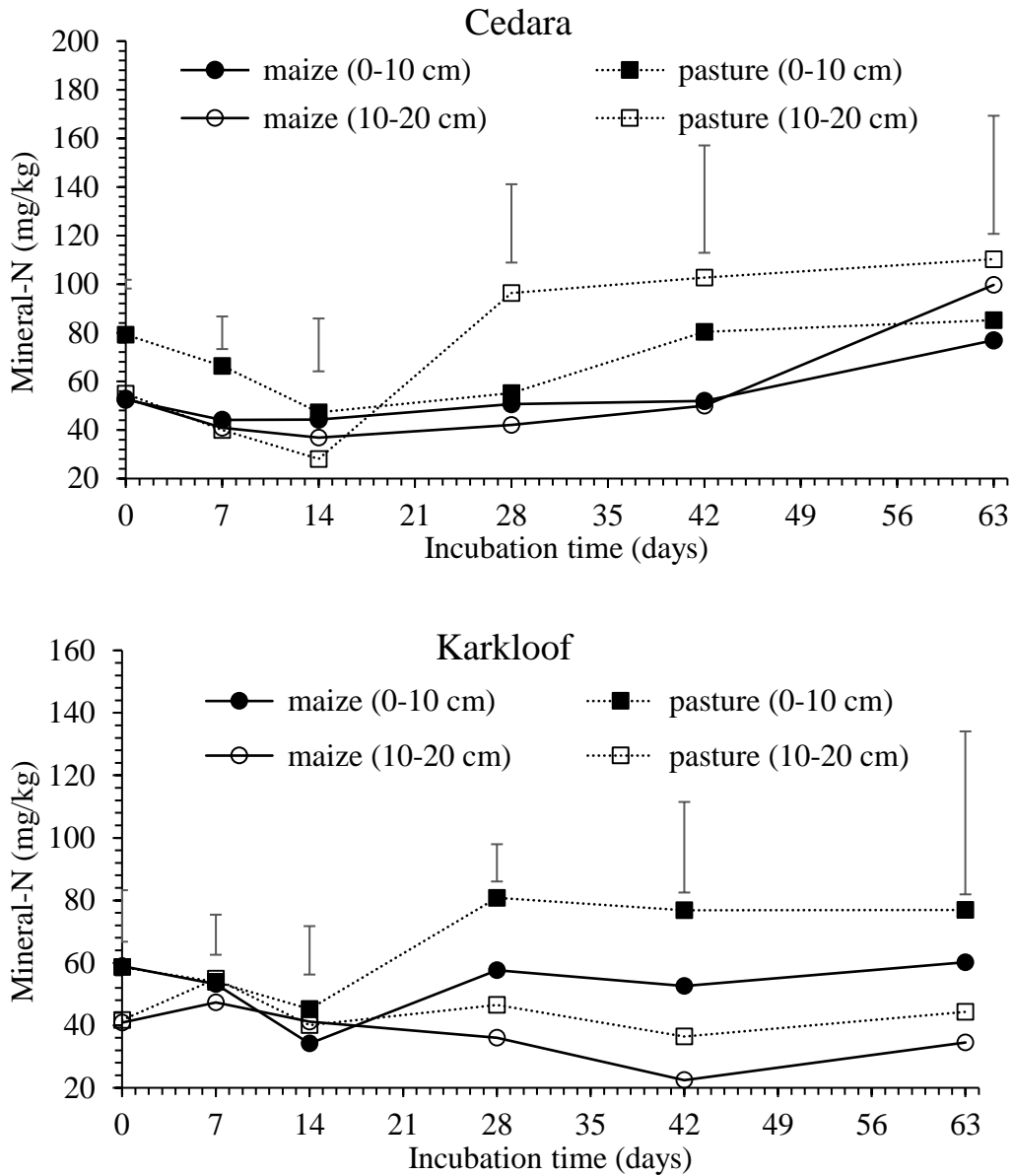


Figure 4.8: Mineral-N released during incubation of soils from Cedara and Karkloof. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

4.3.5 Extractable phosphorus

Extractable P showed a rapid decline to day 14, with the lowest being after 28 days for all land uses and depths of all the soils. There was a general increase in extractable P between 28 and 63 days of incubation, with the greatest increase being in the 0-10 cm depth of the arable soil from Eston (Figure 4.7). The 0-10 cm depth of the arable soil had significantly higher extractable P (> 30 mg/kg) than all other soils from Eston at all sampling times from 14 days of incubation. The 10-20 cm depth of the arable soil had significantly higher extractable P than both depths of the non-arable at 42 and 63 days of incubation (Figure 4.7). There were no significant differences among the land uses and between the depths (all < 20 mg/kg after 7 days and beyond) for the Eshowe soils, except at day 63 when extractable P was significantly higher in the 0-10 cm depth of the arable than the other three soils (Figure 4.7). Soils from Cedara showed high variability (large LSDs) as such there were no significant differences observed in extractable P (all < 20 mg/kg after 7 days and beyond) (Figure 4.8). The 0-10 cm depth of the non-arable soil had significantly higher extractable P than both depth under arable and 10-20 cm depth under non-arable from Karkloof throughout the incubation except days 0 and 42. For soils from the 10-20 cm depth, non-arable had higher extractable P than arable only after 63 and 84 days of incubation (Figure 4.8). All soils had < 20 mg P/kg throughout the incubation except, on the first day.

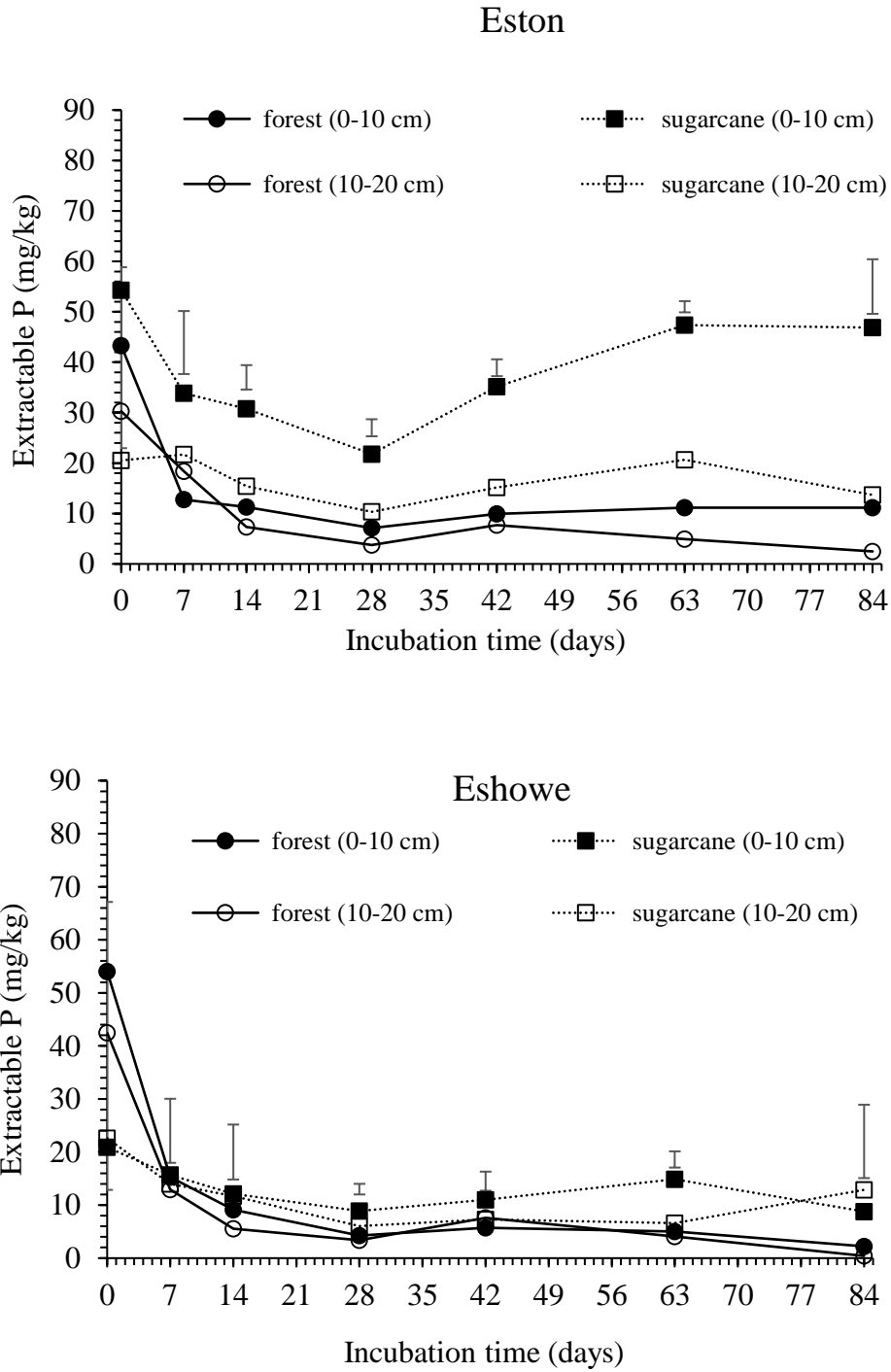


Figure 4.9: Extractable phosphorus (P) released during incubation of soils from Eston and Eshowe. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

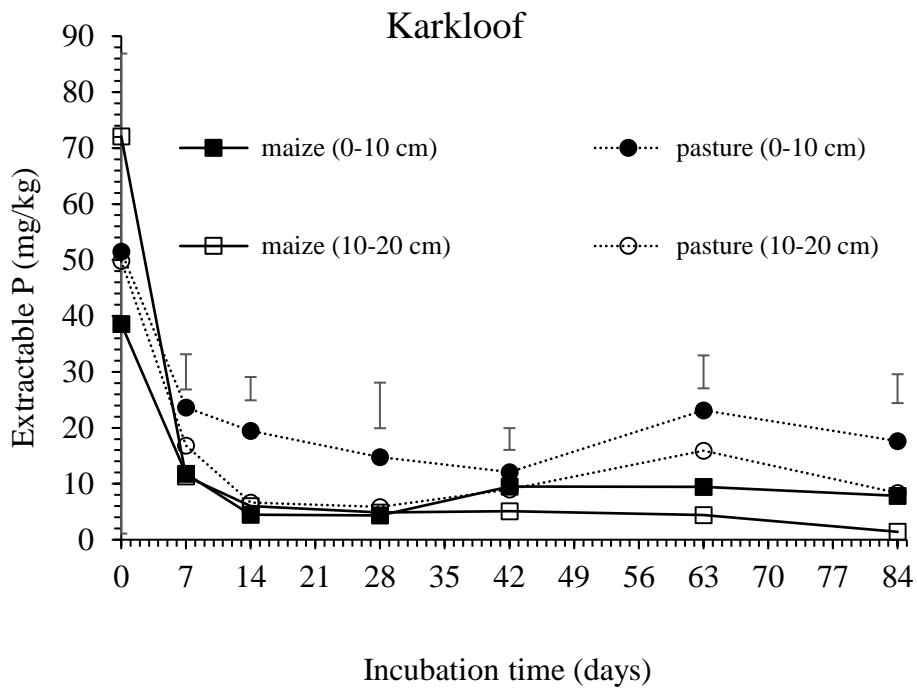
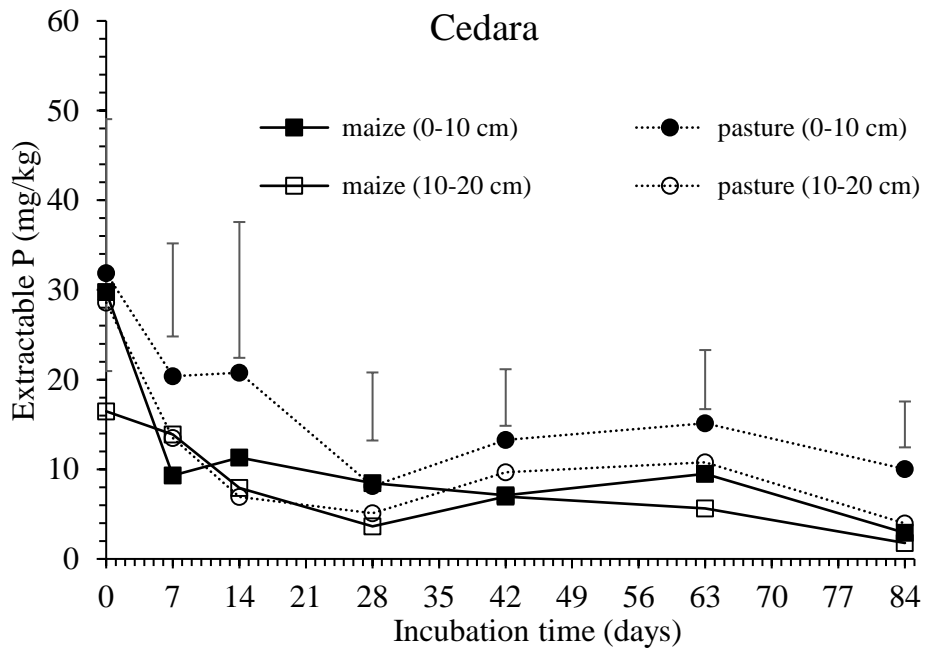


Figure 4.10: Extractable phosphorus (P) released during incubation of soils from Cedara and Karkloof. Vertical error bars represent LSD ($p < 0.05$) for each sampling period.

4.3.6 Inorganic phosphorus fractions

Eshowe arable (sugarcane) soil had significantly higher ($p < 0.05$) Al and Fe bound-P and lower reductant-P at the end of incubation compared to the unincubated soil, whereas residual-P and soluble and loosely bound-P did not show significant changes as a result of incubation. Non-arable soils did not show any effect of incubation on the P fractions (Table 4.1). At the end of incubation, the arable soil had significantly higher Al bound-P and Fe bound-P and lower reductant-P than non-arable soil. It is important to also note that the data had high variation (large LSDs), which explains the lack of statistical significant differences even where the absolute values look different.

Table 4.1: Inorganic phosphorus (P) fractions after incubation for 84 days of soils from 0-10 cm at Eshowe under sugarcane and forest.

Land use	Incubation	Soluble/ loosely bound-P	Al-P	Fe-P	Reductant- P	Residual- P
Sugarcane	<i>Unincubated</i>	101 ^{a#}	122 ^a	102 ^a	309 ^b	70.2 ^a
	<i>Incubated</i>	93.9 ^a	210 ^b	226 ^b	106 ^a	116 ^a
Forest	<i>Unincubated</i>	219 ^a	114 ^a	73.3 ^a	482 ^b	87.9 ^a
	<i>Incubated</i>	185 ^a	125 ^a	69.8 ^a	420 ^b	76.6 ^a
<i>LSD (p<0.05)</i>		116.3	17.17	17.64	159.5	47.68

#Values followed by the same letter in the same column are not significantly different at $p < 0.05$.

Soils from Karkloof arable (maize) had significantly higher ($p<0.05$) Fe bound-P and reductant-P at the end of incubation compared to the unincubated soil, whereas Al bound-P, residual-P and soluble and loosely bound-P did not show significant changes as a result of incubation (Table 4.2). Soils under non-arable (pasture) had significantly higher ($p<0.05$) Al and Fe bound-P after incubation compared to the unincubated soil, with no differences in reductant-P, residual-P or soluble and loosely bound-P (Table 4.2). At the end of incubation, the arable soil had significantly higher Fe bound-P and reductant-P and lower Al bound-P than non-arable soil. It is important to also note that the data had large LSDs, which explains the lack of statistically significant differences even where the absolute values look different.

Table 4.2: Inorganic phosphorus (P) fractions after incubation for 84 days of soils from 0-10 cm at Karkloof under maize and pasture.

Land use	Incubation	Soluble/ loosely bound-P	Al-P	Fe-P	Reductant- P	Residual- P
Maize	<i>Unincubated</i>	212 ^{a#}	183 ^a	242 ^a	162 ^a	83.5 ^a
	<i>Incubated</i>	196 ^a	181 ^a	319 ^b	262 ^b	101 ^a
Pasture	<i>Unincubated</i>	226 ^a	157 ^a	206 ^a	90.5 ^a	122 ^a
	<i>Incubated</i>	208 ^a	270 ^b	348 ^b	142 ^a	134 ^a
<i>LSD</i>		40.79	39.62	69.29	94.42	57.55

($p<0.05$)

#Values followed by the same letter in the same column are not significantly different at $p<0.05$.

4.4 Discussion

The general decline in soil pH with incubation time corresponded with a general increase in nitrate-N, suggesting that nitrification acidified the soil during incubation. As expected under the imposed conditions, the ammonium-N and nitrate-N trends were complementary to each other, with nitrate-N increasing in line with the decrease in ammonium-N. The degradation of the organic matter by a wide group of heterotrophic microorganisms resulted in N mineralization in soils from all the sites (Oberson *et al.*, 2001). A decrease in ammonium-N, coupled with an increase in nitrate-N with time during incubation was also shown in the study by Mchunu *et al.* (2018), who studied mineralization of N from different organic sources added to a humic soil. Although ammonium-N was nitrified to nitrate-N, the absolute amounts of decrease in ammonium-N did not exactly correspond with the quantity of nitrate-N measured. The lack of accumulation of ammonium-N after 14 days, suggested that the ammonium-N in the system at the beginning was nitrified, while additional ammonium-N released during incubation was nitrified immediately.

While land use and depth did not significantly affect nitrate-N in any of the soils from all the sites, the increase in nitrate-N could make a contribution to the N requirements of crops grown on these soils, particularly at Eston and Cedara. On average the nitrate-N increased by 52 mg/kg (from 22.4 to 74.4 mg/kg) in soils from Eston, 26.7 mg/kg (19.5 to 46.2 mg/kg) at Eshowe, 31.2 mg/kg (17.2 to 48.4 mg/kg) at Karkloof and 83.8 mg/kg (24.2 to 108 mg/kg) at Cedara. Assuming a bulk density of 1 000 kg/m³ and a depth of 0.2 m, these nitrate figures translate to 104, 53.4, 62.4 and 168 kg N/ha for Eston, Eshowe, Karkloof and Cedara soils, respectively. Assuming these laboratory results can be replicated in the field, the calculated N figures would be the maximum amounts that could be available. For the soil from Cedara, that would be more than the required 120 kg N/ha for a 6 t/ha maize crop. This was despite the Cedara soil having lower total N than the other soils. The higher nitrate-N could be a result of higher pH and lower

acidity, which may have supported greater microbial activity. Although acidity was high in the soils from Eston, the higher total N than the Eshowe and Karkloof sites could explain the relatively higher nitrate-N results. During the summer, soil temperatures and moisture are high, and aeration is not limited (the soils are well drained although they could be briefly saturated in the event of high precipitation), so microbial decomposition of organic matter in humic soils could make a major contribution to the N requirements of crops. However, the amount of nitrification in the incubation experiment would be higher than in the field due to favoured conditions and the nitrate remained in situ while in the field it would be taken up by plants or leached.

While nitrate-N increased with incubation time, extractable P rapidly declined to its lowest after 28 days of incubation. The decrease in pH due to the nitrification process would not favour an increase in the P availability unless lime was applied (Abolfazli *et al.*, 2012). The higher extractable P in soil under sugarcane than the wattle plantation at Eston, could be a result of lime and poultry manure applications for sugarcane production. The liming had been practiced to neutralize the high acidity from both the strong weathering and leaching and the acidic wattle litter added in the years prior to sugarcane cultivation. The increase in extractable P beyond 28 days of incubation, particularly for the soil from the 0-10 cm depth at Eston under sugarcane, could be due to the release of microbial P and N, when the microorganisms died upon possible decrease in labile organic matter. This was around the same time when significant increase in nitrate-N occurred, which support the idea of P and N being released from died microorganisms. The absence of plants during incubation eliminated plant uptake as a mechanism of removal of P from the soil. During organic matter decomposition some of the Fe and Al associated with organic matter might have been released into solution and most likely will have precipitated with P, especially with the decline in pH of these acidic soils during incubation. The high amounts of Al and Fe in these (Section 3.3.3) suggest a high probability

of P complexing with Al and Fe. This view was supported by the results of P fractionation at the end of incubation, which showed an increase in Al and Fe phosphates in soils from both Eshowe and Karkloof, when compared to the initial unincubated soils. These differences in P fractions were not all clear from all the land uses, which might suggest other factors in addition to land use were at play. An increase in Al- P and Fe-P in arable soil from Eshowe after incubation could be accounted for by the low rate of lime application to reduce acidity and increase soil pH, which can then increase the available P fraction. The reason for no differences in non-arable from Eshowe soil is not clear, with incubation having insignificant effects on P fractions. However, the lower pH and higher concentration in this soil could have limited microbial activity, and mineralization. After incubation, reductant-P decreased in the sandy arable soil of Eshowe but increased in the clayey arable of the Karkloof. The decrease in reductant-soluble P within the matrices of retaining aggregates/mineral from Eshowe arable soil and increase in the Karkloof arable suggests that this fraction responds differently under different textural class and land use management such as tillage practices. Both non-arable soil of both sites show no changes in reductant-P because with the minimal soil disturbance reductant-P remained more associated with mineral and well protected organic matter within the aggregates. While mineralization would have released P, its fixation resulted in limited changes in available and residual-P in the soil from both Eshowe and Karkloof. The >30 mg P/kg in the 0-10 cm depth of the arable soil from Eston could support plant growth without the need for fertilization while all other soils from the different sites and land uses would require P fertilizer addition for optimal crop production.

Soil amendments that facilitate microbial activity in humic soils could be essential to limit fixation of mineral P, making it more available to plants. Amendments such as goat manure have been reported to increase soil microbial biomass P, which then could improve the efficiency of fertilizer P (Gichangi *et al.*, 2010).

4.5 Conclusions

Incubation of humic topsoils decreased pH for the different land uses and depths. Under conducive moisture and temperature conditions humic soils released significant amounts of mineral N. Mineralization did occur on the studied soils. The amounts of released N, of up to 103 mg/kg (as nitrate-N), could significantly contribute to crop productivity. Extractable P released was higher in arable soil than non-arable soils, and it initially declined within the first 28 days and then increased gradually till it remained constant. Incubation increased Al and Fe phosphates fractions when compared to the unincubated soil. Reductant-P decreased in the sandy arable soil of Eshowe but increased in the clayey arable of the Karkloof after incubation. Non-arable soils P fractions were not affected by incubation. The high N and low P in these soils need to be considered in fertilizer management to avoid over or under applications.

CHAPTER FIVE

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE WORK

5.1 Discussion

Humic soils are among the most important agricultural soils in South Africa. Their natural characteristics are affected by land use and management. The effects of land use on the natural characteristic, including high organic matter and acidity, could influence nitrogen (N), phosphorus (P) dynamics, and crop productivity. The aims of this investigation were to (i) determine effects of different land uses on some of the characteristics of topsoils of some humic soils and (ii) to investigate the mineralization of N and P from the organic matter and its implications on plant available N and P.

Change of land use resulted in the humic topsoils undergoing a significant change in soil quality, as evidenced by increasing pH and basic cations, and decreasing exchangeable acidity, total carbon (C), and total N in arable compared to non-arable soils. The higher soil pH, concentrations of calcium (Ca), magnesium (Mg) and potassium (K) and lower exchangeable acidity in the arable than non-arable soils was explained by lime and fertilizer application in these soils. Kristaponyte (2005) demonstrated that liming and fertilization increase pH and nutrient availability in acid soils. Enwezor *et al.* (1990) also showed that more P, K, Ca and Mg are available in the topsoil of limed and fertilized as compared to unlimed and unfertilized soils. However, in the current study these effects were more evident at some sites than others, possibly as a result of differences in site characteristics, such as climate, parent material and management practices. For example, the non-arable soil at Eshowe had higher pH, Mg and K, particularly in the 0-10 cm depth than the arable one, while arable soils had higher pH at all other sites, and higher Mg and K at Eston and Karkloof, with no land use effects on bases at Cedara. Land use did not affect Ca concentrations at all sites except Karkloof, where the arable soil was higher than the non-arable. Although soils at Eston and Eshowe were both formed

from sandstone, the non-arable soil from Eshowe was under natural forest, while at Eston it was wattle forest, and the litter from the wattle increased acidity and lowered pH. *Acacia* species, including wattle, has been reported to alter soil physico-chemical properties to favour their growth, which include acidifying the soil (Matali and Metali, 2015). The soils at Karkloof and Cedara were formed from dolerite, with the arable ones being under maize and non-arable were under pasture. The higher Ca, Mg and K in the arable than non-arable at Karkloof, with no differences between land uses at Cedara, could be a result of differences in management of the maize and the pastures at the two sites. At Cedara the arable soil was treated with 40 kg K /ha once every year, calcitic lime once every 3 years, guided by acid saturation, while 200 kg K /ha was applied once every year without any liming on the non-arable. The lower content of exchangeable bases in the non-arable humic soils, which was combined with higher acidity than the arable soils and higher extractable iron (Fe) at Eshowe and Cedara, indicates that management approaches, such as lime and fertilizer application make a positive contribution to some soil quality parameters. For example, increasing soil pH and reduction in exchangeable acidity, will reduce possibility of Mn toxicity, and improve soil biological activity (Kuehn *et al.*, 2004). However, the results of total C and N showed that monocropping systems with intensive tillage (sugarcane and maize although tillage frequencies are not the same) adversely affected soil C and N compared to the less disturbed land uses (forest and pasture), as indicated, for example, by the higher total C in the soils under the latter land uses. Higher total C and N and the low C/N ratio suggested the high potential for N mineralization. The lower C and N contents in the arable humic soils were explained by decomposition of the organic matter and mineralization of N as a result of tillage, combined with lower organic matter inputs. Tillage has been reported to affect soil organic C by Needelman *et al.* (1999) who compared conventional tillage practices against no-till system of 5 years and found that there was 15 % more soil organic C in a no-till 0-5 cm layer than on the conventional tillage system. Pre-

harvest burning of cane in the soils of Eston and Eshowe may have lowered C inputs and transfer of N as part of the cane after harvest. Dengia and Lantinga (2018) estimated that 14.4 t/ha of organic matter and 66 kg/ha of N are lost during cane burning. This burning also reduces the crop residues that could be kept over the soil, which have proven to increase soil N stock and N recovery by sugarcane (Trivelin *et al.*, 2013). The result of the lower N is the need for higher N fertilizers to sustain the production of sugarcane as compared to other land uses. Although the incubation experiment resulted in N mineralization, the process was not as rapid as suggested by some of the C/N ratios. This was perhaps because of the high acidity in some of the soils since there was more N mineralized from the arable soils from Eston, Karkloof and Cedara, as a result of liming.

Curtin *et al.* (1998) found that although acidity did not prohibit mineralization, raising pH of acidic soils using lime, stimulated C and N mineralization. In addition, management activities such as addition of chicken litter and residue incorporation to the soil after harvest on the sugarcane sites might have influenced the process of mineralization. However, the amounts of N released could make a significant contribution to crop N nutrition, particularly in the arable soils from Eston and Eshowe. The mineralization study gave a picture of what could be potentially mineralized from these soils under ideal conditions. Under field conditions, the N mineralization could be lower as a result of wetting and drying cycles due to rainfall and irrigation, and fluctuating temperatures. Mikha *et al.* (2005) compared cumulative N mineralization at constant water content with four series of drying and rewetting cycles of soils and found that drying and rewetting cycles decreased N mineralization cumulatively, while N mineralization increased under constant moisture content. In the field, there could be a flush of C mineralized after each rewetting period, which may result in the decrease of inorganic N because of it being assimilated by microbes as result of rapid increase in microbial activity. In the event of large pulses of water availability which may results in full soil saturation there

would be slower release in mineralization products as compared to small pulses of water which fuel rapid cycle in C and N mineralization- immobilization (McIntyre *et al.*, 2009).

The incubation of the soils also resulted in a decline in pH, and extractable P with incubation time mainly during the first 28 days of incubation. The decomposition of the organic matter could have released P, resulting in fixation, as phosphates of Al and Fe, which occurred at high concentration in these soils (Table 3.3). This was supported by higher Al and Fe phosphate and reductant P in the soils after incubation than in the unincubated soils. These findings were supported by the high affinity of the soils for P, and the high sorption maxima, particularly the sandy clay loams from Eston and Eshowe, which generally had higher extractable Al and Fe. The highly weathered nature of humic soils (MacVicar *et al.*, 1984) result in a high P fixation capacity and the studied soils were no exception. All the humic soils in the present investigation showed high to very high P sorption, as indicated by the Langmuir isotherms. The isotherms also showed further 'sorption' beyond the initial sorption maximum. Such stepped behaviour may represent P more firmly held, perhaps by Al and Fe, although mechanisms were not investigated in the present study. This fixation could explain the decline in extractable P during increase, while immobilization as microbial biomass P could have contributed, as shown by slight increases in extractable P at later stages of incubation.

The increase in extractable P after 28 days of incubation in most of the soils but much so for 0-10 cm depth of the Eston soils suggests that soil microbial biomass P could have contributed to the decline in P in the first 28 days and that when the microbes died, they released the microbial P. This supports the view that microbial P could increase availability of P for crop uptake (Gichangi *et al.*, 2010). There was significant increase in N around about the same time as P, which suggest the idea of P and N being released from the same source which could be dead microorganisms. However, across the entire time period of the incubation experiment the amount of available P declined. This was supported by the measurements of pH, exchangeable

acidity, P sorption maxima, Al and Fe contents and nitrification. The interaction of these factors likely played a role in the decrease in extractable P over time. Understanding the factors that influence both inorganic and organic P fractions could be a useful tool to manage P and improve on the supply of P from mineralization (Nziguheba *et al.*, 1998). The findings of the present study suggest that decomposition of the organic matter triggered other processes that led to not only a decline in available P but also changes in other characteristics of the soils that are not desirable for crop growth.

5.2 Conclusions

Land use affected a range of humic topsoil characteristics. Arable humic topsoils contained more exchangeable bases, higher pH, extractable P and lower acidity compared to non-arable soils (forest and pasture). Non-arable soils (not regularly tilled) had higher C and N contents, than arable soils. During incubation, arable soils released more nitrate N than non-arable soils. The nitrate N contributed more in the total mineral N. Humic soils could contribute significant plant available N via mineralization. High sorption of P on humic soils reduced its availability, which declined with incubation time for all land uses. Decomposition of organic matter in humic soils could significantly contribute for N nutrition in these soils, but liming and additional P may be required for optimal crop production. As such N mineralized may need to be accounted for when making N fertilizer recommendations on humic soils. The changes in physico-chemical properties of humic topsoils as a result of change to arable cropping could contribute significantly to soil fertility but may have long term negative effects on soil organic C.

5.3 Future work

Sugarcane (before harvesting), and the brash of timber, are often burnt and the effects of these activities on humic soil C and N need to be investigated. The results of P sorption on humic soils showed that multiple mechanisms are at play, which requires further research to

understand these mechanisms. Soil amendments, such as lime and poultry manure, that can potentially reduce solubility of Al and Fe and fixation of P, and increase microbial biomass, may need to be studied for the contribution of the microbial biomass P pool in lowering P fixation and increasing availability in humic soils. The effects of lime application on N mineralization need to be studied, in case it may result in extremely large quantities of N, particularly nitrate-N, being released with potential risks for leaching to groundwater.

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APPENDICES

Appendix 3.1: Particle size analysis (Gee and Bauder, 1986).

Moisture content was determined by drying a sub-sample at 105°C to a constant mass for moisture correction. Soil (20.0 g) was wetted with de-ionized water followed by treatment with 30 mL of 30% hydrogen peroxide to oxidize organic matter (further additions of peroxide were made for soils with >4% organic matter). The beaker was allowed to stand for a few minutes before placing on a hot plate, where the mixture was heated until the reaction subsided and finally boiled to remove all the unreacted H₂O₂. Dispersing agent solution (20 mL of sodium hydroxide plus 10 mL of sodium hexametaphosphate) was added to the sample in a stirrer cup, and stirred on a high-speed stirrer for 10 minutes. The dispersed sample was transferred into a 1 L measuring cylinder with de-ionized water. The soil was brought into suspension by at least 40 up and down strokes with a plunger. The temperature of the liquid was recorded. After the appropriate settling time for sand, a 20 mL sample was collected at 100 mm below the surface with the pipette to represent the fine silt plus clay content. The sample was discharged into a pre-weighed beaker, placed in an oven at 105°C and dried overnight. After the required settling time for silt, a 20 mL sample was collected at 75 mm below the surface to represent the clay content. The sample was dried at 105°C. The beakers were removed from the oven, allowed to cool in a desiccator, and re-weighed. The calculation data sheet was completed.

Calculation

m1 = mass of empty beaker for silt + clay reading

m2 = mass of beaker containing dry silt + clay

m3 = mass of empty beaker for clay reading

m4 = mass of beaker containing dry clay

b = mass of reagent blank *ie.* 20 ml sample pipette at 20°C and dried at 105°C

% moisture = [(mass of air-dry soil - mass of oven-dry soil) / mass of oven-dry soil] x 100

% Silt and Clay = 250(m2 - m1 - b) (1 + % moisture)

% Clay = 250(m4 - m3 - b) (1 + % moisture)

% Silt = (% Silt + Clay) - % Clay

% Sand = 100 - (% Silt + Clay)

Appendix 3.2: Mehlich 3 method (Wolf and Beegle, 2009).

A 4 g sample of air-dry soil was weighed into a 100 mL centrifuge tube and 40 mL of Mehlich 3 extracting solution (0.2 M CH₃COOOH + 0.25 M NH₄N₀3 + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA) added. The mixture was shaken for 5 minutes on a horizontal shaker at 180 cycles/minute, and then centrifuged at 7 000 rpm for 5 minutes and filtered through a Whatman No 1 filter paper, before analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Varian 720-ES). Each soil sample was replicated three times.

Appendix 3.3: AMBIC-2 method used for phosphorus (P) extraction (Van der Merwe et al., 1984).

A 2.5g (oven dried equivalent) soil sample was mixed with 25 mL of the AMBIC-2 solution (0.25 M NH₄CO₃ + 0.01 M Na₂EDTA + 0.01 M NH₄F + 0.05 g L⁻¹ Superfloc, adjusted to pH 8 using concentrated ammonia solution) in a 50-mL centrifuge tube, the suspension shaken for 15 minutes, and filtered through a Whatman No.1 filter paper. The extractable P was determined using the molybdenum blue method (Murphy and Riley, 1962), with a spectrophotometer UV-5500(PC) at a wavelength of 670 nm. Each soil sample was replicated three times.

Appendix 4.1: Sequential extraction procedure for inorganic phosphorus (P) fractions (Kuo, 1996).

