Nake, Steven (2010) ***Potassium fixation and release in alluvial clay soils of Milne Bay, Papua New Guinea: effects of management under oil palm.*** **Masters (Research) Thesis, James Cook University.**

https://doi.org/10.25903/hr1c%2Dt329

POTASSIUM FIXATION AND RELEASE IN ALLUVIAL CLAY SOILS OF MILNE BAY, PAPUA NEW GUINEA: EFFECTS OF MANAGEMENT UNDER OIL PALM

Dissertation submitted by:

Steven Nake

in August 2010

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science (by Research) in the School of Earth and Environmental Sciences at James Cook University, Cairns, Queensland

JAMES COOK
UNIVERSITY
AUSTRALIA

STATEMENT OF ACCESS

I, the undersigned author of this thesis, understand that James Cook University will make it available for others to use. All users consulting this thesis will have to sign the following statement:

"In consulting this thesis, I agree not to copy or closely paraphrase it in whole or part without the written consent of the author; and to make proper written acknowledgement for any assistance which I have obtained from it".

Beyond this, I do not wish to place any restriction on access of this thesis.

28/2/2011

……………………….. ……………………..

Steven Nake Date

DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

28/2/2011

……………………….. ……………………..

Steven Nake Date

ACKNOWLEDGEMENT

First, I would like to express my sincere gratitude to Australian Centre for International Agricultural Research (ACIAR) for kindly offering me the scholarship under the “John Allwright Fellowship” to study in Australia.

I am deeply obliged to my supervisor, Dr. Paul Nelson. His great supervision and bright ideas helped me complete this thesis. I thank him very much for his patience, enthusiasms in reading, discussing and rewording the drafts of this thesis. I am also indebted to Sue Berthelsen for helping me out with all the soil analysis for this work and with the interpretation of some of the analysis results. I wish to thank Nick Salmon for his technical support. Thanks to John Broughton and Jeremy Kinley for helping out with the laboratory work. I would like to convey thanks to John Armour (Department of Environment and Resource Management) for providing some of the equipments used in the laboratory work.

Many thanks to Ian Orrell (Managing Director, PNGOPRA) for allowing me time away from work to conduct this study. Special thanks to Dr. Harm van Rees for providing technical advice and support, especially with the field work. Thanks to Dr. Murom Banabas for his assistance in providing some of the information required for the completion of the thesis. Thanks also to Mrs Pole Crompton (Administrator, PNGOPRA) for providing the logistical support. I am indebted to Wawada Kanama (Agronomy Supervisor) and all his field staff in Milne Bay Research Centre for helping out with the field work.

The following people also provided moral support and encouragement and I am heartily thankful to them: Dr. Mike Webb (CSIRO), Elizabeth Smyth, John Berthelsen, Hanington Tate, Titus Kakul and Anton Lata.

Finally, but not the least, special thanks to my wife (Barbra) and the kids (Genesis, Nathan and Crystal) for their invaluable support and encouragement throughout this adventure. I dedicate this thesis to them.

ABSTRACT

Potassium deficiency is pronounced in oil palm and other crops on alluvial clay soils of Milne Bay Province in Papua New Guinea. These clay soils contain clay minerals that can fix K. This, coupled with large amounts of exchangeable Mg and Ca, triggers the K deficiency problem in oil palm growing in this area. Oil palm yield and other growth parameters had responded positively to K fertiliser application for the last 12-13 years in long-term factorial fertiliser trials. However, a K use efficiency study showed that 40% of the added K was taken up by the oil palm while more than 50% had accumulated in the top 60 cm of the soil. There is currently limited information to explain why K accumulated in the soil and the implications for management. Fixation of K could be one of the factors contributing to K accumulation. Therefore, this study was carried out to determine fixation and release characteristics of K in alluvial clay soils under oil palm cultivation in relation to soil and management factors.

All the work was carried out using soil samples collected in 2007 from plots with different K fertiliser history in two long-term fertiliser trials, trial 502b and 504, which had been operating since 1995 and 1994, respectively. Soil mineralogy was predominantly smectite in trial 502b and vermiculite in trial 504. In Experiment 1 (Chapter 3), the effects of management (K fertiliser history and surface management) on the amounts and forms of K in the soil was examined by measuring exchangeable (ammonium acetate extractable) and non-exchangeable (sodium tetraphenyl borate extractable minus ammonium acetate extractable) K. The results showed that in both trial sites, the management zones receiving K fertilizer (frond pile [FP], frond tip [FT] and between other zones [BZ]) had significantly ($p<0.001$) higher concentration of both exchangeable and non-exchangeable K than the other zones (weeded circle [WC] and harvest path [HP]). The exchangeable and non-exchangeable K concentrations differed significantly between sites, and there was a significant interaction between sites and K fertiliser history. In the plots and zones that had received fertiliser, exchangeable and non-exchangeable K contents were higher in trial 502b than 504, whereas in the plots that had received no fertiliser they were higher in trial 504 than 502b. In the plots that had received no K fertiliser, contents of exchangeable and non-exchangeable K were very low and could be considered deficient at both sites. The difference between the two sites was related to the mineralogy of the soils.

In Experiment 2 (Chapter 4), the effects of site and previous management on K fixation were determined. Solutions with nine different concentrations of KCl (equivalent to 0, 3.2, 9.6, 12.8, 16.0, 19.2, 22.4 and 25.6 mmol K kg^{-1} soil) were added to the soil, centrifuged and decanted.

Exchangeable K was then extracted from the soil with 1 M ammonium acetate. The decanted equilibrium solutions and ammonium acetate extracts were analysed for K using an atomic absorption spectrophotometer. Fixed K was determined using the formula: Fixed K = added K minus decanted equilibrium solution K minus ammonium acetate extractable K. Potassium fixation was significantly ($p<0.001$) affected by the K fertiliser history and surface management. In soils and zones that had received no K fertiliser, an average of 27% of added K was fixed in both trials, whereas in the plots with a history of K fertiliser, there was little net fixation or release in the WC zone and a considerable release of non-exchangeable K in the BZ and FP zones.

In Experiment 3 (Chapter 5), the release of K from non-exchangeable form into solution was studied. Firstly, the exchangeable K in the soil was removed by rinsing the soil three times with 0.25 M $CaCl_2$. Then the soil was equilibrated with 0.01 M $CaCl_2$ for 480 hours. At various intervals during that period, the supernatant was removed, analysed for K, and replaced with fresh 0.01 M $CaCl_2$. In the plots that had received no K fertiliser, more K was released from the native non-exchangeable pool in trial 504 than trial 502b. In the plots that had received K fertiliser, a substantial amount of K was released. In those plots more K was released in trial 502b than 504. In both trials, more K was released from the FP zones than the other zones, and K release in both trials increased in the order; HP<WC<BZ<FT<FP. The kinetics of K release from non-exchangeable K pool was described well by the Elovich function in all samples (r^2 = 0.957-0.989; se = 0.002-0.179). Over all samples, the parameters α and $1/\beta$ were linearly related to the amount of non-exchangeable initially present; i.e. the rate of release of non-exchangeable K was positively related to the amount present. The rate of release was greater for trial 502b than trial 504.

This study showed that management has a large effect on the fixation and release of K in alluvial soils of PNG under oil palm cultivation. Soil behaviour differed considerably between management zones, suggesting that K fertiliser placement might have a considerable effect on uptake efficiency.

Table of Contents

List of Tables

List of Figures

CHAPTER ONE

1 Introduction

1.1 Background and aims

With the world's ever increasing population, it becomes more critical for researchers to examine factors that improve food production, so that a particular land would be able to sustainably maintain and support crop growth and yield. In light of this, plant nutrition is one of the most important factors that is worth considering. Nutrient deficiencies are mainly attributed to the limited availability of soil nutrients to the plants, and can be caused by extensive mining of nutrients by crops without replenishment. Other factors such as amounts of nutrients in the parent material from which the soils are derived, fixation and immobilization of nutrients, losses due to leaching or erosion in high rainfall areas can also contribute to nutrition deficiencies.

Potassium deficiency is reported worldwide, and Papua New Guinea (PNG) is no exception. Potassium deficiency is a problem in coconuts grown along the coast of New Ireland where the soils have very low pH and mostly derived from limestone and coral (Hartemink and Bourke, 2000). Harding and Hombunaka (1998) reported K deficiency in coffee grown in certain parts of the highlands of PNG where soil K uptake is affected by very high Mg levels. Hartemink (1998) reported a significant decline in exchangeable K in Ramu soils between the 1980s and 1990s. The decline in the exchangeable K was caused by a significant drop in the soil pH within the same years. Potassium deficiency is also prevalent in the south coast of the eastern tip of the mainland, particularly in Milne Bay and Central Provinces (Best 1977).

In Milne Bay, the soil origin is alluvial with clay content of 30-50 % (Bleeker 1988). These clay soils are high in exchangeable Ca and Mg and low in exchangeable K (Best 1977, Bleeker 1983, Bleeker 1988) and at the same time are dominated by vermiculite and smectite clay minerals which are K-fixing. Long term fertiliser trials on these soils have established clear responses to K in yield and leaflet K concentrations. Application of muriate of potash (MOP) fertiliser, which is a source of K, increased both yield and K concentration in the leaf tissues (PNG Oil Palm Research Association Annual Reports 2007). Despite the positive response, it was uncertain whether the K fertiliser was efficiently utilised by the palms. In 2006, a study to investigate nutrient use efficiency by the oil palm revealed that only a small proportion (25 %) of the applied K was taken up by the palms, whereas a large proportion (75 %) had accumulated in the top 30-40 cm and had not been lost through leaching (Webb *et al*. 2009). There is limited information to explain why K had accumulated in the soil. Due to the presence of vermiculite and smectite in these soils, fixation could be one of the factors contributing to K accumulation or uptake was limited by factors other than fixation. Therefore, this study was carried out on alluvial clay soil in Milne Bay to determine (1) fixation and release characteristics of K and (2) the influence of management (K fertiliser history and placement) on K fixation and release in alluvial clay soils under oil palm in Milne Bay.

1.2 Literature review

1.2.1 Role of K in plant nutrition

Potassium is important for both plant and animal growth and is regarded as one of the three main macronutrients with N and P. Potassium is not incorporated into the structures of organic compounds like N and P but exists as an ion in solution or bound to negative charges of clay surfaces. As a result of its strictly ionic structure, K plays major roles relating to ionic strength of solutions within plant cells. Fixation of N in leguminous plants, manufacture of starch and, more importantly, mobilization of sugars within the plant cells are enhanced by K. Potassium also improves plants’ adaptability to stressful environmental conditions such as drought and improves resistance to fungal diseases and insect pests. Potassium also enhances formation of flowers and subsequent development of fruits in crops. When K levels are low, some fruit crops such as peaches are more vulnerable to certain diseases (Mengel 2006). Some of the major functions of K in plants are discussed below.

Enzymes activated by monovalent cations such as K play a key role in metabolic processes. Potassium is responsible for activating over 80 cellular enzymes responsible for plant processes such as photosynthesis, starch synthesis, nitrate reduction and energy metabolism (Tisdale *et al.* 1993). These enzymes are present at the growing points of the plants. When K binds to the surface of the enzyme, it changes the enzymic conformation and activates it. For example, K increases the activity of the plasmalemma H^+-ATPase enzyme. This enzyme is responsible for H^+ excretion from the cell. The H^+ concentration in the aploplast of the root cells is important for nutrients and metabolites taken up by the H^+ cotransport. Starch synthetase and nitrogenase are two other important enzymes activated by K. They are responsible for conversion of soluble sugars into starch and for converting atmospheric N_2 to NH_3.

Potassium is required in every major step of protein synthesis. This includes synthesis of ribosomes and aminoacyl-tRNA, peptidyl transfer, GTP utilization, protein synthesis from charged tRNA transfer and messenger RNA turnover (Evans and Wildes 1971). Potassium plays a major role in transporting N which is the key ingredient in protein to the sites of protein synthesis.

Studies have shown that the transport and uptake of NO_3^- was stimulated when K is the accompanying cations compared with the other cations (Blevins 1985).

The presence of K and other ions in the cytoplasm also maintains osmotic concentration necessary to keep the plant cells turgid. The role of K in osmotic regulation is particularly important because of its abundance over other cations in plants. The osmotic pull that draws water into the plant roots is triggered by K. Plants deficient in K are more susceptible to water stress conditions because of their inability to fully utilize available water (Tisdale *et al*. 1993). It was found that K increased the turgor and promoted growth in the cambial tissue (Koch and Mengel 1974).

Potassium has an important role in plant photosynthesis and respiration. Low levels of K reduces the rate of photosynthesis and translocation and increases rates of dark respiration, and this contributes to reduction in plant growth (Huber 1985). Transport of K^+ across chloroplast and mitochondrial membranes is closely related to the energy status of the plants (Mengel 2006). ATPase in the chloroplast pumps H^+ out of the stroma and stimulates a K influx into the stroma via selective channels, thus K is essential for pumping the H^+. Without the pumping of the H^+ from the chloroplast, the increase in stromal pH which is required for efficient conversion of light into chemical energy would rapidly dissipate. An increase in leaf K concentration directly increases CO_2 assimilation and reduces mitochondrial respiration (Peoples and Koch 1987).

1.2.2 Potassium bearing minerals

The earth's crust contains about 2.6% K making it the seventh most common element (Sheldrick 1985; Sparks and Huang 1985). The igneous rocks of the earth's crust have higher K contents than sedimentary rocks. Granites contain 46-54 g K kg^{-1}, basalts 7 g K kg^{-1} and peridotites 2.0 g K kg^{-1}. Limestones and clayey shales contain 6 and 30 g K kg^{-1} respectively. Mineral soils contain 0.4-3.0 kg^{-1} of K (Sparks 1980), which is lower than the average K content of igneous rocks but higher than that of some sedimentary rocks. The most important potassium-bearing minerals in soils are K-feldspars (20 to 30 g K kg^{-1}), muscovite (K mica, 60 to 90 g K kg^{-1}), biotite (Mg mica, 36 to 80 g K kg^{-1}), and illite (32 to 56 g K kg^{-1}) (Mengel 2006).

Potassium-feldspars are one of the main sources of K bearing minerals. They directly release K to the soil solution, and subsequently to exchange surfaces, through their dissolution (Singh and Goulding 1997). This process is promoted by very low K concentrations in the soil solution as a result of K uptake by plants and microorganisms and K leaching. Feldspars constitute 5-25 % of silt and clay fractions of soil and up to 40 % of clay fraction of unweathered soils, but generally 5 % or less of the clay fraction of most soils (Jackson 1979).

Mica is another important K bearing mineral and is widely distributed in clay soils. In micas, interlayer K (fixed K) is held tightly by electrostatic forces. This ‘fixed’ K can be replaced either by ion exchange and the transformation of micas into 2:1 layer silicates, or by dissolution, particularly through acidification of the rhizosphere by excretion of H^+ from the plant roots (Singh and Goulding 1997). Micas consist of two Si-Al-O tetrahedral sheets between which an M-O-OH octahedral sheet is located (Figure 1). M represents Al^{3+}, Fe^{2+}, Fe^{3+}, or Mg^{2+}. The three sheets form a unit layer, and are bounded together by K ions (Filep 1999). Micas exist as smaller particles (silt and clay) and smaller particles release the most K per unit weight. For example, biotite, which is a form of mica, weathers faster and releases K more readily than other feldspars (Munn *et al*. 1976). Most of available K in New Zealand soils came from weathering of mica (Surapaneni *et al*. 2002).

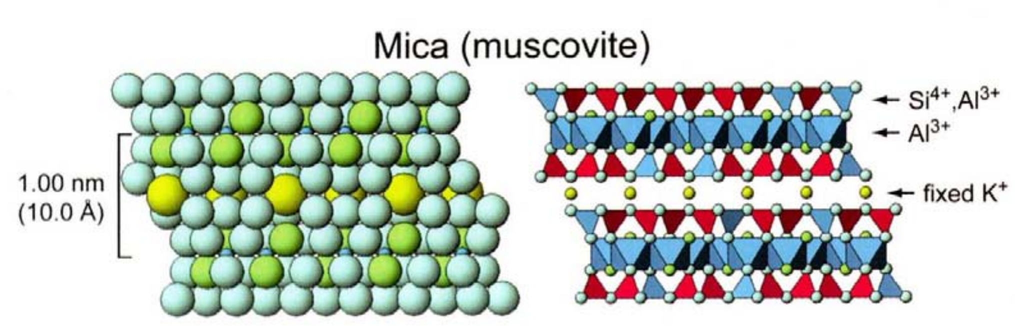

Figure 1. Chemical structure of mica (muscovite) (from Schultze, 2002)

1.2.3 Crystalline silicate clays

Most soils (except Andisols, Oxisols, and Histosol) are dominated with crystalline silicate clays. Silicate clays are composed of two basic building blocks; (i) Silicon - Oxygen Tetrahedron (Si_2O_{5-2}) and (ii) Aluminum Octahedral - $Al(OH)_{6-3}$. Tetrahedral sheets are composed of individual tetrahedrons which share every three out of four oxygens. They are arranged in a hexagonal pattern with the basal oxygen linked and the apical oxygen pointing up/down.

The tetrahedral sheets are combined with another sheet-like grouping of cations (Al^{3+}, Mg^{2+}, Fe^{2+}) or in six fold coordination with O_2- and OH- anions. With the six fold coordination, the negatively charged ions are arranged around the positively charged cations in an octahedral configuration (Olson *et al*. 2000). Crystalline silicate clays are divided into the 1:1 and 2:1 silicate clays depending on the number of tetrahedral and octahedral sheets in the layer structure (Schulze 2002).

1.2.4 The 1:1 silicate clays

A 1:1 silicate clay is formed when only one surface of an octahedral sheet is shared with a tetrahedral sheet. Halloysite, nacrite, dickite and kaolinite which are most common types of 1:1 silicate clay (Brady and Weil 2008). The kaolinite layer consists of one Si tetrahedral sheet and one Al octahedral sheet, which are tightly held together because the apical O atom in each tetrahedron also forms a bottom corner of one or more of the octahedra in the adjourning sheet. Most soils of the world contain kaolinite in the clay size fraction (<2µm). In highly weathered soils, such as those of Southeastern U.S. and tropical regions of Africa, Asia, and S. America, kaolinite is usually the dominant clay mineral because of its relative resistance to chemical weathering (Olson *et al*. 2000). Since kaolinite only has negative sites at the edge of the mineral that are not satisfied, the CEC is low (3-15 meq100g^{-1}). This makes the soil easy to acidify because the ability to hold on the basic cations is low.

1.2.5 The 2:1 silicate clays

The basic structure of 2:1 clay minerals is two silicon tetrahedral layers and one aluminum octahedral layer. This layer is weakly held to another 2:1 layer to make the 2:1 family of clay minerals. An interlayer or the space between the sheets becomes an important difference between 2:1 and 1:1 clay minerals. Smectite and vermiculite are two important expanding-type clay minerals in this group. The 2:1 clay minerals are the most important sources of soil K apart from inorganic fertilizers because they hold bulk of K and release it only when there is low concentration of soil solution. Barre *et al*. (2007) reported that 2:1 clay minerals behave as a huge, renewable reservoir whose amounts in fertile soils could exceed 3 t ha^{-1}.

Smectite clay

Smectites are 2:1 layer silicate with a high cation exchange capacity and highly variable interlayer spacing. They have a permanent layer charge because of the isomorphous substitution in either the octahedral sheet (typically from the substitution of low charge species such as Mg^{2+}, Fe^{2+}, or Mn^{2+} for Al^{3+}) or the tetrahedral sheet (where Al^{3+} or Fe^{3+} substitutes for Si^{4+}). It is common for smectites to have both tetrahedral charge and octahedral charge. The isomorphous substitutions lead to net negative charges on the clay structure which must be satisfied by the presence of charge-balancing cations somewhere else in the structure. The interlayer is hydrated, which allows cations to move freely in and out of the structure. The separation between individual sheets varies according to the type of interlayer cations present (monovalent cations like Na^+ cause more expansion than the divalent cations like Ca^{2+}), the concentration of ions in the surrounding solution and the soil moisture. Because the interlayer is open and hydrated, cations may be present within the interlayer to balance negative charges on the sheets themselves (Foth 1990). These cations between the layers are part of the cation exchange capacity of the soil. Smectites have a CEC of 80 to 150 $cmol_c kg^{-1}$ (Brady and Weil 2008).

Smectites are important minerals in soils in the temperate region because of their high surface area and relatively high adsorptive properties (Schulze 2002). The interlayers in smectites are not only hydrated, but are also expandable. Because of this characteristic, smectites are often known as the “swelling clays”. Soils that have high concentrations of smectites can undergo as much as a 30% volume change due to wetting and drying. The expansion upon wetting contributes to high degree of plasticity, stickiness and cohesion which makes the smectite soils difficult to cultivate. Wide cracks form in these soils when they are dry (Brady and Weil 2008).

Smectites have a lot of commercial uses. They can be utilized as lubricants, water proofing agents and binding agents for molding sands in metallurgical castings. Apart from that, they are also used to slow down the rate of water movement and chemical waste. Smectites can also be used as a decolouring agent for vegetable oil. They are a major component in the making of bricks, tiles and other building products (Olson *et al.* 2000).

Vermiculite clay

Vermiculite is a high-charge 2:1 phyllosilicate clay mineral. They are regarded as hydrated mica from which K^+ has been removed and replaced by Ca^{2+} and Mg^{2+} (FitzPatrick 1983). Though the charge in vermiculites can be both tetrahedral and octahedral, most vermiculites have mainly tetrahedral charge due to the substitution of Al^{3+} for Si^{4+}. Normally, around 0.6 to 0.9 out of 4 Si are replaced by Al. This negative charge must be balanced by the presence of positively-charged sites somewhere else in the mineral structure. Generally vermiculite is like smectite except for more tetrahedral charge (Troeh and Thompson 2005).

The presence of vermiculite in the soil allows Mg^{2+} ions in the interlayers to be exchanged with other cations, giving vermiculite an even higher cation exchange (100 to 200 $cmol_c\ kg^{-1}$) capacity for storing available plant nutrients (Brady and Weil 2008).Vermiculites do not swell and shrink very much like smectites, because the greater layer charge of vermiculites causes the exchangeable cations to electrostatically pull the layers together limiting the extent of layer separation. Vermiculites are also hydrated and somewhat expansible than smectite because of its relatively high charge. Vermiculite soils do not display the high shrink-swell characteristics of highly smectite soils.

Vermiculites also have a variety of commercial uses. They are often used to loosen and aerate soil mixes. When mixed with soil, vermiculites improve water retention and fertilizer release. Exfoliated vermiculite has a high insulation value and can absorb and hold a wide range of liquids. Exfoliated vermiculite is used in the friction brake linings market, high temperature insulation, loft insulation, fire proofing, sound proofing, various construction products, and animal feeds.

1.2.6 Forms of soil potassium

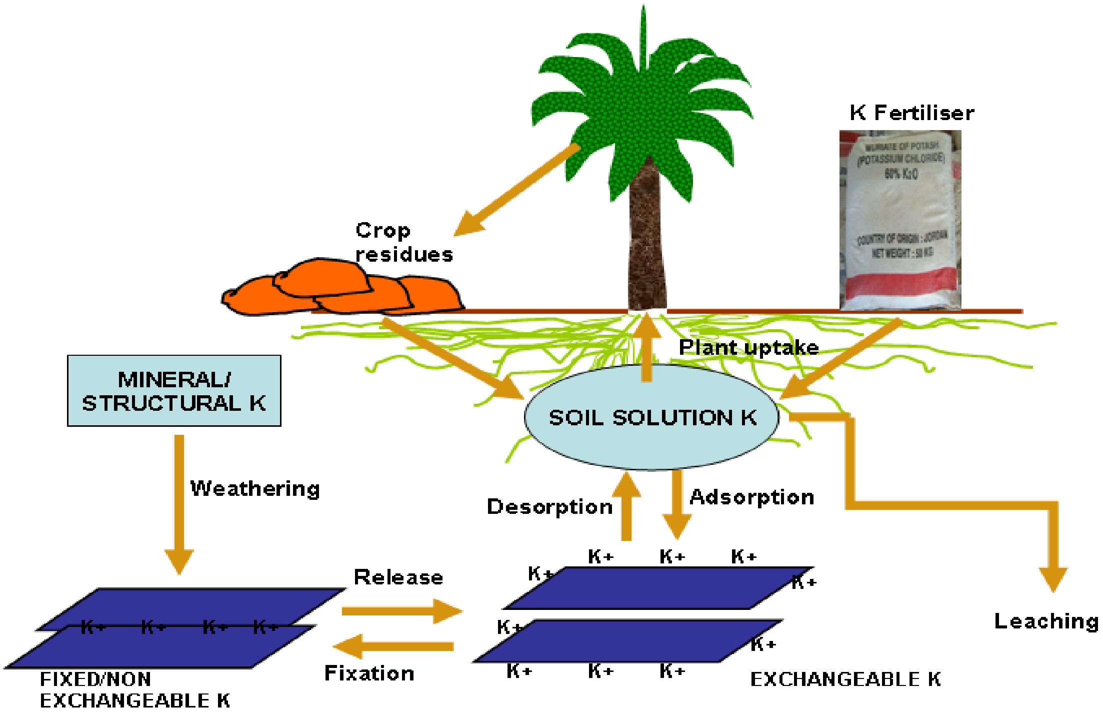

Figure 2. The Potassium Cycle

Potassium exists in four forms in soil (Figure 2). These forms, in increasing order of availability to the plants with their approximate amounts are: structural or mineral K (5000-25000 mg kg^{-1}); fixed and non-exchangeable K (50-750 mg kg^{-1}); exchangeable K (40-600 mg kg^{-1}) and K in the soil solution (1-10 mg kg^{-1}) (Sparks 2000, Gourley 1999). The amount of K in each of these forms is determined by the type and amount of clay, uptake of K by the plants, K fertiliser application, crop and leaching losses and the relative effectiveness of K fixation and release processes that occur in the soil (Kirkman *et al*. 1994).

Mineral K

Mineral K, also known as the structural K constitutes 98 % of the total K in any soil and its quantity depends on the composition of parent rocks and the stage of development of the soil (Sparks and Huang 1985). Mineral K is bound within the crystal structures of K bearing minerals such as micas, feldspars and volcanic glasses (Kirkman *et al*. 1994). As a result, it is assumed to be slowly available to plants, however, its availability depends on the levels of other forms of K, the degree of weathering of K bearing minerals like feldspars and micas (Sparks 1987). Most of these minerals are found in the coarser fractions of soils and have not undergone any alterations during soil development (Metson 1980). The degree of alteration is increases with decreasing particle size. The alteration of these K-bearing minerals forms the secondary layer silicates which retain some structural K.

Weathering of primary minerals that contain high reserves of K must occur first before considerable amounts of K becomes available to plants. The rate at which weathering takes place is dependent on the environment as well as the composition and structure of the primary minerals. While biotite and volcanic glasses weather easily, feldspars and other acidic volacanic glass weather slowly. Weathering of micas proceeds by other cations such as Mg^{2+}, Ca^{2+} and Al^{3+} replacing the interlayer K^+, which results in the formation of illite, vermiculite and smectite minerals. Feldspars and volcanic glasses weather through the process of hydrolysis and results in the formation of X-ray amorphous gels and crystalline clay minerals like halloysite (Kirkman 1981).

Non-exchangeable K

Non-exchangeable K differs from mineral K in that it is not bound within the crystal structures of the clay minerals. Instead, non-exchangeable K is trapped between the adjacent tetrahedral layers of dioctahedral and trioctahedral structure of micas, vermiculites and other clay minerals that fix K (Sparks 2000). Potassium is fixed when the binding power of the between clay and the surface of the clay surpass the hydration forces between the individual K^+ ions. This results in the partial collapse of the crystal structure which subsequently traps the K^+ ions, making the release of K a slow process (Classen *et al*. 1990).

Goulding (1987) mentioned several types of adsorption site for K^+ on clay minerals. These include the adsorption sites on the planar surfaces (p-positions), those on edge (e-positions), the wedge (w-positions), those in the interlayer sites (i-positions) and the cracked positions. Adsorption sites on planar surfaces have a low K^+ selectivity, while those on the edge and wedge positions have a medium K^+ selectivity. Adsorption sites in the interlayer and cracked positions have a high K^+ selectivity. Non-exchangeable and fixed K can also be found in the wedge zones of weathered micas and vermiculites and this K can only be exchanged with ions like NH_4^+ and H_3O^+, which both have a similar size to K^+.

The amount of fixed K is dependant on various factors like particle size distribution, types and amount of clay minerals and the addition and removal of K from the minerals. Addition of K to the soils with 2:1 clay minerals such as vermiculites and smectites results in a strong K^+ adsorption or fixation, whereas removal of K through leaching or plant uptake enables the release of K from the sites non-exchangeabe pool and the fixed K (Rich 1964).

Exchangeable K

The exchangeable K is electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and is readily exchanged with other cations and is available to plants (Sparks 2000). The distribution of K between negatively charges sites on the clay minerals is a function of the kinds and amounts of complementary cations, the anion concentration and the properties of the soil cation exchange materials.

The amount of K^+ attached to the exchange sites of the clay minerals depends on the kinetics as well as the thermodynamic factors. The affinity of the exchange sites for K^+ is related to the nature of the soil surface and the concentration of other exchangeable cations. The displacement of exchangeable K^+ by Ca^{2+} is important in soils where Ca^{2+} is present in large quantities, which could result in leaching of K^+ (Parfitt 1992).

Solution K

Soil solution K is readily available and plants and soil microbes take up K^+ mostly from the soil solution. The level of K in the soil solution at any given time is generally low, and depends on the depletion (plant uptake and leaching) as well as the replenishment from exchangeable and non-exchangeable K forms. The quantity of soil solution K also depends on the buffering capacity of the clay minerals (Kirkman *et al.* 1994). Well buffered micas and vermiculites maintain the level of the solution K, while weakly buffered allophanic clays do not readily replenish the soil solution.

Equilibrium and kinetic reactions exist between these forms of K that affect the level of solution K at any particular time, and thus the amount of readily available K for plant uptake (Sparks 1987). Solution and exchangeable K are in an extremely dynamic equilibrium because a change in one causes an immediate change in the other.

1.2.7 Methods of evaluating K availability in soil

Various methods have been described in the literature to measure different forms of soil K (Table 1). K in the soil solution can either be measured as a soil solution K concentration, or by using 0.005 M $CaCl_2$ to extract K. The method of extracting K using 0.005 M $CaCl_2$ is well suited for routine determination (Moody and Bell 2006).

K extraction from the exchangeable pool using 1 M NH_4OAc is more widely used than the other two method in Table 1. Soil solution K is not measured separately but included along with the extracted (soluble and exchangeable) because solution K is a small fraction of the total extractable K using the 1 M NH_4OAc-method (McLean and Watson 1985). Other methods of measuring exchangeable K include the Mehlich no. 1 method (i.e. 0.05 M HCl in 0.025 M H_2SO_4). This method is considered best for acid soils with low CEC. The Mehlich no. 2 method is also used in a wide range of soils. Apart from extracting exchangeable K, it can be used to measure P and other trace elements from the same extractant. Gillman *et al*. (1982) however mentioned that there is little difference in the amount of exchangeable K extracted using these different methods.

A number of extractants have been used to study the rate of release of non-exchangeable K from soils and clay minerals. These include dilute salt solutions (Dhillon *et al.* 1989; Lopez-Pineiro and Garcia 1997), cation exchange resins (Martin and Sparks 1983; Dhillon and Dhillon 1990), organic acids (Song and Huang 1988; Zhu and Luo 1993), sodium tetraphenyl boron (Dhillon and Dhillon 1992; Cox and Joern 1997), nitric acid (Gil-Sotres and Rubio 1992), and electro-ultrafiltration (EUF) technique (Rubio and Gil-Sotres 1996).

The amount of K present in each form by using any of the analytical procedures in Table 1 is determined by factors like types and amounts of clay, plant K uptake, fertiliser additions, crop and leaching losses and the fixation and release characteristics of the soil (Kirkman *et al.* 1994).

Table 1. Methods used to measure various conceptual soil K pools (Moody and Bell 2006)

K pool in soil	**Methods**	**References**
Solution K	Soil solution K	Menzies and Bell (1988)
	0.01M $CaCl^2$ extraction K	McLean and Watson (1985)
Exchangeable K	1M NH_4Cl	McLean and Watson (1985)
	1M NH_4OAc	McLean and Watson (1985)
	0.1M $BaCl_2$ + 0.1M NH_4Cl	Gillman and Sampter (1986)
Mineral (fixed) K	Boiling HNO_3	Martin and Sparks (1985)
	Sodium tetraphenyl borate	Cox *et al*. (1996)

1.2.8 Factors affecting K availability in clay soils

Availability of K to plants is influenced by soil and plant factors. Soil factors include those influencing K diffusion and exchangeable K, soil solution parameters and plant water use related to mass flow (Haby *et al*. 1990). Factors related to the plants include plant age, rate of transpiration, root distribution and proliferation, root morphology and growth rate and root absorption mechanisms. Some of these factors will be discussed in this section.

Mass flow, diffusion and retention by exchange complex

The most available form of K for plant nutrition is the one present in the soil solution. Despite this, the concentration of soil solution K is very low at any one time. Potassium in the soil solution K is replenished by K fertilizer application or other forms of K. The soil solution mobilizes K^+ to the plant roots for uptake (Brady and Weil 2002), however, only a small proportion of the required K is obtained by direct contact through root interception (Stucki and Huo 1997). A large proportion of it is transported in the soil solution to the roots via two processes; mass flow along with water molecules or diffusion along a concentration gradient built up by the absorbing roots (Sparks 2000; Troeh and Thompson 2005). These two processes have an important influence on K availability. From these two processes, diffusion is the dominant mechanism of transportation of K to the plant roots (Classen *et al*. 1990; Foth 1990). Diffusion and K uptake by the plant roots from the soil solution are also influenced by the concentration of K in the soil solution. Potassium uptake by the roots is increased when the concentration of K in the soil solution is high (Sparks 2000).

Clay minerals and organic matter possess different exchange sites that hold onto the K^+. This exchangeable K is in equilibrium with the K^+ ions in the soil solution. Any decrease in the soil solution K concentration due to plant uptake or leaching will result in the release of K from the soil exchange sites (Stucky and Huo 1997). Evidence of exchange sites with different selectivity for K^+ ions was obtained by Bolt *et al.* (1963), in which three different sites were recognized. These were the basal surface, edge-interlayer and the interlayer sites. Potassium ions held on the basal surface and edges are exchangeable with other cations while those at the interlayer sites have high K^+ selectivity and very slow K release (Bolt *et al.* 1963). The ability of any soil to supply K over a growing season depends on the quantity of exchangeable K held on the exchanges sites. The removal of K^+ and other cations from the exchange site involves a cation exchange reaction (Best 1977). It is the energy of this exchange that determines whether K supply is enough for adequate plant nutrition.

Fixation of K into the interlayers of 2:1 clay minerals

Potassium fixation is the movement of K ions from the soil solution into mineral forms (Troeh and Thompson 2005). When the concentration of K^+ in the soil solution increases due to K fertiliser addition or K release from the minerals through weathering, the equilibrium is shifted resulting in the fixation of K^+ onto the specific sites on the clay minerals. Fixation of added K may be appreciable in soils that contain substantial amounts of K depleted micaceous and vermiculite minerals. Page *et al.* (1963), for example, demonstrated the need for large K fertiliser applications of 175 kg K ha^{-1} to high K fixing soils in California to alleviate K deficiency problems in cotton.

It was initially believed that fixation of applied K drastically reduces plant available K. However, the negative effect of K fixation on plant nutrition was challenged by several researchers who all suggested that fixation of added K is beneficial because it assists in retaining and recycling K and protecting K from leaching (Reitemeier 1951; McLean and Simon 1958a; Troeh and Thompson 2005). Fixed K should not be seen as lost but as stored K since it eventually becomes available for plant uptake.

Soils containing 2.1 type of clay minerals can fix considerable amounts of K (Brady and Weil 2008; Sparks and Huang 1985). The major clay minerals responsible for K fixation are smectite, vermiculite and fine-grained micas (illite). However, smectites and vermiculites can fix considerable amounts of K compared to the other 2:1 clay minerals because they have high surface area and very high negative charge density compared to the other 2.1 clay minerals (Guzel *et al.* 2001; Carter & Singh 2006; Brady and Weil 2008). The very high negative charge density in these two 2:1 clay minerals increases their capacity to absorb cations like K, thus contributing to their high K fixing capacity. Vermiculites however have greater fixing capacities than smectites and other montmorillonites (Malla, 2002). Through fixation, smectites and vermiculites can hold up to 3 tonnes of K per hectare in fertile soils, making them behave like huge renewable K reservoir (Barre *et al*. 2007). Furthermore, soils with high fixing capacity are capable of sustaining available K to the plants over many years of production, thus buffering removal of K by the plants.

Several factors influenced K fixation in soils and these include type and abundance of clay in soils, wetting and drying, freezing and thawing, soil pH, K fertiliser application, soil moisture content and the concentration of K ions as well as that of other competing cations such as Ca and Mg (Brady and Weil 2008; Sparks 2000). Of all these factors, K fixation is greatly affected by the type and amount of clay. The major clay minerals responsible for K fixation are smectites, vermiculites and weathered micas. Vermiculites are the mainly responsible for K fixation in acid soils, whereas weathered micas fix K in both moist and dry conditions. Smectites fix K only under dry conditions (Sparks 2000).

Release of K from the interlayers of 2:1 clay minerals

The release of K from interlayers of 2:1 clay minerals is considered to be the reverse process of fixation. Non-exchangeable K (fixed K) is only released to exchangeable pool when the K level in the exchangeable and soil solution pool is depleted by either crop removal or other factors like leaching (Tisdale *et al.* 1993). Unlike the fixation process, K release is a slow process because of the strong binding of the K ions. However, plants differ in their ability to take up fixed K. Release of K from the interlayers of the clay minerals is limited by the rate of diffusion of K ions and the other cations with which it exchanges through the interlayer space. Generally, the rate of K release increases when the K concentration in the solution decreases. Soil properties such as texture and structure that alter K concentration in the soil solution also influence the release of K from the non exchangeable (fixed) pool (Munn *et al*. 1976).

Fixation and release of K by clay minerals are closely related to the soil pH and the CEC (Mengel 2006). When there is an increase in the soil pH, the H ions are replaced from the exchange sites by the K ions resulting in a subsequent increase in the fixed K thereby reducing the amount of K in the soil solution. Similarly, clay soils with higher CEC will attract more K ions, thus these soils have large reserves of fixed or non-exchangeable K which are slowly available for plant uptake (Brady and Weil 1999; Gourley 1999).

Kinetics of K release from interlayers of 2:1 clay minerals

Research in soil K is now being focused mainly on the kinetics of K release to labile forms than the previous interest on simple measurements of exchangeable or non exchangeable forms. Most studies on Kinetics of K release from non-exchangeable form considered the effects of the mineralogy of the soil and the concentration of K in the different K pools and not so much on the K fertilizer effect.

The concentration of K in the soil solution and that absorbed by the plant roots is affected by equilibrium and kinetic reactions among the various forms of K (Brady and Weil 1999; Kirkman *et al*. 1994; Moody and Bell 2006) (Figure 3). Continuous supply of K to the plants is only ensured when the rate of K released to the soil solution and transported to the roots keeps pace with the rate of nutrient uptake by the roots. The rate and direction of reactions between the soil solution and the exchangeable pool of K influence whether applied K is absorbed by the plant roots, leached, converted or released into exchangeable or non-exchangeable K phase. Thus it is important to know whether K release rates from the interlayers of K-rich 2:1 clay minerals are fast enough to supply K needs of the plants.

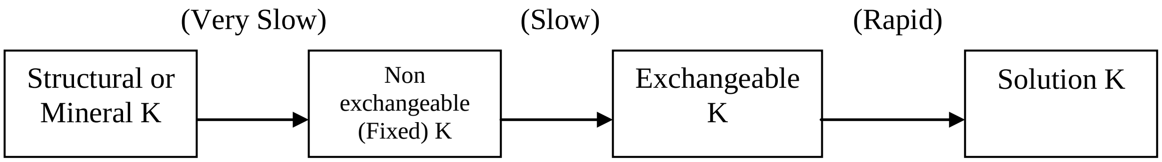

Figure 3. Equilibrium relationship between the three K pools in soils.

The rate and magnitude of release is influenced by the degree of exposure of edges of the 2:1 clay minerals to the soil solution and the position of non-exchangeable K with respect to the outer layers (Sparks 2000). This is the reason why the rate of release from non-exchangeable K is slow in some clay soils, limiting crop yield while in other clay soils release is rapid to meet the K demand of the crop during the growing season. Srinivasarao *et al*. (2006) studied release kinetics of non-exchangeable K on six soil series of India and found that the release of non-exchangeable K was greater in smectite soils than in illitic soils. K release was greatest in surface horizons of smectite and illitic soils, whereas subsurface soils had larger K release in kaolinitic soils. Eick *et al*. (1990) also mentioned that the kinetics of K fixation and release on montmorillonite are rapid whereas that on vermiculites and micaceous minerals are very slow.

The ability of soils to release K from the non exchangeable to the labile form has been studied using various techniques (Havlin *et al*. 1985; Sparks and Jardine 1981). Batch techniques and miscible displacement are popular and have been used often with great success and are also known to come up with similar results when the similar time intervals are used. However, the batch method is used more frequently than miscible displacement. With the batch method, the absorbent and the desorptive are mixed then separated to provide a clear supernatant for analysis. Alternatively, K release from the non exchangeable to exchangeable form is simulated using extraction with Ca-resin, which represents the plant roots.

The rate of release of K from the non exchangeable forms depends 3 factors; quantity of the K bearing minerals present, amount of edge exposure to the soil solution, and the distance which the K^+ must travel to reach the outer edge of the soil colloid. As soon as the exchangeable K is removed to some critical level unique for that soil, further growth and K uptake by the plants may be regulated by the rate of release from the non exchangeable pool. The rate of release may in some cases limit yield while it may be very rapid in some cases to meet the plant demand for K. These differences are due to the type of parent material present in the soil.

Cation exchange capacity (CEC)

Cation exchange capacity is the net ability of a soil to hold, retain and exchange cations such as Ca^{2+}, Mg^{2+}, K^+, Na^+, NH^{4+}, Al^{3+} and H^+. The amount of clay or humus determines the CEC of any soil. Clay has a greater capacity to attract and hold cations because of its chemical structure (Bray and Weil 2002). CEC varies with the type of clay minerals depending on the clay content, types of clay and organic matter content. Each clay type has different types of CEC of soils (Tan 1994). For instance, vermiculites have the highest CEC, followed by smectites, illites and kaolinites (Table 1).

Table 2. CEC Values for different soil colloids

Soil Colloid	CEC (meq/100g)
Humus (humic acids)	>150
Vermiculite	150
Smectite	100
Illite	30
Kaolinite	10
Sesquioxides	4

Source: Tan, 1991

Likewise, CEC of the soil reflects on the soils ability to hold K and other cations and store them in the soil for plants uptake. Clay surfaces are negatively charged and they attract positively charged cations like K^+, Ca^{2+}, Mg^{2+}, Na^+ and H^+. The negative surface charges attract the positively charged cations and prevent them from leaching down the soil profile (Brady and Weil 2002). Soils with high CEC have a much lower percentage of cations in the soil solution, thus are far less susceptible to leaching. The positively charged cations that are retained can then be replaced or exchanged by other cations in the soil solution. Through the cation exchange process, K is constantly available for plant growth, so long as the soil contains adequate available K at the start of the growing season. The availability of K increases as the percentage of the exchange sites occupied with the K^+ increases (Brady and Weil 2002). Generally, the higher the CEC of the soil, the greater the storage and supplying power of K.

Influence of other cations on K availability

The availability of K in soil is greatly influenced by other exchangeable cations such as Ca^{2+} and Mg^{2+}. K availability and uptake is reduced as Ca^{2+} and Mg^{2+} levels are increased, and the opposite happens when the available supply of K is increased. Thus availability of K is more dependent on its concentration relative to Ca^{2+} and Mg^{2+} than on the total quantity of K present (Tisdale *et al*. 1993).

Influence of other cations on K uptake

Plant roots take up nutrients directly from the soil solution which is saturated not only with K ions, but also with Ca, Mg and Na. K uptake depends to a large extent on its concentration relative to these other cations, thus excessive Ca or Mg or an imbalance between these two cations and K can reduce K uptake. Bethelsen *et al*. (2006) reported that severe deficiency of K and Mg on oil palm in Bialla, West New Britain Province was due to high exchangeable Ca in the soils. High quantities of K and Mg fertilizers must be applied in these soils. Likewise, high Mg concentrations in the exchange complex triggered K deficiency in the south-eastern part of the Papuan region (Bleeker 1983), therefore high K rates with N must be applied to increase crop yield.

Experiments, in which limestone (Ca source) was applied to increase soil pH and improve soil structure, also reduced K availability to the plants (Gourley 1999). This is because liming increased plant growth and thereby boosting the demand for potassium. However, investigations in Hawaii, New York and Alabama (Reitemeier 1951, quoted in Troeh and Thompson 2005) reported that addition of Ca to acid soils improved K uptake. The Ca ion was more strongly attracted by cation exchange than the K ions, therefore adding Ca in the form of lime can move exchangeable K out into the soil solution. The ratio of Ca-K in soil solution is much narrower than the exchangeable cation ratio because Ca is held more tightly on the exchange sites. However, plants containing twice as much potassium as calcium show a tenfold preference for absorbing K over Ca.

Not all cations involved in cation exchange reactions are held with equally tenacity by exchange sites. Some cations are held more tightly than others and are less likely to be displaced from the clay surface. This is influenced by the charge and the hydrated radius of the cations. For instance, a cation with higher charge and smaller hydrated radius will attract itself tighter to the exchange site than a cation of lower charge and larger hydrated radius (Brady and Weil 2002). Therefore K ions are less tightly held than Al, Ca and Mg ions.

The selectivity of clay minerals for K also depends on the K adsorption site. Adsorption sites on planar surfaces have low K selectivity, while those on the edge and wedge position have medium K selectivity. Interlattice and crack positions have high K selectivity (Kirkman *et al*. 1994). Potassium held at the interlattice positions are generally non exchangeable or fixed. Fixation of K does not occur when most of the planar positions are occupied by K. This scenario is reached only when there is adequate concentration of K in the soil solution. Therefore, availability of K increases as the exchange sites occupied with K also increases.

Soil moisture

Soil moisture affects K uptake through its effects on root growth and activity. Increasing the soil moisture increases the diffusion of K ions in the soil solution and the uptake efficiency of applied K fertilizer (Stucky and Huo 1997). Low soil moisture on the other hand limits K diffusion and uptake because K movement into the roots is reduced. Therefore, crop response to K fertilizers is often greater during drier periods than in wet seasons (Mengel *et al*. 2001).

Too much water in clay soils is more limiting to K uptake than too little water. Mackay and Barber (1985) reported that increasing the moisture content above the optimum level resulted in slow root growth due shortage of oxygen. This is because water movement down the soil profile is slow, even when the soil is completely saturated. Additional input of K fertilizer is required to counterbalance the diminished nutrient uptake capacity by the plant roots (Troeh and Thompson, 2005).

Wet and dry cycles promote potassium fixation and reduce potassium availability in soils containing 2:1 clay minerals, particularly vermiculites and smectites. The clay minerals expand and contract when the soil is wet and dry respectively. When the clay soil is dry, the interlayers of the 2:1 clay minerals contract and thus trapping the potassium ions making them temporarily unavailable for uptake. Zeng and Brown (2000) in their study on soil potassium mobility and uptake by corn under different soil moisture regimes concluded that wet and cycles enhance soil potassium fixation, reduce soil potassium mobility, and therefore reduce potassium uptake by corn. Flooding of dry lowland soils containing vermiculite, smectite, illite and other 2:1 layer clay minerals increased K fixation and decreased soil solution concentration. The proportion of added K fertilizer that was fixed in the soil ranged from 46-56 % in a wet and dry cycle and fixation was linear with increase in the rates of K added up to 25 mM K kg^{-1} of soil (Regmi *et al*. 2002).

K absorption is also related to water in the soil and is increased if water is added to the dry soil. However, when the soil becomes too wet, K absorption is reduced due to lack of oxygen supply.

This is because the energy required by the plant roots comes from oxidation of sugars transported from the tops to the roots of the plants (Troeh and Thompson 2005). K absorption is rapid when the water content is near the field capacity.

Plant factors

A plant root system is often as unique in structure as its other parts above the ground. However, the roots are more irregular in shape. The root development of any plant into a genetically determined configuration is greatly influenced by the chemical and physical environment. Because K enters any growing plant through the root system, any factor that affect the nature and development of the root system also affects potassium uptake.

The very rapid growth of root hairs in the young part of the root zone increases the root's surface area. Because root hairs are the main site for both water and nutrient adsorption, an increase in the surface area will mean that the plant roots are able to be supplied with more K by the process of diffusion through the water films instead of actual contact of the roots with the K ions on the soil particles (Mengel 2006; Nelson 1985). Potassium is taken up more in the surface layer of the soils because of highly concentrated root mass which are also responsible for direct K uptake.

Monocotyledons, especially cereals, utilise K reserves better than dicotyledons and this is attributed mainly to the root hairs. Root hairs can double the surface area of the root system and contribute substantially to nutrient uptake, especially nutrients like K which have low mobility and are required in large quantities (Jungk 2001).

Root length differs greatly between plant species and influences their ability to absorb K from the soil. For example, ryegrass could take up exchangeable K longer than red clover because it has longer and denser root system allowing it to grow and survive at a relatively low K concentration (Steffens and Mengel 1985).

Surface applied K may be leached to the subsoil but can be used later by deep rooted crops. This uptake of K from subsoils can affect the response of crops to surface applied K fertilizer, for instance no response to added K due to mining of K from the subsoil. If plant roots can reach K supply that is retained in deeper layers, they can utilise them in severe conditions. In an experiment in which 42K was introduced, there were large differences in the rooting depth, root distribution and 42K uptake amongst plant species. All the plant species obtained their K from the soil surface layer, however the deep rooted species utilised K in the sub-soil to a greater extent than the shallow rooted species (Gourley 1999).

Root elongation is affected by soil moisture. At the optimum soil moisture content, root elongation is promoted which in turn improves K uptake. When the moisture is further increased beyond the optimum soil moisture content, root elongation is reduced leading to lower K uptake. Kafkafi (1991) reported that the rate of root elongation in annual crops is crucial for the uptake of cations like K that are tightly adsorbed to the soil.

The ability of plants to take up K appears to be related to the plant species. For example, rye grass could take up non-exchangeable K longer without yield reduction, whereas red clover could not. This is because rye grass has a longer root system which would allow it to grow at a relatively low K concentration (Mengel 1985). The difference in root mass, length and morphology between monocots and dicots could be the reason why monocots feed better than dicots from the non-exchangeable K.

Marschner (1995) mentioned that roots are smooth and cylindrical in friable soils but root growth is impaired in compact soils, where the roots are stubby, thus reducing K uptake. Soil structure also determines root system morphology and hence K uptake.

The supply of nutrients and other resources for plant growth are intrinsically heterogeneous and plant roots have developed foraging mechanisms such as proliferation to assist them obtain adequate amounts of nutrients from the soil (Robinson 2001). Therefore plants are found to grow preferentially in areas of the soil with high concentration of inorganic nutrients.

Plants that do not change their root morphology and physiology in response to local nutrient enrichment will acquire fewer nutrients. This again depends on the plant species, the soil physical and chemical properties and the fertilizer and management practices. Jackson and Caldwell (1989) when studying the timing and degree of root proliferation for three perennial species found that there was root proliferation with increased root growth from thin, laterally branching roots in zones of N and P enrichment only but not K. Drew (1975) compared the effects of localized supply of phosphate, nitrate, ammonium and K on the root system of barley and also found that localized promotion of both first and second root laterals were directly related to phosphate, nitrate and ammonium but not K. In contrast, Qifu *et al*. (2007) reported that roots of wheat proliferated in compartment fertilized with both P and K. They also found that the root growth of wheat fertilized with both P and K in one compartment of the root-split system was significantly improved.

1.3 Conclusions

Potassium is essential for plant growth and yield. Potassium in soil solution and exchangeable form are the two forms that are readily available for plant uptake. Non available forms (non exchangeable and mineral) can also be released to the soil solution through weathering and other processes but at a much slower rate. These forms of K are always in equilibrium with each other so that a change in one will result in a change in the other. K availability in soils with 2:1 clay minerals (especially vermiculite and smectite) and its uptake by the plant roots is dependent on various factors such as:

- concentration of K in the soil solution,
- fixation and release by the clay minerals and the kinetics of release of trapped K in the interlayers of these clay minerals,
- Influence of other cations like Al, Ca and Mg on K uptake and retention
- Soil moisture status
- and root factors such as distribution and length and proliferation.

Therefore, an understanding of these factors limiting K availability and its uptake is of paramount importance in order to alleviate K nutrition problems in the 2:1 clay mineral soils.

CHAPTER TWO

2 Site description

2.1 Introduction

The research described in this thesis involved field work in Papua New Guinea (PNG) and laboratory work in Australia, using soils collected from the PNG field sites. The field sites were two oil palm fertiliser trials (trials 502b and 504) in Milne Bay Province (Figure 4). The trials are run by the PNG Oil Palm Research Association (PNGOPRA) in collaboration with the plantation and milling company Milne Bay Estates (MBE). Milne Bay Estate is one of the four oil palm companies in PNG owned by CTP Holdings, a joint venture between Cargill and Temasek Holdings. The company was first established in 1983 as an oil palm and cocoa producing and exporting company. Milne Bay Estates now covers an area of about 12 000 ha of oil palm plantings, extending from Giligili estate in the east to Mariawatte estate in the west. The company operates a 30 tonne per hour palm oil mill, including storage and loading facilities in Alotau, the township of Milne Bay.

Physical and chemical properties of soils in Milne Bay are well documented (Bleeker 1983; Bleeker 1988; Hartley 2005). The soils were grouped into three major categories; floodplains, interfluves and terraces and moderate to steeply sloping hilly terrain. Soils in the flood plains are recently formed alluvial soils with poor profile development, generally of clayey texture. The interfluves and terraces have poorly to imperfectly drained soils with gravelly top soils and clayey subsoils. Slightly to moderately weathered soils with slightly acid to acid soils (pH 4-5) exist on moderately to steeply sloping hilly terrain. Fertiliser trials have been established on a range of soil types throughout the plantation.

Figure 4. Map of Papua New Guinea, indicating location of Milne Bay Province. (Source: ***www.lib.utexas.edu/maps/papua_new_guinea.html***)

2.2 Trial 502b and 504 descriptions

2.2.1 Trial 502b

Trial 502b is located in block AM2160 (previously 6503), in Waigani estate, which is about 15 m.a.s.l and at the latitude and longitude of 10° 18' 36" S and 150° 15' 32" E, respectively. The soil in trial 502b is categorised under the Plantation family, which is derived from recent alluvial origin. It is located on the 'interfluves and terraces' area of an extensive alluvial plain. The plain is about 3 km wide in the west, but increases to 12 km wide in the east. The major features of this plain includes floodplains, drainage depressions, interfluves and low terraces. The plain is surrounded by strongly dissected terraces which merge into hilly terrain at higher altitudes (Bleeker 1988).

The oil palm block was planted in 1986 at 127 palms per hectare. The trial, however, commenced in 1995 to investigate the response to N, P, K in factorial combination, with and without empty fruit bunches (EFB), with view of using EFB to replace or supplement inorganic fertilizer. The EFB is the empty bunch after the oil palm fruits are removed from the oil palm fresh fruit bunch for processing. It is applied in the oil palm plantations as a form of mulch.

The trial was laid out using a factorial design with 4 levels of ammonium sulphate (SOA), 4 levels of potassium chloride [Muriate of potash (MOP)], 2 levels of triple superphosphate (TSP) and 2 levels of empty fruit bunches (EFB) (Table 3). The 64 treatment combinations were not replicated, but split into four blocks, with each block with 16 plots per block. Each plot had 16 core palms, which were surrounded by one guard row, giving a total of 36 palms per plot. Fertiliser amounts were split into 3 applications in a year and applied anytime between April and October.

Table 3. Amount of fertiliser and EFB used in Trial 502b

Fertiliser type	Amounts (kg of fertilizer palm^{-1}year^{-1})			
	Level 0	Level 1	Level 2	Level 3
SOA (N)	0.0	2.0	4.0	6.0
MOP (K)	0.0	2.5	5.0	7.5
TSP (P)	0.0	2.0	-	-
EFB	0.0	300	-	-

Significant ($p<0.05$) effects on yield and tissue nutrient concentrations were observed with the SOA, MOP and EFB application. TSP fertiliser did not have any significant effects on both yield and tissue nutrient concentration (Figure 5).The oil palm yield responded more positively to N fertiliser in 2002 and thereafter, which the plots with highest level of N fertiliser yielded better than the plots that received no N fertiliser. The highest level of N had an average of 25.4 t ha^{-1} of fresh fruit bunch compared with 21.8 t ha^{-1} from the plots that received no N fertilizer, a yield difference of 5 t ha^{-1}. Leaf N levels also responded well to N fertilizer.

The oil palm yields responsed significantly to MOP application from 2003 onwards. In these years (2003-2007), the yields favoured the plots which received the highest rate of MOP (7.5 kg palm^{-1}year^{-1}). The highest rate of MOP had an average of 24.2 t ha^{-1} of fresh fruit bunch compared with 21.0 t ha^{-1} from the plots that received no MOP fertilizer, a yield difference of 3.2 t ha^{-1}. MOP also had a significant effect on the K levels in the oil palm fronds (Rachis K concentration). The concentration of K in the rachis was increased to 1.5 % with MOP application, whereas the K concentration in the rachis was below 1.0 % in the treatment where MOP was never applied.

EFB application increased yields by 3 tonnes in plots where N and K fertiliser was not applied and could be a substitute for these two nutrients, especially K. Since 2004, there had been very little response to TSP application. The response to TSP was significant only in 2005 and was probably an aberration.

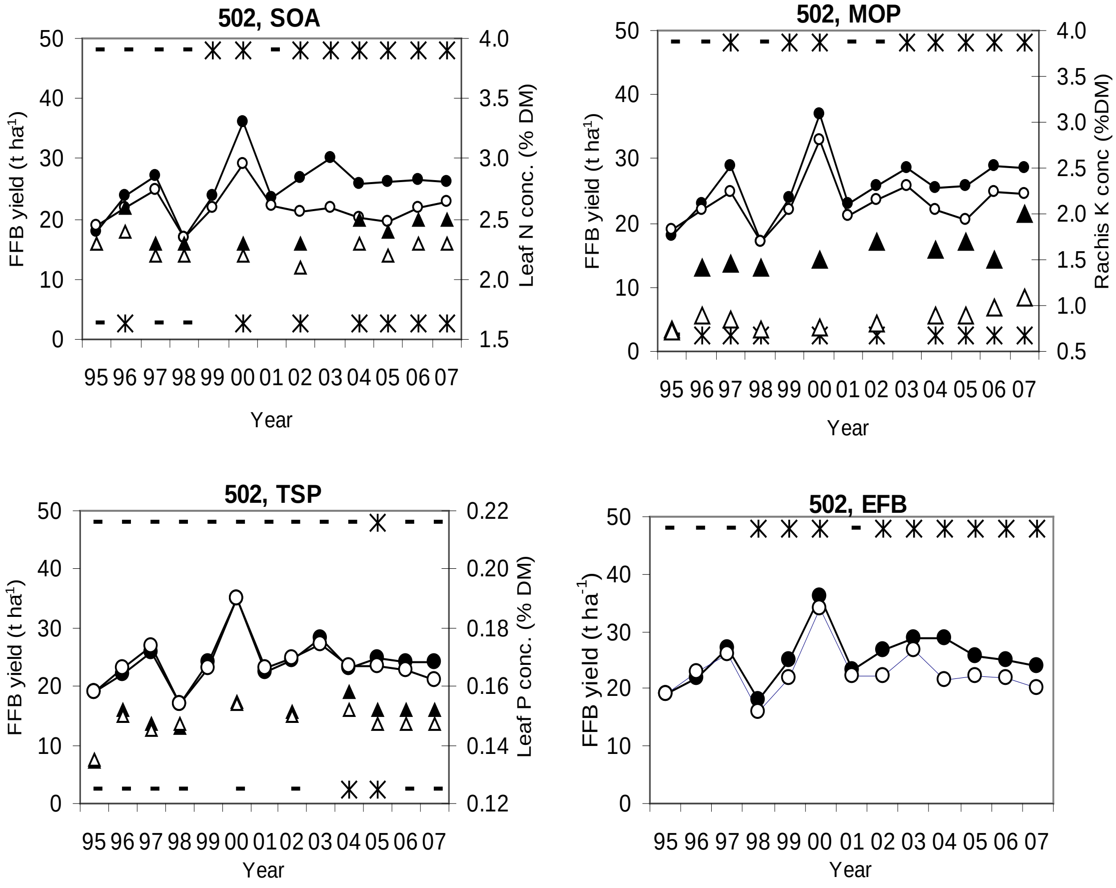

Figure 5. Trial 502b, main effects of SOA and MOP on yield and tissue nutrient concentration over the duration of the trial. (Lines are FFB yields and triangles are tissue concentrations. Full symbols represent the maximum level of application, and empty symbols zero application. Symbols along the top of the graph indicate significance of the main effect on yield, and along the bottom indicate significance of the main effect on tissue concentration. Stars indicate significance and dashes non-significance)**.**

2.2.2 Trial 504

Trial 504 was set up in blocks 0610, 0611, 0612 of Sagarai estate. It is approximately 5 m above sea level and has a latitude and longitude of 10° 25' 53" S and 150° 11' 27" E, respectively. The trial is located on the floodplains of the Sagarai River which are poorly drained, although levee banks and low terraces are also found in the eastern part of the estate (Bleeker 1988). The predominant soil found in this area is the Tomanau family, derived from recent alluvial origin, with deep clay loamy soils and reasonable drainage status.

The trial block was planted in 1991 at the planting density of 127 palms. Fertiliser treatment application commenced in 1994, with the aim of testing oil palm yield and growth response to N and K in the Tomanau soils. The trial was laid out in a factorial design with four levels each of N and K (Table 4), giving a total of 16 treatment combinations. The 16 treatments were replicated 4 times, giving a total of 64 plots. Each plot had 16 core palms, which were surrounded by one guard row, giving a total of 36 palms per plot. Similar to Trial 502B, the fertiliser treatments were applied in 3 doses per year.

Table 4. Amount of fertiliser used in trial 504

Fertiliser type	Amounts (kg of fertilizer palm^{-1}year^{-1})			
	Level 0	Level 1	Level 2	Level 3
SOA (N)	0.0	2.0	4.0	6.0
MOP (K)	0.0	2.5	5.0	7.5

The fertiliser main effects on the yield and tissue nutrient concentration are shown in Figure 6. The yield and the tissue nutrient concentration responded well to the fertiliser treatments, particularly SOA. Since 2003, higher yields were obtained from the plots receiving N than those receiving no N fertiliser. The N fertiliser significantly increased N levels in the leaflets.

The response to MOP has been increasing over the last few years. The effect of MOP fertiliser although significant on the yield from 2004 to 2008, is less marked compared to the SOA. Generally, the plots with MOP fertiliser exhibited higher yield (26.2 t ha^{-1}) that those without MOP (22 t ha^{-1}), a difference of 4.2 t ha^{-1}. Similarly, MOP fertiliser significantly increased K concentration in the rachis to over 1.5 % in those years where rachis K was analysed. The rachis K levels were low (<1.0 %) in the zero K treatment. With very low values of K in the rachis in the plots without K fertiliser, the palms will be experiencing increasing K deficiency and the subsequent yield drop in the future.

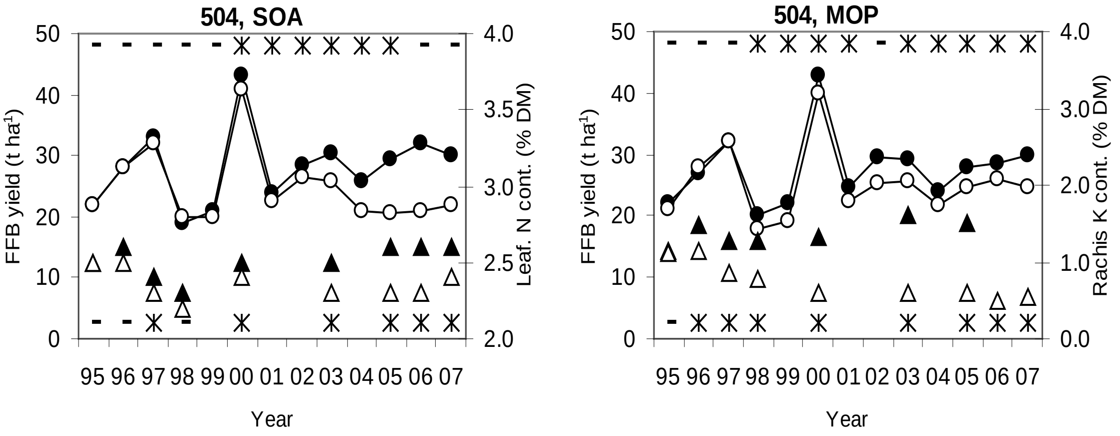

Figure 6. Main effects of SOA and MOP on yield and tissue nutrient concentration over the duration of Trial 504. (Lines are FFB yields and triangles are tissue concentrations. Full symbols represent the maximum level of application, and empty symbols zero application. Symbols along the top of the graph indicate significance of the main effect on yield, and along the bottom indicate significance of the main effect on tissue concentration. Stars indicate significance and dashes non-significance).

2.3 Climate

The climate of the field sites has been classified as lowland humid climate (Bleeker 1988; McAlpine *et al*. 1983). This type of climate has an annual rainfall range of 2000 – 3500 mm, with the temperature range of 23-30 °C, and covers most of the coastal lowlands of PNG.

The annual and monthly rainfall from 1987 to 2008 years is similar at the two sites (Figure 7, Figure 8). Both trial sites are approximately 0.5 km away from the Waigani and Sagarai estate office where the rainfall was recorded. The average annual rainfall for the period was between 2500-3000 mm, however 2008 was the wettest year with over 4000 mm of rain at both sites. There was no pronounced dry season at either site. The wettest part of the year is from March to August. Climatic parameters other than rainfall have not been recorded at the trial sites or nearby estates.

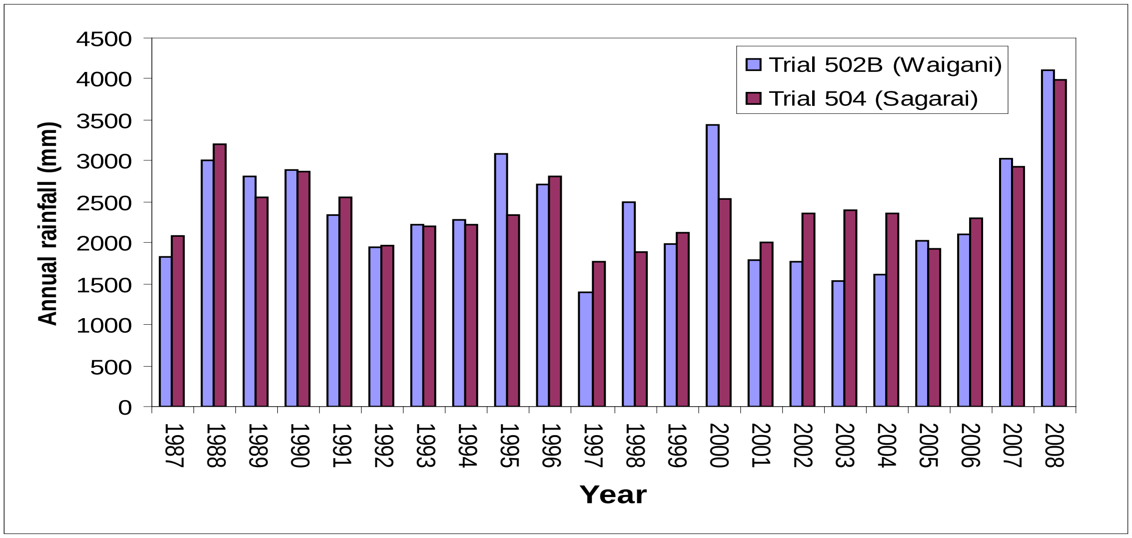

Figure 7. Annual rainfall recorded at Waigani and Sagarai estate for the last 23 years (1987-2008).

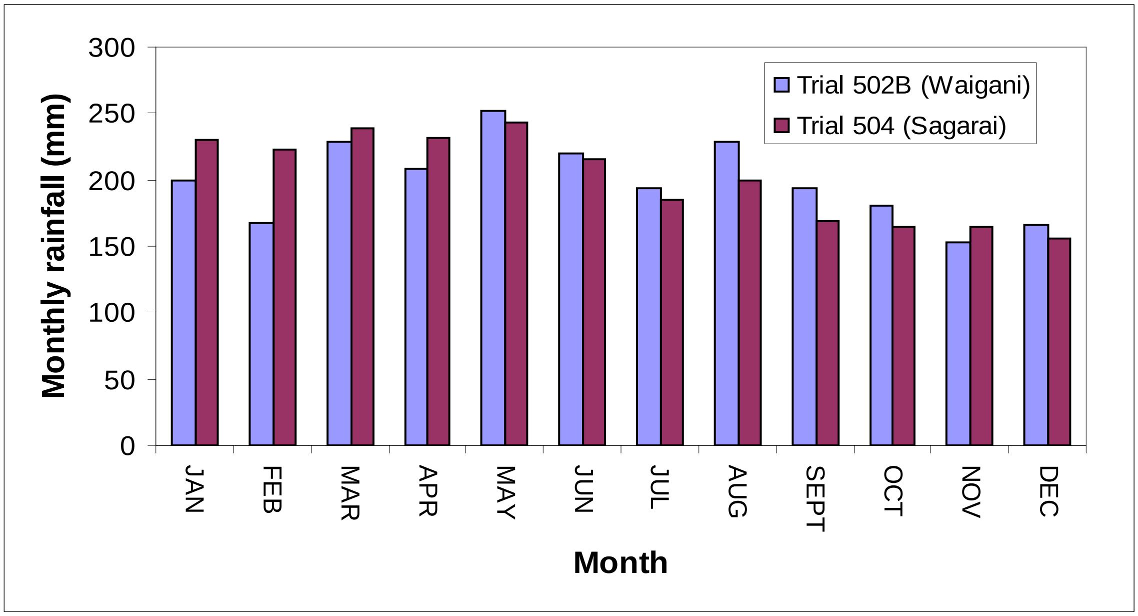

Figure 8. Monthly rainfall recorded at Waigani and Sagarai estate for the last 23 years (1987-2008)

2.4 Soil characteristics

2.4.1 Soil physical characteristics

In 2006, a pit was dug in the control plot of each trial for soil profile description. A brief description of the various depths in soil profile of each trial is described in this section (Table 5, Table 6).

The soil on which trial 502b is established is known as the Plantation family. The Plantation family comprises of recent alluvial origin deposited by the Waigani river. The soils of trial 502b are imperfectly drained, medium to fine textured soils with dark top soils, with mottling commonly found at the 50-100 cm depth. The soil profile (Table 5) is well structured clay throughout the profile (0-100 cm), whereas beyond 100 cm dark black brown course granular ferruginous/manganiferrous stony materials were found. From 0 to 40 cm depth the soil is dark grayish brown colour, light to medium clay. At 40-60 cm, some isolated layers of dark reddish brown granular concretions were found. The water table was at approximately 70 - 100 cm depth, but mottling below 30-40 cm suggests that water table can rise to that level.

Soils in trial 504 are of the Tomanau family, which is of recent alluvial origin, with deep clay loam soils and reasonable drainage status. These soils have little profile differentiation and become sandier at depth (Table 6). The soil colour in the first horizon (0-15 cm) was dark yellowish brown, then dark brown from 15 to 200 cm depth. Texture was light to medium clay throughout the profile and mottles were found at 30-85 cm depth. The water table was reached at 170 cm depth. Similar to trial 502b, drainage is a major problem here with water logged conditions during the wet season.

Table 5. Trial 502b soil profile description (control plot)

Depth (cm)	**Colour (moist)**	**Texture**
0-30	10YR3/2	light-medium clay, moderate structure sub-angular blocky (5-10mm), gradual change to
30-40	10YR 4/2	transitional zone, light-medium clay, moderate structure, some mottles appearing, gradual change to
40-60	10YR 5/4	light-medium clay, ~ 50% general distinct mottling (10YR 5/8), (some isolated layers of dark reddish brown granular concretions were found), gradual to
60-90	10YR 4/3	sandy light clay, weak structure, ~ 50% mottled (10YR 5/8) to
90-100	10YR 4/3	sandy light clay, weak structure, ~ 50% mottled (5YR 3/4) + many (20%) black medium size (5-15mm) ferromanganiferous and manganiferous nodules, some soft, some hard, clear change to
100+	dark black brown	coarse granular ferruginous/manganiferous stony material, 10YR 2/1

Table 6. Trial 504 soil profile description (control plot)

Depth (cm)	**Colour (moist)**	**Texture**
0-15	10YR 3/4	light - medium clay, moderate - strong structure
15-30	7.5YR 4/4	light - medium clay, moderate - strong structure
30-85	7.5YR 4/4	light medium clay with ~ 50% evenly distributed mottles of 7.5YR 5/6, strong structure parting easily into distinct polyhedral peds down to 2-5mm with clean shiny faces
85-150	7.5YR 4/4	as above but more gleyed patches and some weak ferruginous segregations
170	7.5YR 4/4	water table
170-200	7.5YR 4/4	medium clay, very mottled with many (20-50%) manganiferrous and ferromanganiferous, soft, medium (2-6mm) segregations

2.4.2 Soil chemical properties

Soil samples were taken from the 0-10 cm and 70-80 cm depth increments of the pits described above, for chemical analysis. Soil chemical properties were similar at the two sites (Table 7). The pH was slightly acid. Exchangeable K levels were below the commonly quoted critical level (20 mmol(+) kg^{-1}). Exchangeable Ca and Mg contents were high at both sites. These high Mg/K and Ca/K ratios are typical of clay soils in this region. Mg/K and Ca/K ratios greater than 10 and 20 respectively are unfavourable and can reduce K uptake by the plant roots (Bleeker 1988; Bleeker 1983). Organic C and extractable P concentrations were higher in trial 504 than trial 502b.

2.4.3 Soil mineralogy

The soil mineralogy and analysis for major elements is shown in Table 8. The soils in both trials are dominated by silica (SiO_2), making up almost 50% of the total soil mass. For both trials, a higher proportion of SiO_2 was present in the 70-80 cm layer compared to the top layer (0-10 cm). Silica concentration was slightly higher in trial 504 than trial 502b. Apart from SiO_2, there were also reasonable amounts of Al_2O_2 and Fe_2O_3 in both trials. K concentration was much higher in trial 504 than 502b. Trial 502b soil is dominated by smectite while vermiculite dominates in Trial 504 soil.

Table 7. Soil chemical properties for trial 502b and 504. Analytical methods are described in Chapter 3.

		Trial 502b		**Trial 504**	
		0-10 cm	70-80 cm	0-10 cm	70-80 cm
Exchangeable Ca	$mmol^+/kg$	333	304	309	264
Exchangeable Mg	$mmol^+/kg$	174	189	131	210
Exchangeable K	$mmol^+/kg$	1.2	0.7	1.8	1.4
Exchangeable Na	$mmol^+/kg$	6.7	7.5	4.7	5.1
CEC	$mmol^+/kg$	498	516	438	237
TPB Extractable K	mg/kg	142.9	89.6	258.5	321.9
EC	µS/cm	84	28	72	34
pH (water)		5.81	6.52	5.96	6.81
pH ($CaCl_2$)		5.69	5.99	5.53	6.06
Organic C	%	4.80	0.60	5.12	0.99
Olsen P	mg/kg	13.87	4.24	80.62	106.0

Table 8. The soil mineralogy and total elemental analysis from the 0-10 and 70-80 cm depth increments from trials 502b and 504 (from Webb *et al*. 2009).

		Trial 502b		**Trial 504**	
		0-10 cm	70-80 cm	0-10 cm	70-80 cm
Major Elements					
SiO_2	%	39.7	46.8	43.2	47.1
Al_2O_2	%	15.2	17.4	15.3	17.8
MgO	%	2.7	3.5	3.7	4.7
Fe_2O_3	%	13.1	16.2	11.6	14.5
CaO	%	3.2	3.7	2.9	2.5
Na_2O	%	1.1	1.4	1.3	1.2
K_2O	%	0.3	0.2	2.3	2.1
TiO_2	%	1.5	1.7	1.0	1.1
P_2O_5	%	0.23	0.09	0.57	0.52
MnO	%	0.40	0.32	0.25	0.27
SO_2	%	0.04	0.03	0.06	0.05
Mineralogy					
Quartz		T	T	T	T
Pyrophylite		T	T	-	-
Anorthite		SD	SD	M	M
Smectite		D	D	M	M
Laumontite		T	T	-	-
Halloysite		T	-	T	M
Cristobalite		?T	?T	?T	?T
Maghemite		T	T	-	-
Amphibole		-	T	T	T
Vermiculite		-	-	D	D

D- dominant (>60%), SD – sub-dominant (20-60%), M – minor (5-20%), T – trace (<5%), ? – possible component

Pyrophylite – $Al_2Si_4O_{10}(OH)_2$; Anorthite – (Ca.Na) $Al_2Si_2O_8$; Laumontite – (zeolite group) $Ca(Al_2Si_4)O_{12}.4H_2O$

2.5 Conclusions

Both trial sites have deep clay soils, which are from recent alluvial origin. Trial 502b is located on an extensive alluvial plain, while trial 504 is located on a flood plain. Both trial sites experience waterlogged conditions during prolonged wet season. Presence of smectite and vermiculite clay minerals at both sites, coupled with high levels of Ca and Mg are the common features of the soils at these two sites. There are positive responses to K fetiliser at both sites.

CHAPTER THREE

3 Forms of potassium in soil

3.1 Introduction

Previous studies showed that the clay soils in Milne Bay Province have high contents of exchangeable Ca and Mg and low contents of exchangeable K (Best 1977, Bleeker 1983, Bleeker 1988). Best (1977) attributed the K deficiency symptoms in coconut palms in Cape Rodney and surrounding areas in Milne Bay Province to low exchangeable K (10 mmol (+) kg^{-1}) and high exchangeable Mg (117 mmol (+) kg^{-1}) contents in the soils. Bleeker (1988) found exchangeable K contents to be very low (<10-20 mmol (+) kg^{-1}) and thus recommended regular fertiliser applications of K. Webb *et al*. (2009), also found exchangeable K contents to be within the same range (10-20 mmol (+) kg^{-1}). These studies all confirmed that exchangeable K contents in the Milne Bay soils are very low.

However, there is little information on the availability of other forms of K particularly, non-exchangeable K, and how these forms of K are affected by K fertiliser application and management.

The objective of this study was to determine the effects of soil properties (site) and management (K fertiliser history and surface management) on exchangeable and non-exchangeable K, and on selected soil chemical properties in the alluvial soil of Milne Bay Province, PNG.

3.2 Materials and methods

3.2.1 Experimental design and soil sampling

The aim was achieved by measuring chemical properties of soils differing in 3 factors: soil type (2 sites), K fertiliser history (2 levels), and management practices (5 zones within the oil palm plantation), in a factorial design involving all combinations of the factors. The sites were fertiliser trials 502 and 504, described in Chapter 2. The K fertiliser history factor was obtained by sampling plots that had or had not received potassium fertiliser (MOP) over the life of the trials (Table 9). The management zones were the weeded circle (WC), harvest path (HP), frond pile (FP), frond tips (FT) and between other zones (BZ) areas (

Figure 9). The weeded circle is kept weed-free using herbicides in order to facilitate harvesting. The harvest paths, in every second row, are bare and compacted due to wheelbarrow traffic used to remove harvested fruit bunches. The frond piles, in alternate rows to the harvest paths, are the main area to which pruned fronds are added (about 25 fronds per palm per year). Pruned fronds are also added to the frond tips areas, which project perpendicularly from the frond piles. The remaining area is designated as the 'between other zones' area. It is vegetated with herbaceous legumes and other shrubs. The approximate proportion of the plantation occupied by each zone is 3% HP, 10% WC, 73% BZ, 6% FT and 7-8 % FP (Banabas pers.com). All the plots sampled had a history of adequate N fertiliser. Two replicates of each treatment were obtained by sampling different plots. Trial 502b had only one replicate of each treatment, so the replicates required were obtained by sampling plots with different P fertiliser rates. There has been no response to P in the trial. Overall then, 40 soil samples were used: 2 trial sites x 2 K fertiliser rates x 5 zones x 2 replicate plots.

The soil samples were taken on 19th and 20th of September 2007 at trials 502b and 504, respectively. Each soil sample was a composite of 4 samples taken from around the 4 inner-most palms of each plot. A sampling depth of 0-30 cm was chosen because most oil palm root activity is within this depth zone (Nelson *et al.* 2006). The 4 soil samples from each plot and zone were put into the same bucket and mixed thoroughly. The samples were taken back to the Agronomy Field Office, where they were tipped out of the bags onto a flat surface. Soil lumps were broken down into smaller aggregates, while stones and plant materials were discarded. The samples were then reduced to approximately 1.5 kg using a quartering technique. The samples were air dried at room temperature for two weeks and packed into airtight plastic bags. The soil samples were then air freighted to the AQIS accredited soils laboratory at JCU, Cairns, Australia, where they were again air dried at room temperature until they were properly dried, then crushed through a 2 mm mesh. Water content of each sample was determined gravimetrically and was used to convert all results to an equivalent oven-dry soil weight basis.

Results were statistically analysed using analysis of variance using SPSS. In the results section, the mean of the two replicate plots is shown in all cases.

Table 9. Treatment details for plots from which soil samples were taken.

Trial	Plot	MOP	SOA	TSP
		kg palm^{-1} year^{-1}		
502	43	0	6	0
	64	0	6	2
	38	7.5	6	0
	59	7.5	6	2
504	1	0	6	0
	35	0	6	0
	6	7.5	6	0
	40	7.5	6	0

MOP - muriate of potash (KCl); SOA - sulfate of ammonia; TSP is triple superphosphate

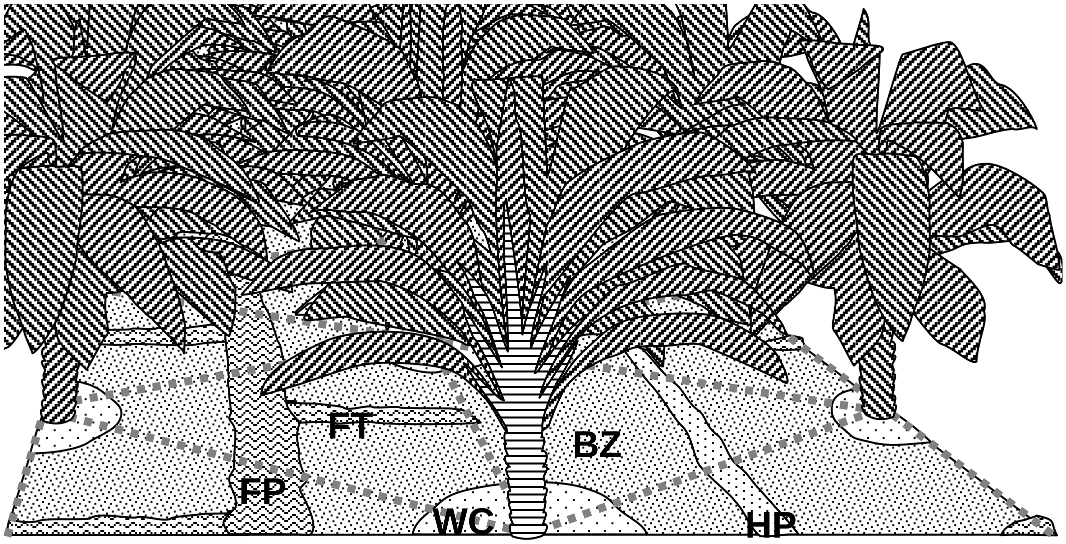

Figure 9. Surface management zones in two inter-rows (pattern is repeated throughout plantation) at the two sites. Surface management zones are ‘frond tips’ (FT), ‘frond pile’ (FP), ‘weeded circle’ (WC), ‘harvest path’ (HP) and ‘between other zones’ (BZ). Dashed lines show equilateral triangular spacing of palms. Figure derived from Nelson *et al*. (2006).

3.2.2 Laboratory analysis

Various laboratory tests were performed on the same 40 samples (described above) for the work described in this chapter as well as Chapters 4 and 5. The analyses performed for this chapter are described here.

Exchangeable Ca, Mg, K and Na contents were determined using extractions with 1 M ammonium acetate (NH_4OAc) (McLean and Watson 1985; Dhaliwal *et al.* 2006). For each analysis, approximately 2g of air dried soil (sieved <2mm) was weighed into a 50mL centrifuge tube. Next, 20 mL of 1 M NH4OAc was added. The centrifuge tube was then tightly capped and put in an end-over-end shaker for 30 minutes. Following shaking, the sample was centrifuged at 3000 rpm for 10 minutes and the supernatant was decanted into 50 mL sample bottle. The procedure was repeated and the supernatant from the second extraction was combined with the first. Blanks were prepared in an identical way, except without soil. The combined extract was analysed for exchangeable cations using an atomic absorption spectrophotometer (AAS). Standards were produced using different concentrations of KCl.

Exchangeable acidity was measured using titration of a 1 M KCl extract using the pyrocatechol violet method. For each analysis, about 4g of air dried soil (sieved <2mm) was weighed into a centrifuge tube. Next, 40 mL 1M KCl was added and the tube was placed on an end-over-end shaker for 1 hour. The sample was centrifuged, then 25 mL was pipetted into a beaker and 25 mL of water was added and mixed well. The solution was then titrated to the end point of pH 8.3-8.6 as indicated by phenolphthalein, and the titre was recorded as V_S (mL). A blank sample was analysed in the same way. The titre was recorded as V_B (mL).Exchange acidity was calculated as:

Exchangeable acidity (cmol(+)/kg) = $\underline{[(V_S - V_B) \text{ x (molarity of NaOH) x } 1000]/25}$

Effective cation exchange capacity (ECEC) was calculated by adding up the exchangeable cation contents and exchangeable acidity.

Non-exchangeable K in the interlattice of the clay minerals was extracted using sodium tetraphenylborate (NaTPB) solution (Carey *et al*. 2003; *Cox et al.* 1996). Exchangeable K was subtracted from NaTPB to get the non-exchangeable K. For each analysis, about 1.25 g of soil together with 0.25 g of NaTPB was weighed into a 100 mL digestion tube (calibrated at 100 mL). Then 3.75 mL of 1.7 M NaCl:0.01 M EDTA extraction solution was added. The tube was swirled to mix the contents and allowed to stand for 1 hour. After 1 hour, 25 mL of 0.5 M NH_4Cl solution was added to precipitate any remaining NaTPB. Then 3.75 mL of 1 M $CuCl_2$ was added, mixed well and the tube was placed on a digestion block at 125°C. The tube was gently boiled for 20 minutes until the TBK precipitate completely disappeared. The tube was removed from the block and left to cool and then 1 mL 50% HCl was added to prevent the EDTA from precipitating. The tube volume was then made up to 100 mL with deionised water, the top of the tube covered with parafilm, mixed thoroughly and left to stand overnight giving a clear solution. The tube contents were then diluted 1:1 with deionised water to prevent the AAS burner from clogging up due to high salt concentration. The clear solution was then analysed for K using the AAS at 766.5 nm over a standard range of 0-25 mg L^{-1} of K. Standards were prepared in an identical way, except without soil and with known quantities of K.

Organic C content was measured using the Heanes wet oxidation procedure. For each analysis, 0.5g of air dried soil (sieved <2 mm) was weighed into a digestion tube, then 10 mL of 0.167 M potassium dichromate was added. After that, 20 mL of sulphuric acid was slowly added to the tube, and the tube was placed on a preheated (135 °C) digestion block and heated for 30 minutes. The tube was then removed and allowed to cool, deionised water was then added into the digestion tube and it was secured with a stopper and mixed thoroughly. The solution was transferred to a centrifuge tube and centrifuged to clear. The clear supernatant was transferred to a spectrophotometer tube and absorbance was measured at 600 nm. Nine different sucrose solution (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mL) were used as standards in this experiment.

For measurement of pH and electrical conductivity (EC), 1:5 soil:water suspension was prepared by weighing air dried soil (sieved <2 mm, mass equivalent to 6 g oven-dried soil) into a centrifuge tube and adding 30 mL of deionised water. The suspension was then shaken for 30 minutes. After shaking, the suspension was allowed to settle for 20 minutes. The conductivity cell was then dipped into the supernatant, moving it up and down slowly. The EC was read when the reading stabilised. The cell was rinsed thoroughly with deionised water between samples.

The pH electrode was then dipped into the supernatant, while stirring continuously. The pH was read when the meter stabilized. Before measurements, the pH meter was standardized according to manufacturer’s instructions, using a buffer at pH 7.0 and 4.0. Before measuring the EC, the conductivity cell and meter was calibrated in accordance with manufacturer’s instruction with KCl reference solution.

3.3 Results

3.3.1 Soil organic C content, pH, exchangeable acidity, electrical conductivity (EC) and clay content

Soil organic C content differed significantly between trial sites and management zones, but not with K fertilizer history (Table 10, Table 11). There were no significant interactions between treatments. Generally, the organic C content decreased in the order FP>FT>BZ>WC>HP (Figure 10). Organic C content in trial 504 (24 mg kg^{-1}) was slightly higher than that in trial 502b (21 mg kg^{-1}).

Soil EC was significantly different between trial site, K fertilizer history, zones and their interactions (Table 10, Table 11). Trial 504 had higher EC than trial 502b. The EC was highest in the WC, BZ, FT and FP zones in the plots with a history of K fertiliser application (Figure 10).

Soil pH was significantly higher in trial 502b than trial 504 and differed significantly between management zones, but was not significantly affected by K fertiliser history (Table 10, Table 11). Generally, the management zones with the highest to the lowest pH followed the order; HP>WC>BZ>FT>FP (Figure 10).

Exchangeable acidity differed significantly between management zones (Table 10, Table 11). The zones with a history of K fertiliser application (BZ, FT and FP) had higher exchangeable acidity than the zones with a history of no K fertiliser. The highest exchangeable acidity was measured from BZ zone (Figure 10). Exchangeable acidity was closely related to pH in that it was high in zones where soil pH was low (Figure 10).

Table 10**.** Significance (p values) of treatment effects on soil chemical properties.

				Exchangeable cations							
Treatments	OC	pH $_{1:5}$	EC $_{1:5}$	K	Na	Ca	Mg	Acidity	ECEC	K sat	K_{nex}
Main effects											
Trial (T)	**0.017**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.109	**<0.001**	0.100	0.112
K fert (K)	0.203	0.212	0.780	**<0.001**	0.073	0.116	0.704	0.700	0.073	**<0.001**	**<0.001**
Zones (Z)	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.468	0.072	**0.017**	0.313	**<0.001**	**<0.001**
2 way interaction											
T x K	0.745	**0.047**	0.277	**<0.001**	0.468	**0.012**	0.749	0.228	0.075	**0.023**	**0.007**
T x Z	0.781	**0.046**	**<0.001**	**0.003**	**0.048**	0.809	0.820	0.159	0.830	**0.042**	**0.011**
K x Z	0.941	0.386	0.004	**<0.001**	0.640	0.427	0.64	0.858	0.618	**<0.001**	**<0.001**
3 way interaction											
T x K x Z	0.780	0.891	**0.006**	**0.001**	0.761	0.996	0.976	0.677	0.998	**0.030**	**0.007**

OC – organic C content

EC – electrical conductivity of 1:5 soil:water extract

ECEC – effective cation exchange capacity

K sat – exchangeable K content as proportion of ECEC

K_{nex} – non-exchangeable K

Table 11. Soil chemical properties (mean of 2 replicate plots). Significance of treatment effects are given in Table 10.

Trial	K fert	Zone	OC (g kg^{-1})	pH 1:5 (water)	EC 1:5 (µS cm^{-1})	Exchangeable cations (mmol (+) kg^{-1})					ECEC (mmol (+) kg^{-1})	K sat (%).	K_{nex} (mmol (+) kg^{-1})
						K	Na	Ca	Mg	Acidity			
502b	-K	HP	13.7	6.6	44	1.5	8.4	309	149	2	470	0.3	1.9
	-K	WC	21.4	6.1	59	2.1	7.1	297	145	3.2	454	0.5	2.2
	-K	BZ	19.9	5.8	76	1.4	7.3	289	128	4.5	430	0.3	1.9
	-K	FT	20.8	5.7	73	1.3	6.6	286	128	8.1	430	0.3	1.6
	-K	FP	27.6	6.1	96	1.5	6.8	319	154	2	483	0.3	1.8
502b	+K	HP	15.2	6.8	57	7.3	9.3	381	161	2	561	1.3	5
	+K	WC	20.2	6.5	73	15.3	7.4	357	160	2	542	2.8	11.3
	+K	BZ	20.3	6.2	79	31.3	6.7	342	132	2.6	515	6.1	19
	+K	FT	23.2	6	78	64.6	4.9	318	117	3.5	508	12.7	34.8
	+K	FP	30.2	6.2	99	66.7	4.7	343	136	1.9	552	12.1	35.6
502b -K Mean			*20.7*	*6.1*	*70*	*1.6*	*7.2*	*300*	*141*	*4.0*	*453*	*0.3*	*1.9*
502b +K Mean			*21.8*	*6.3*	*77*	*37.0*	*6.6*	*348*	*141*	*2.4*	*536*	*7.0*	*21.1*
502b mean			*21.3*	*6.2*	*73.4*	*19.3*	*6.9*	*324*	*141*	*3.2*	*495*	*3.7*	*11.5*
504	-K	HP	17.6	6.3	61	1.9	2.9	249	109	1.9	365	0.5	6.6
	-K	WC	20.6	5.9	119	2.5	2.7	261	109	2.9	378	0.7	7.1
	-K	BZ	24	5	131	2	2.6	242	82	10.6	339	0.6	6.1
	-K	FT	26.5	5.9	138	2.2	2.6	273	89	3.8	371	0.6	6.9
	-K	FP	27.7	5.8	129	2.2	2.9	270	99	2.6	377	0.6	6.6
504	+K	HP	19.9	6.3	63	7	3.4	276	121	2	409	1.7	11.6
	+K	WC	24.5	6	145	12	2.6	265	120	2	402	3	18.5
	+K	BZ	25.4	5.1	194	21.5	2.4	231	92	9.2	356	6	21.6
	+K	FT	24.5	5.6	205	18.3	2	236	101	7	364	5	20.2
	+K	FP	31.4	5.4	140	26.6	1.9	226	80	5.7	340	7.8	26.9
504 -K Mean			*23.3*	*5.8*	*116*	*2.2*	*2.7*	*259*	*98*	*4.4*	*366*	*0.6*	*6.7*
504 +K Mean			*25.1*	*5.7*	*149*	*17.1*	*2.5*	*247*	*103*	*5.2*	*374*	*4.7*	*19.8*
504 mean			*24.2*	*5.7*	*133*	*9.6*	*2.6*	*253*	*100*	*4.8*	*370*	*2.7*	*13.2*

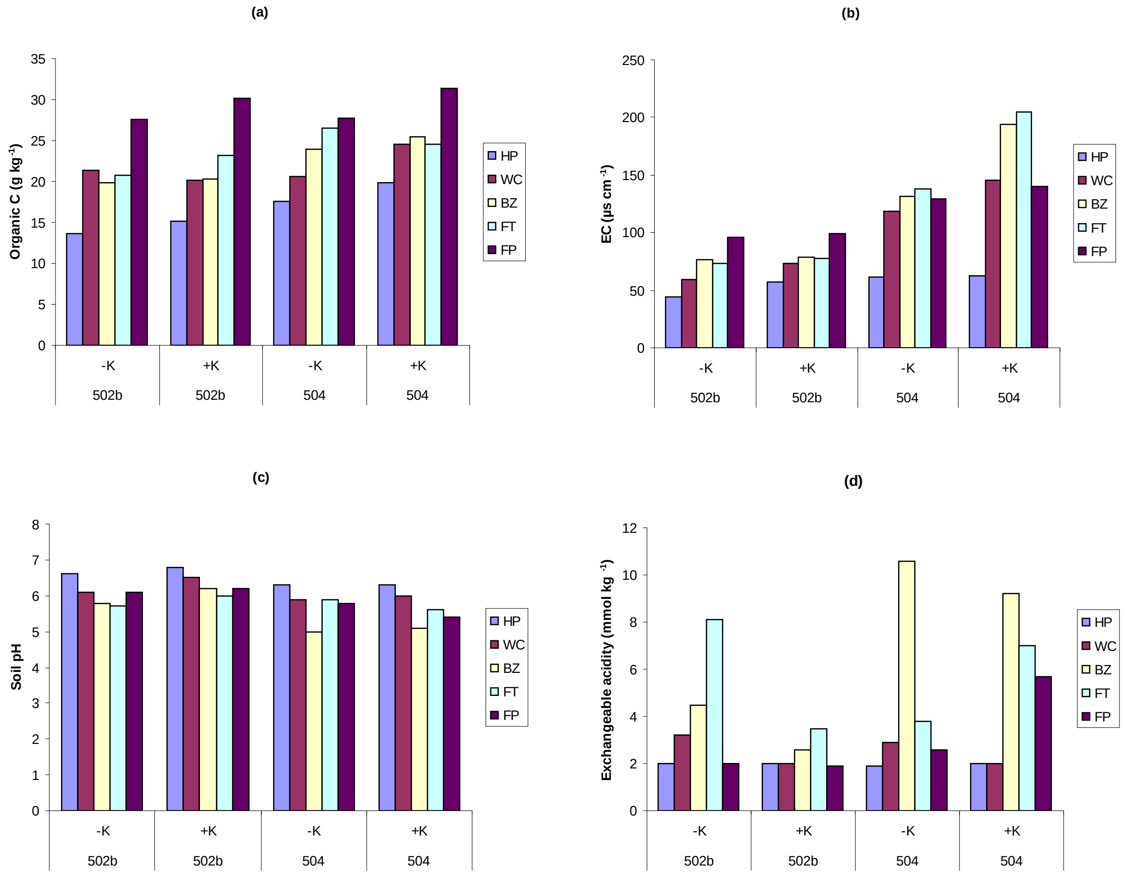

Figure 10. Mean contents of soil (a) organic C content, (b) electrical conductivity (EC), (c) pH and (d) exchangeable acidity for the different treatments. Significance of treatment effects is given in Table 10.

3.3.2 Particle size distribution

The proportion of coarse and fine sand, silt and clay are given in Table 12. The proportion of both fine and coarse sand was higher in trial 502b than 504, whereas trial 504 had more silt than trial 502b. The clay content for both trials was below 50 %, although trial 502b had more clay content trial 504. Trial 502b had an average of 41 % clay, while trial 504 had 37.4 %. A soil pit description on the same sites (unpublished data) also categorized these soils to have light to medium clay.

Table 12. Particle size distribution of the soils in trial 502b and 504

	% of total			
	Coarse Sand (2000-200 µm)	**Fine Sand** (200-20 µm)	**Silt** 20-2 (µm)	**Clay** <2 (µm)
502b-43 (-K)	3.3	18.2	33.8	44.6
502b-64 (-K)	10.3	22.8	29.6	37.3
502b mean	***6.8***	***20.5***	***31.7***	***41.0***
504-1 (-K)	3.3	11.5	47.2	38.0
504-35 (-K)	2.7	15.0	45.5	36.8
504 mean	***3.0***	***13.2***	***46.4***	***37.4***

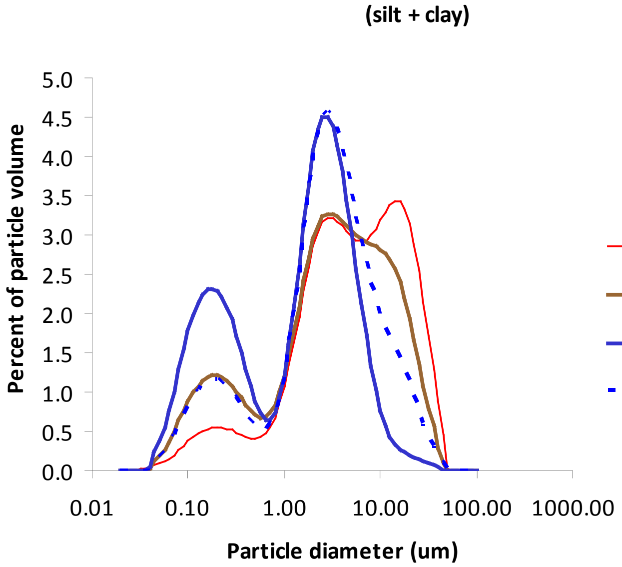

Figure 11. Proportion of silt and clay found in the plots with a history of no K fertiliser in trials 502b and 504

3.3.3 Exchangeable cations and non-exchangeable K

Soil ECEC differed significantly between the two sites but was not affected by the other treatments (K fertilizer history and management zones) or the treatment interactions either (Table 10, Table 11). Trial 502b had a significantly higher ECEC (495 mmol (+) kg^{-1}) than trial 504 (370 mmol (+) kg^{-1}) (Figure 12). This is probably due to the difference in clay content (Table 12), whereby trial 502b had more clay content than trial 504.

The exchangeable Ca contents found in the soils in both trial sites were reasonably high (Figure 12). The exchangeable Ca level was significantly ($p<0.001$) affected by the trial sites and the two way interaction between trial site and K fertilizer (Table 10, Table 11). The exchangeable Ca contents found in the soils in trial 502b (324 mmol (+) kg^{-1}) were higher than trial 504 (253 mmol (+) kg^{-1}).

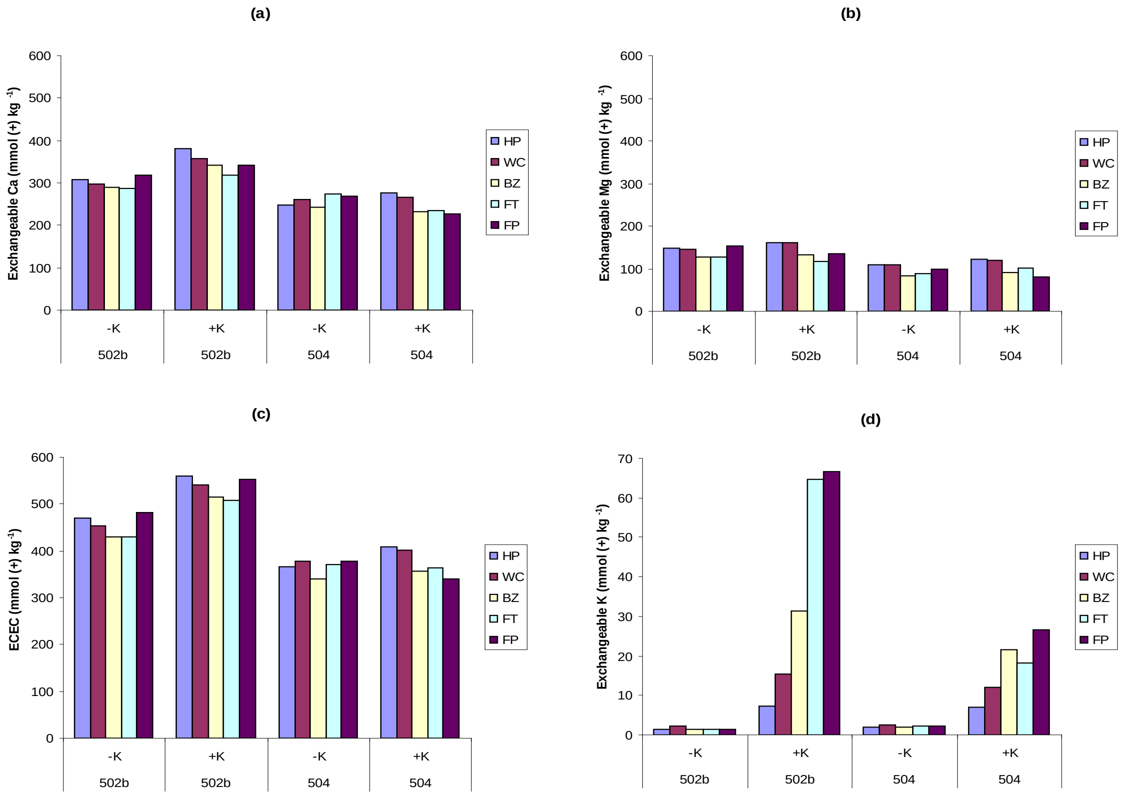

Figure 12. Mean contents of exchangeable (a) Ca, (b) Mg, (c) effective cation exchange capacity (ECEC) and (d) K. Significance of treatment effects is given in Table 10.

The exchangeable Mg content was significantly higher in trial 502b (was 141 mmol (+) kg^{-1}) than trial 504 (100 mmol (+) kg^{-1}) (Table 10, Figure 12).

Exchangeable K content responded significantly ($p<0.05$) to all the treatments and their interactions (Table 10, Table 11). Trial 504 had higher native exchangeable K content (-K fertiliser treatment) than trial 502b. However, in the plots with a history of K fertiliser application the exchangeable K content was higher in trial 502b than 504 (Figure 13). The soils from plots and zones with a history of K fertiliser application had higher exchangeable K content than the soils with a history of no K fertiliser.

The treatment effects on non-exchangeable K contents were similar to the effects on exchangeable K. Non-exchangeable K content differed significantly ($p<0.001$) between the plots with a history of no K fertiliser and those with a history of K fertiliser application and the 5 management zones (Table 10). Trial 504 had higher native non-exchangeable K content (-K fertiliser treatment) but in the plots with a history of K fertiliser, the exchangeable K content was higher in trial 502b than 504 (Table 11). The surface management zones where K fertiliser is normally applied during application (BZ, FT and FP) had significantly higher non-exchangeable K content than the zones that receive very little or no K fertiliser (HP and WC). Non-exchangeable K contents were slightly higher than the exchangeable K contents (Figure 13).

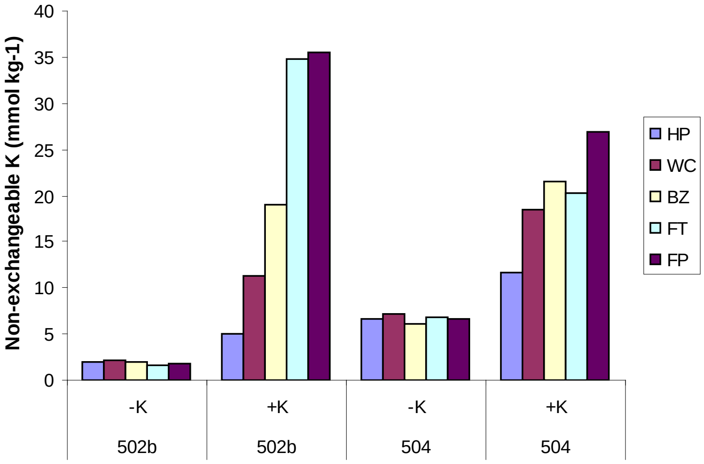

Figure 13. Mean non-exchangeable K contents for the different treatments. Significance of treatment effects is given in Table 10

3.4 Discussion

The soil organic C and pH values obtained in this study were similar to those obtained previously by Bleeker (1988). Despite that fact that the organic C contents were found to be higher in trials 504 (Tomanou soils) than 502b (Plantation soils), the organic C contents at both trial sites all found to be within the low (1.0-2.5 %) and medium range 2.6-5.0 %) (Bleeker 1988). Soil pH values at both trial sites were generally high for soils of the wet tropics. Trial 502b had an average pH of 6.2 while trial 504 had an average pH of 5.7. Previous studies on these soils also found the soil pH to be within the same range (Bleeker 1988, Webb *et al*, 2009).

Irrespective of the fertilizer and the surface management zones, all the other cation contents, except for exchangeable K, were more or less similar to the values obtained in previous studies (Bleeker 1988, Webb *et al*, 2009). In this study, the average exchangeable Ca content in the soil was 324 mmol kg^{-1} and 253 mmol kg^{-1} at trial 502b and 504 respectively. Bleeker (1988) found the exchangeable Ca contents to be within the range of 126-307 mmol kg^{-1} and 115-391 mmol kg^{-1} in the Plantation and Tomanou soils, the two soil types predominantly found at trial 502b and 504. Webb *et al*. (2009) also found the exchangeable Ca contents in both trials to be around the same range reported in this study. The exchangeable Mg contents in this study ranged from 117-161 mmol kg^{-1} in trial 502b and 80-121 mmol kg^{-1} in trial 504, which were also similar to previous studies Webb *et al*. (2009).

The exchangeable K contents increased considerably with K fertilizer and where it had been applied. The concentration of exchangeable K was higher in the BZ, FT and FP zones because most of the K fertiliser is placed in these three zones compared to the HP and WC which receive very little or no fertiliser

The exchangeable K levels found in the plots and zones with a history of no K fertiliser had low contents of exchangeable K (1.2-2.2 mmol kg^{-1}). These low levels may be natural or due to depletion by oil palm uptake. Oil palm removes large quantities of nutrients, including K, from the soil (Hartley 1988). Continuous exploitation of K from the soil by the oil palm without supplementation from sources such as fertiliser results in a gradual drop in the level of K in the soil to a point where the K is seen to be deficient. However, low exchangeable K values were also reported by Bleeker (1988) and Webb *et al.* (2009) in the native soil. Bleeker (1988) attributed the low levels of K to high levels of Mg and Ca in these soils. High levels of exchangeable Ca or Mg in soils generally affect K uptake or vice versa, which is why Bleeker (1998) recommended high application rates of K to boost the exchangeable K levels in these soils.

Similarly, the non-exchangeable K contents were also affected by the K fertiliser and its placement. Within the plots with a history of K fertiliser, the BZ, FT and FP zones, where K fertiliser is normally applied, had higher contents of non-exchangeable K than the HP and WC zones. The non-exchangeable K contents in all the five management zones within the plots with a history of no K fertiliser were very low. K stored in the non exchangeable form is released into available forms such as exchangeable K and soil solution K, becoming available for plant uptake. This process, although slow, still results in the depletion of non-exchangeable K (Moody and Bell 2006). This is because K fertilizer application increases the concentration of K in the soil solution, which then affects the K level in the exchangeable pool as well over time (Sparks 1987). Where fertilizer K is not applied, K uptake from solution causes K to be depleted in both the exchangeable and solution pools.

Soil organic C content, ECEC and pH differed significantly between zones. The high organic C contents observed in the FP and FT zones were attributed to the decomposition of the oil palm fronds placed on these two zones during harvesting. The decomposition of the frond over time has contributed to the buildup of organic C within these two zones. Generally, the zones with a history of no K fertiliser had lower soil pH than those zones with a history of K fertiliser application. All plots used in this study have also been receiving 1.26 kg N (equivalent to 6 kg SOA) per palm per year for the duration of the trial, and it is likely that a high proportion of the N fertiliser was applied in the BZ, FT and FP zones with little to no N applied in the WC and HP zones, respectively. Therefore prolonged use of ammonium based N fertiliser and loss of nitrate by leaching in these three zones was probably responsible for the low soil pH.

ECEC was closely related ($r = 0.690^{**}$) to pH but not to organic C ($r = -0.167$), suggesting that acidification caused loss of CEC (Table 13). This is presumably associated with variable charge of the organic matter, as vermiculite and smectite do not have much variable charge. The fact that ECEC was related to pH but not to total organic C content suggests that the difference in organic C content between zones was mainly due to organic matter with low CEC.

Table 13. Correlation coefficients (r) between selected soil chemical properties in trial 502b and 504

	OC	pH	EC	Exch K	Non-exch K	ECEC	K sat %
OC							
pH	-0.386*						
EC	0.287	-0.688**					
Exch K	0.322*	0.000	-0.060				
Non-exch K	0.443**	-0.148	0.095	0.938**			
ECEC	-0.167	0.690**	-0.449**	0.215	0.000		
K sat %	0.354*	-0.125	-0.008	0.977**	0.958**	0.053	

*** Correlation is significant at the 0.01 level*
** Correlation is significant at the 0.05 level*

3.5 Conclusions

The soil chemical properties were very much affected by the K fertiliser history. The differences in the soil chemical properties as affected by the different surface management zones were only obvious in the plots or areas that received K fertiliser. Soil organic C content and pH did not differ much between the two trial sites, but the EC, exchangeable and non-exchangeable K contents did. Trial 502b had lower native contents of exchangeable and non-exchangeable K than trial 504, but higher contents in the fertilized plots and zones for the same rate of applied K.

Since high Mg and Ca contents can impede K uptake, the very high exchangeable levels of these two cations mean that large K fertiliser applications may be required to allow adequate K uptake on these soils.

CHAPTER FOUR

4 Fixation of potassium

4.1 Introduction

Potassium fixation in soils is defined as the transformation of available K forms (i.e. soil solution K and exchangeable K) into non-exchangeable K forms. This transformation has a direct effect on K availability and on the degree of fertiliser K uptake by plants (Malavolta 1985, Troeh and Thompson 2005). The study of fixation in soils is of particular agronomic and practical interest. It permits a better understanding of the soil's behaviour in response to application of K fertiliser and it generally contributes to more effective evaluation for crop needs for K (Sharpley 1990). Therefore, it is important to know the fixation characteristics of soils in order to make rational recommendations about K fertilisers. Soils differ in their tendency to fix applied K into forms unavailable to plants, and each soil has its own fixing capacity for K which must be satisfied before a change in soil solution concentration occurs.

Various factors affect the K fixation capacity of soils; among them clay type and quantity constitute the most important ones (Sparks and Huang 1985). Clay type and quantity determine the magnitude of soil fixing capacity and thus control K fixation and release processes (Kirkman *et al.* 1994). Studies on the effect of clay mineralogy on soil K dynamics showed that K fixation occurs when the soil clay minerals are of 2:1 type (Sardi and Csitari 1998; Conti *et al.* 2001; Dhaliwal *et al.* 2006; Simonsson *et al.* 2009).

The long-term use of K fertilisers (or K fertiliser history of soil) is another important factor that determines the K concentration in the various K pools (solution, exchangeable and non-exchangeable) in the soil, which subsequently affects K fixation. According to Kirkman *et al.* (1994), when the addition of K fertiliser increases the concentration of K in the soil solution, the resulting shift in equilibrium may result in fixation of K ions at specific sites on the clay minerals. Simonsson *et al.* (2007) also looked at K release and fixation as a function of fertiliser application rate and soil parent material. They found that release and fixation rates were highly dependent on soil K balance, and confirmed that the processes of K fixation and release are reversible and depend on the plant uptake and K fertiliser input. Other work done on the effects of K fertiliser history on K fixation included Etchevers and Hidalgo (2005), Dhaliwal *et al.* (2006) and Li *et al.* (2010).

In Milne Bay Estates, K is applied to in oil palms in the form of K fertiliser. Unfortunately, a nutrient use efficiency study showed that out of the 6191 kg of K applied per hectare in fertiliser, 2498 or 40% was taken up (808 kg in standing biomass and 1690 kg exported in fresh fruit bunch), and 57% remained in the top 60 cm of the soil (Berthelsen *et al.* 2010). The soils in trial 502b and 504 are dominated by vermiculite and smectite clays, which are forms of 2:1 clay minerals. The presence of these clay minerals could have contributed to the chronic K deficiency at these two sites in the absence of K fertiliser application. However, there is limited knowledge on the K fixing capacity of these soils as affected by K fertiliser history and surface management. This study will permit a better understanding of the soil behaviour in response to fertiliser K application, and by knowing the fixation characteristics of these soils, rational K fertiliser recommendations can be made.

The objectives of the study were to (1) compare and determine the relative ability of the soils at each site to fix K, (2) determine the influence of surface management on K fixation and (3) determine the effect of long term K fertiliser history on K fixation.

4.2 Materials and methods

4.2.1 Field work – soil sampling

The soils used in this experiment were the same as those described and used in Chapter 3.

4.2.2 Soil treatment and laboratory analysis

The soils were equilibrated with different concentrations of KCl, and the amount of fixed K was measured using a procedure similar to that used by Dhaliwal *et al.* (2006). Two g of each soil sample (air dried, sieved <2mm) was weighed into a 50 mL centrifuge tube. Then 10 mL KCl solution was added to each sample, using a soil:solution ratio of 1:5. The additions had concentrations of 0, 47.7, 143, 190.7, 238.3, 286, 333.7 and 381.3 mg KCl L^{-1} or 0, 0.6, 1.3, 1.9, 2.6, 3.2, 3.8, 4.5 and 5.1 mmol L^{-1} which was equivalent to 0, 125, 375, 500, 625, 750, 875 and 1000 mg K kg^{-1} soil, or 0, 3.2, 9.6, 12.8, 16.0, 19.2, 22.4 and 25.6 mmol K kg^{-1} soil. The soil samples were equilibrated with the KCl solution by shaking gently over a period of 72 hours on an end-over-end shaker. After shaking, the samples were centrifuged at 2000 rpm for 10 minutes and the equilibrium solution supernatant was decanted into 25-mL sample bottles. The equilibrium solution supernatant was analysed for K using atomic absorption spectrometry and the tubes were weighed to measure the amount of entrained solution. Then 20 mL of 1M NH4OAc was added to the soil samples, which were put into the shaker for 30 minutes and then centrifuged at 2000 rpm for 10 minutes. The ammonium acetate supernatant was decanted to a 25-mL sample bottle. The NH4OAc supernatant was analyzed for K using the atomic absorption spectrometer. Exchangeable K is the NH4OAc extractable K minus the entrained equilibrium solution K. The net amount of K added to the soil was calculated as the amount of K added minus the amount decanted and the amount entrained. The amount of fixed K was calculated as the difference between the amount of K added to the soil and the amount of K extracted from the soil using 1M NH_4OAc.

The experiment was initially conducted using all the soil samples described in Chapter 3 and using an equilibration time of 30 minutes. Very little fixation was observed, so the experiment was repeated using an equilibration time of 72 hours, as described above. In this second experiment, which is the one reported here, soils from the WC, BZ and FP zones only were used. Soils from the HP and FT zones were not analysed because from the results of the first experiment, the fixation rates were more or less the same those from the WC and FP, respectively.

4.3 Results

4.3.1 Exchangeable K content

The concentration of exchangeable K was significantly ($p<0.001$) affected by the treatments at every level of added K (Table 14). The K fertiliser history and the interaction between zones and K fertiliser affected exchangeable K at all levels of added K, whereas the other treatments affected exchangeable K at higher levels of added K.

The effects of the treatments on the amounts of exchangeable K are shown in Table 15. The exchangeable K content extracted from the zones with a history of K fertiliser was higher than from those that received little or no K, and followed this sequence: FP>BZ>WC. In the plots with a history of no K fertilizer there were no marked differences in the exchangeable K contents between the 3 zones, at all levels of added K (Table 15). Irrespective of the other treatments (K fertiliser history and zone), soil from trial 502b had higher exchangeable K contents than soil from trial 504 (Table 15).

The relationship between the exchangeable K content and the net added K is shown in Figure 14. In both trials, exchangeable K content was higher in the plots with a history of K fertiliser addition than the plots that received no K fertiliser, at all levels of added K. Furthermore, the concentration of exchangeable K in the plots with no K fertiliser addition was less than the net amount of K that was added in the experiment. The plots with a history of K fertiliser had more exchangeable K than the net amount added, particularly in the BZ and FP zones in both trials. The graphs clearly illustrate that fixation took place in the plots with a history of no K fertiliser addition, as well as in the unfertilised zones of the plots with a history of K fertiliser (i.e. WC). In contrast, some non-exchangeable K appeared to be released into the exchangeable pool in the zones to which fertiliser had been added (i.e. BZ and FP) in the plots with a history of K fertiliser addition.

Table 14. Significance of treatments effects (p values) on exchangeable K content at each value of added K. Significant values ($p<0.05$) are shown in bold.

Treatments	Added K (mmol kg^{-1} soil)							
	0	3.2	9.6	12.8	16.0	19.2	22.4	25.6
Trial (T)	0.679	0.301	**<0.001**	**0.008**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
K fertiliser (K)	**<0.001**	**0.002**	**<0.001**	**0.023**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Zone (Z)	0.119	0.252	**<0.001**	**0.044**	**<0.001**	**<0.001**	**0.011**	**<0.001**
T x Z	0.153	0.426	**0.020**	**0.032**	**0.006**	**0.007**	**0.039**	**0.001**
Z x K	**0.020**	**0.010**	**0.002**	**0.038**	**<0.001**	**<0.001**	**0.004**	**<0.001**
T x K	0.439	0.172	0.350	0.263	0.568	0.101	0.980	0.163
T x K x Z	0.156	0.496	0.186	0.865	0.883	0.220	0.398	0.206
CV %	40.6	6.0	1.5	4.3	1.6	1.5	2.4	1.4

CV = coefficient of variation

Table 15. Amounts of exchangeable K (mmol kg^{-1}) in the different treatments and at various levels of added K

Treatment			**K added to soil (mmol kg^{-1} soil)**							
Trial	**K fert.**	**Zone**	**0.0**	**3.2**	**9.6**	**12.8**	**16.0**	**19.2**	**22.4**	**25.6**
502b	-K	WC	0.2	1.1	6.5	8.3	9.4	14.2	16.2	18.3
502b	-K	BZ	0.1	1.0	6.3	8.3	10.0	13.7	15.5	18.5
502b	-K	FP	0.2	1.0	6.3	9.1	10.4	14.3	15.3	17.8
502b	+K	WC	1.5	2.2	11.7	14.5	13.5	18.6	20.3	22.1
502b	+K	BZ	3.7	4.4	16.1	19.9	19.9	24.1	26.2	27.8
502b	+K	FP	7.5	7.8	28.1	30.7	31.6	36.2	37.7	39.8
502b -K mean			***0.2***	***1.0***	***6.4***	***8.6***	***9.9***	***14.1***	***15.7***	***18.2***
502b +K mean			***4.2***	***4.8***	***18.6***	***21.7***	***21.7***	***26.3***	***28.1***	***29.9***
502b mean			***2.2***	***2.9***	***12.5***	***15.1***	***15.8***	***20.2***	***21.9***	***24.1***
504	-K	WC	0.3	1.3	6.8	7.6	9.5	12.6	13.5	14.6
504	-K	BZ	0.3	1.3	6.9	7.9	9.3	13.6	13.3	16.2
504	-K	FP	0.3	1.3	6.5	8.4	9.4	13.0	14.5	15.6
504	+K	WC	1.5	2.3	9.2	9.4	12.2	14.8	14.8	16.8
504	+K	BZ	2.9	3.9	14.1	15.3	16.3	20.1	19.9	22.3
504	+K	FP	3.9	4.8	14.3	17.0	18.4	22.0	22.4	25.1
504 -K mean			***0.3***	***1.3***	***6.7***	***8.0***	***9.4***	***13.1***	***13.8***	***15.5***
504 +K mean			***2.8***	***3.7***	***12.5***	***13.9***	***15.6***	***19.0***	***19.0***	***21.4***
504 mean			***1.5***	***2.5***	***9.6***	***10.9***	***12.5***	***16.0***	***16.4***	***18.4***

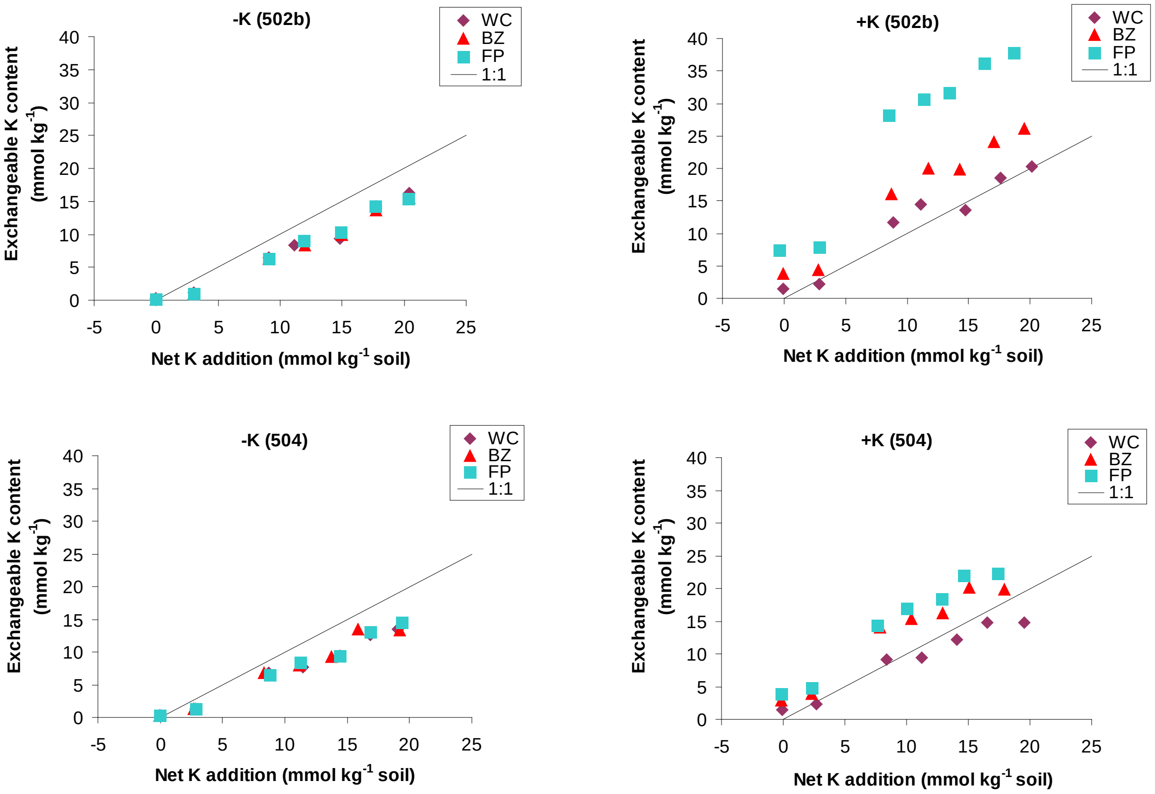

Figure 14. Soil exchangeable K content versus net added K in the two trials (502b and 504) in plots with (+K) or without (-K) a history of K fertiliser application

4.3.2 Net fixation of K

Fixed K was significantly ($p<0.01$) influenced by all treatments and their interactions at all levels of added K (Table 16). In both trials, there was net fixation of added K in the plots that had received no K fertiliser. In those plots, there was a small net release of non-exchangeable K in samples to which no K was added (Table 17). The amount of K fixed increased with the level of added K but was the same in all zones at each level of added K, and was also similar in the two trials (Table 17).

In plots with a history of K fertiliser addition, there was little net fixation or release in the WC zone, and considerable release of non-exchangeable K in the BZ and FP zones (Table 17, Figure 14). The amount of K released from the BZ and FP zones in the K fertilised plots generally increased with levels of added K. Release of K from the non-exchangeable pool was much higher in trial 502b than trial 504.

Table 16. Significance of treatment effects (p values) on fixed K content at each value of added K. Significant values ($p<0.05$) are shown in bold.

Treatments	Added K (mmol kg^{-1} soil)							
	0	3.2	9.6	12.8	16.0	19.2	22.4	25.6
Trial (T)	0.259	0.604	**<0.050**	**0.009**	**0.031**	**0.017**	**0.006**	**0.004**
K (K)	**<0.001**	**<0.001**	**<0.001**	**0.003**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Zone (Z)	**0.002**	**<0.001**	**0.008**	**0.002**	**<0.001**	**<0.001**	**0.001**	**<0.001**
K x Z	**0.002**	**<0.001**	**0.006**	**0.004**	**<0.001**	**<0.001**	**0.002**	**<0.001**
T x K	0.055	0.090	**0.023**	**0.013**	**0.023**	**0.011**	**0.017**	**0.036**
T x Z	0.154	0.206	0.096	0.263	**0.050**	0.060	0.379	0.169
T x K x Z	0.147	0.232	0.141	0.265	0.109	0.130	0.192	0.207
CV %	41.6	10.0	11.5	24.3	31.6	21.5	12.4	11.4

CV = coefficient of variation

Table 17. Amounts of K fixed (mmol kg^{-1} soil) with the different treatments and at various levels of added K

Treatment			K added to soil (mmol kg^{-1} soil)							
Trial	**K fert**	**Zone**	0.0	3.2	9.6	12.8	16.0	19.2	22.4	25.6
502b	-K	WC	-0.2	1.8	2.3	1.3	5.3	3.8	3.6	5.2
502b	-K	BZ	-0.2	1.9	2.5	3.2	5.1	4.1	4.4	3.6
502b	-K	FP	-0.2	1.9	2.7	2.5	4.7	3.6	4.3	5.3
502b	+K	WC	-2.0	0.3	-4.5	-5.5	-0.6	-2.4	-2.4	-1.3
502b	+K	BZ	-5.2	-2.7	-9.9	-12.0	-9.5	-10.5	-11.2	-9.5
502b	+K	FP	-6.3	-3.7	-14.8	-14.4	-13.8	-16.5	-15.5	-15.1
502b -K mean			***-0.2***	***1.9***	***2.5***	***2.3***	***5.0***	***3.8***	***4.1***	***4.7***
502b +K mean			***-4.5***	***-2.0***	***-9.7***	***-10.6***	***-8.0***	***-9.8***	***-9.7***	***-8.6***
502b K mean			***-0.3***	***1.5***	***2.1***	***3.0***	***4.5***	***3.5***	***5.7***	***6.7***
504	-K	WC	-0.3	1.6	2.4	3.2	5.0	4.3	7.0	7.9
504	-K	BZ	-0.3	1.4	1.8	3.6	3.2	2.5	4.8	5.4
504	-K	FP	-0.4	1.6	2.1	2.3	5.2	3.8	5.4	6.8
504	+K	WC	-1.6	0.4	0.8	2.6	2.2	1.4	3.5	5.3
504	+K	BZ	-3.7	-2.2	-7.9	-5.6	-4.4	-7.4	-4.7	-5.0
504	+K	FP	-4.8	-3.3	-10.3	-7.5	-6.6	-9.6	-7.8	-7.7
504 -K mean			***-0.3***	***1.5***	***2.1***	***3.0***	***4.5***	***3.5***	***5.7***	***6.7***
504 +K mean			***-3.4***	***-1.7***	***-5.8***	***-3.5***	***-2.9***	***-5.2***	***-3.0***	***-2.5***
504 K mean			***-1.9***	***-0.1***	***-1.9***	***-0.2***	***0.8***	***-0.8***	***1.4***	***2.1***

4.3.3 K fixation as a proportion of that added (net)

The proportion of net added K that was fixed was highly influenced by the K fertiliser history of the plots and zones (

Figure **15**). In the plots with a history of no K fertiliser, the proportion of added K that was fixed decreased with increasing rates of added K, but there was little or no effect of trial or zone. In general, 40-60 % of the added K was fixed at the lowest rate of K addition and about 10-30 % was fixed at the higher rates of addition.

In the plots with a history of K application, both fixation and release occurred as discussed previously and as indicated by negative 'fixation' values in Table 17. In the WC zone of trial 502b, 0-20 % of the added K was fixed, but in the zones to which fertiliser had been added (BZ and FP), there was net release in both trials.

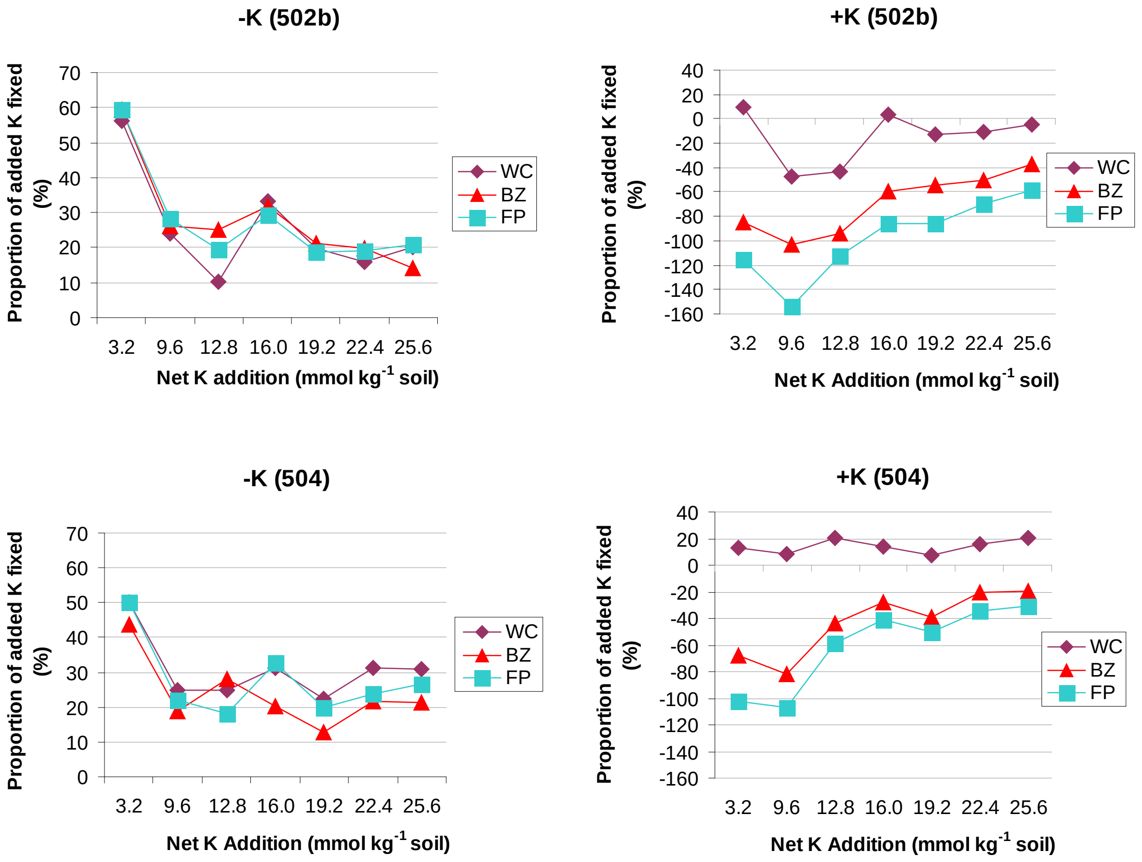

Figure 15. Proportion of net added K that was fixed in WC, BZ and FP zones in trials 502b and 504.

4.3.4 K exchange isotherms

The slopes of the K exchange isotherms differed between the two sites but were not influenced by K fertiliser history (Figure 16). Trial 502b had a greater slope (greater exchange site affinity) than trial 504, irrespective of the K fertiliser history. Thus, a higher exchangeable K content is expected in trial 502b than Trial 504, at the same solution concentration. For instance, in BZ zone of the fertilised plots, at the equilibrium solution concentration of 1.0 mmol L^{-1}, there was 20 mmol kg^{-1} of exchangeable K in trial 504, compared to 39 mmol kg^{-1} in trial 502b.

The graphs in Figure 16 also showed the amount of K that was fixed in relation to equilibrium solution concentration. In the K-fertilised plots, at a given solution concentration of K, more non-exchangeable K was released in trial 502b than 504.The equilibrium solution K concentration reached higher values in the plots and zones with a history of K fertiliser application than in those with a history of no K fertiliser.

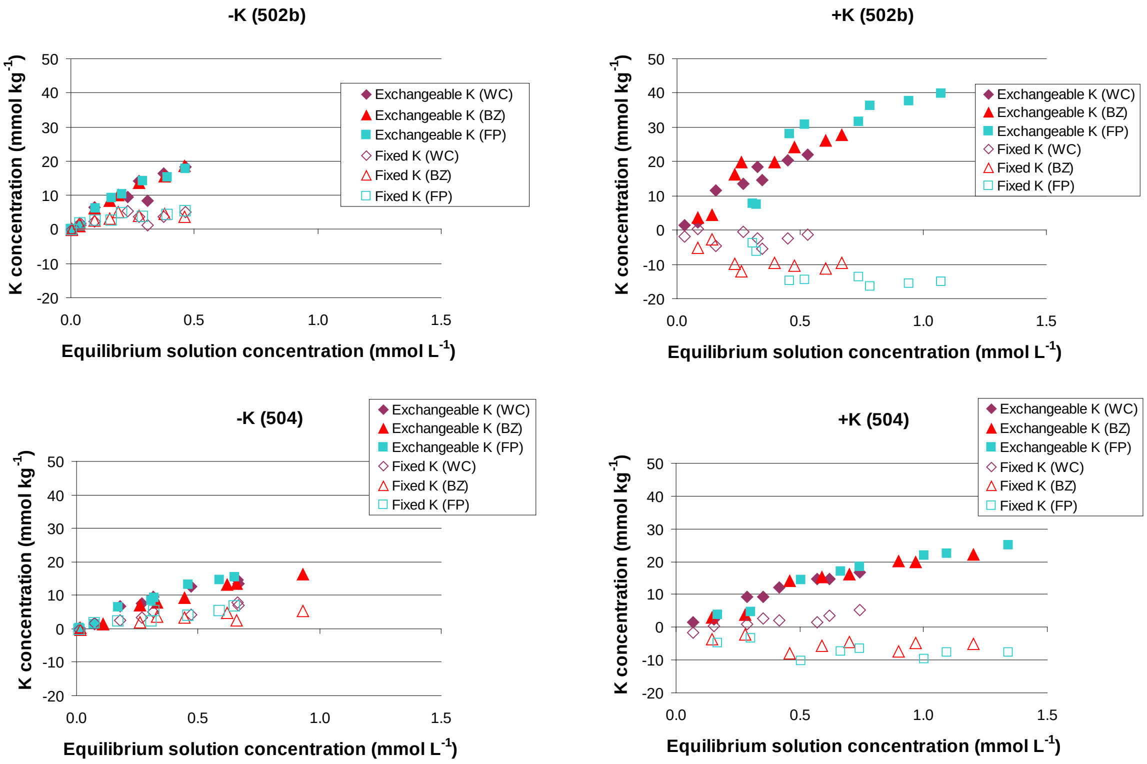

Figure 16. Exchange isotherms and amounts of fixed K in the two trials (502b and 504) in plots with (+K) or without (-K) a history of K fertiliser application.

4.4 Discussion

The experiment in this chapter was designed to measure fixation of K, however in the plots with K fertiliser history there was in fact considerable release of K. In those plots, exchangeable K contents were higher than the amount added to the soil, thus the negative fixation values. In similar studies, Simonsson *et al.* (2007) and Jalali (2007) measured both positive and negative values for K fixation as calculated here. They related the negative sign to the K release and positive sign to K fixation. Some clay minerals, when saturated with K, release most of their absorbed K very easily because mostly their K ion exists as surface K and interlayer K in accessible sites (Mengel and Uhlenbecker 1993). This could be the reason why a substantial amount of K was released as more K was added to the soil. Sparks and Huang (1985) and Fanning *et al*. (1989) reported that partial release of interlayer K seems to proceed near equilibrium and switches to fixation if the concentration of K in the soil solution exceeds a critical level.

Fixation and release in this study were influenced by the K fertiliser history and not by trial sites (which differed in clay content and mineralogy, CEC and organic matter content) or zones (which differed in organic matter content, pH and CEC). In plots with a history of no K fertilizer, about 20-30% of added K was fixed by the soils in both trials, even though they had different mineralogy. In the absence of K fertiliser application, continuous depletion of the non-exchangeable K reserve may build up the capacity to fix added K (Sachdev and Khera 1980). Thus in this experiment, most of the native exchangeable and non-exchangeable K in the plots with no K fertiliser history may have been depleted through continuous uptake by the oil palms to maintain their growth and production. As a consequence, more K was fixed. These results are consistent with those of Mehdi and Ranja (1997) and Dhaliwal *et al*. (2006). Dhaliwal *et al.* (2006) also examined soils with low K content having high K fixation capacity under continuous cropping with little or no K fertiliser application. They measured K fixation values between 44.6 and 86.4 % of that added in low K soil series, compared to 18 and 42 % in the K-rich soil series. In another study by *Li et al.* (2010), higher K fixation was measured in the soil with no applications of K fertiliser than in the soil with a history of K fertiliser application. They concluded that K fertiliser application reduced K fixation in soil.

Application of K fertiliser affects concentration of K in exchangeable and non-exchangeable pools, which influences K fixation (Sparks and Huang 1985; Mittal *et al.* 1990; Conti 2001; Jalali 2007). The lower the concentration of K in exchangeable and non-exchangeable forms, the higher the K fixation capacity of the soil. Therefore, fixation of added K occurred in the plots with a history of no K fertiliser, because the concentration of K in the exchangeable and non-exchangeable pool was low. When soluble K fertilisers are applied, the soil solution K ions and K concentration rises and K moves onto the exchangeable and non-exchangeable pools (Krishnakumari and Khera 1983; Kirkman *et al.* 1994).

The release of K from the non-exchangeable K pool in plots with a history of K fertiliser application was higher in the soil in trial 502b than the soil in trial 504. The difference in K release between sites in the plots with a history of K fertiliser application could be related to the history of the two trials. As the plantation requirement for maximising production, K fertiliser is applied in the plantations every year from the time when the palms start producing crop. The palms in trial 502b were planted in 1986 whereas the palms in trial 504 were planted in 1991, so trial 502b would have received K fertiliser for longer than trial 504; hence the higher concentration of K in exchangeable and non-exchangeable forms in trial 502b, which then resulted in higher K release. Bhonsle *et al.* (1992) found K release was lowest in soils low in exchangeable and non-exchangeable pool. The higher the content of K in the exchangeable and non-exchangeable pool, the higher the cumulative K release from the non-exchangeable pool (Bhonsle *et al.* 1992; Etchevers and Hidalgo 2005). The release of K from the soils is examined further in the next chapter.

The clay mineralogy of the soil appears to have little or no influence on K fixation in this study. If K fixation was dependent on the clay mineralogy of the soil, K fixation values would be higher in trial 504 than that in trial 502b, due to dominance of vermiculite in the clay soil in Trial 504. Vermiculite had been reported to have higher fixing capacity than smectite (Bouabid *et al.* 1991; Brady and Weil 2008). However, that was not the case in this study because the fixation capacities of the soil in both trials were more or less the same.

The results of this study have implications for management of K fertilizer to oil palm on these soils. Applying K fertiliser on soils with depleted soil K reserves will result in a considerable portion of that K being fixed by the soil, whereas if K fertiliser is applied to areas with high K concentration from a prolonged history of K fertiliser application, then there will be no net fixation of K. Therefore, placement of K fertilisers is important in improving K availability in alluvial clay soils.

4.5 Conclusions

K fixation and release was related more to the K fertiliser treatments than the other two treatments (trial site and management zones). K fixation occurred only in the plots and zones with no K fertiliser history and was more or less the same in both trials, irrespective of the presence of different clay minerals at the two sites. In those plots and zones, in both trials, approximately 20-30% of the K added was fixed. In the K fertilised plots, substantial amounts of K were released from the non-exchangeable pool, with trial 502b releasing more than trial 504. More K was released from the BZ and FP zones (to which fertilizer had been added) than the WC zone (to which little or no fertilizer had been added. An implication of the findings is that fixation might be minimized by adding fertilizer continuously to the same zones.

CHAPTER FIVE

5 Release of non-exchangeable potassium into solution

5.1 Introduction

The non-exchangeable K pool is an important reservoir of K in soils (Barre *et al*. 2007) and when released, K from this pool can contribute up to 80-90% of K supply to plants (Hinsinger 2002). Mengel (1985) also mentioned in his review paper that many plants feed from the non-exchangeable source of K, especially the monocots. In order for K to be released from the non-exchangeable pool, first the concentration of K in the solution and exchangeable forms must be depleted to trigger release from the non-exchangeable form to buffer K levels in these two forms. It is therefore important that for maximum plant growth, soil solution and exchangeable K must be replenished continuously by release of K from the non-exchangeable pool (Jalali 2006). The K release from non-exchangeable K forms is influenced mainly by the type and amount of clay, and the concentration of different K forms in the soil (Jalali 2006; Simonsson *et al.* 2007). Other factors affecting K release include CEC, soil reaction, organic C and the application rates of K fertiliser (Sharma and Mishra 1991).

Availability of non-exchangeable K depends not only on the amount of K released from the interlayer of the clay minerals but primarily on the rate at which it is released into more available forms for plant uptake. The type of clay minerals greatly influences the rate of K release from the non-exchangeable pool (Sparks 1987). Soil fertility research has now been shifted from measuring the amounts of K released from the non-exchangeable K pool to determining the rate at which K is released from these forms. Although kinetics of K release have been studied (Cox and Joern 1997; Dhillon and Dhillon 1990; Martin and Sparks 1983; Jalali 2006), most of these studies were more related to the effects of soil mineralogy and other physical and chemical characteristics of the soil. Studies on the effects of K fertiliser application rates are scarce, except some work done by Srivastava *et al*. (2002) and Srinivasa *et al.* (1999). K release rates from the soil under long-term cropping and fertiliser application trials could help to predict the fate of added K in soil as well as the nature of K supply to plants.

Soils in trials 502b and 504 are dominated by smectite and vermiculite 2:1 clay minerals that fix applied K. Work in previous chapters showed that a considerable amount of K is present in non exchangeable forms, mostly originating from K fertiliser applied in previous years. The dynamic equilibrium among the different K pools controls the release of K from the non-exchangeable pool to more available forms. This equilibrium is likely to be influenced by K uptake and K fertiliser application. Therefore, the aim of this experiment was to determine the effects of site and management (K fertiliser history and surface management zones) on release of non-exchangeable K.

5.2 Materials and methods

5.2.1 Field work – soil sampling

The soils used in this experiment were the same as those used and described in section 3.2 (Chapter 3).

5.2.2 Soil treatment and laboratory analysis

For each measurement of K release, about 5 g of air dried, sieved (<2 mm) soil was weighed into a 50-mL centrifuge tube. Solution and exchangeable K was then removed and the soil was saturated with Ca as follows. A 25 mL aliquot of 0.25 M $CaCl_2$ was added and the suspension was shaken on an end-over-end shaker for 30 minutes. After shaking, the sample was centrifuged for 10 minutes at 4000 rpm and the supernatant was discarded. This procedure was repeated 2 times (total of 3 times). Then 25 mL of 0.01 M $CaCl_2$ was added to the soil, and shaken on the end-over-end shaker for 30 minutes. After shaking, the sample was centrifuged for 10 minutes at 4000 rpm and the supernatant was discarded. This procedure was repeated (total of 2 times).

Following saturation with Ca in the manner described above, a further 25 mL of 0.01 M $CaCl_2$ was added to the soil and the sample was shaken for 1 hour, and then centrifuged for 10 minutes at 4000 rpm. A sample of supernatant was removed for analysis and the remaining supernatant was discarded. A further 25 mL of 0.01M $CaCl_2$ was added and the sample was placed back on the shaker. After 24 hours, the sample was centrifuged and the supernatant sampled and discarded. This procedure was repeated, with subsequent removals of supernatant at 1, 24, 48, 72, 120, 264, and 480 hours. There was no replication done in this experiment other than the field plot replication. Potassium concentration in the supernatant was measured using the atomic absorption spectrophotometer. Cumulative release of K from the non-exchangeable pool was calculated by summing the amounts removed at each step. Significance of the treatment effects was examined by ANOVA.

The kinetics of K release from non-exchangeable pools into solution has been described using several functions (Aharoni *et al*. 1991; Cox and Joern 1997). In this work, the commonly used Elovich function (Equation 1) was fitted to the data. In Equation 1, q (mmol kg^{-1}) is the cumulative amount of non-exchangeable K released into solution at time t (hours). t_0, a and β are fitted constants. Equation 1 was fitted to the data using iteration and the least squares method in Sigma Plot. If the data fit the model, then the release process is assumed to be diffusion-controlled (Aharoni *et al.* 1991; Cox and Joern, 1997). Fitting the Elovich function enabled derivation of release-related parameters that could be used to relate K release to soil properties. The parameter α is a quantity inversely related to the energy of activation for desorption. The parameter t_0 has been described as an estimate of the time beyond which release is Elovichian, and the reaction preceding t_0 cannot be described as Elovichian (Cox and Joern, 1997).

$$q = (1/\beta) \ln \alpha\beta + (1/\beta) \ln (t + t_0) \qquad \text{Equation 1}$$

5.3 Results

5.3.1 Cumulative K release

The cumulative release of K from the non-exchangeable K pool was significantly affected ($p<0.001$) by all the treatments (Trial, K fertiliser history and zones) and all their interactions at all times of measurement. The cumulative amount of K released increased with the equilibration time for both trials, with more K released from the native non-exchangeable pool in trial 504 than trial 502b (Table 18). Release of native non-exchangeable K was taken as that released from the non-exchangeable K pool in the plots with a history of no K fertiliser application.

Potassium fertiliser application history had a pronounced effect on the release of K from the non-exchangeable pool (Table 18, Figure 17). A substantial amount of K was released from the plots with a history of K fertiliser application compared to those that did not receive any K fertiliser. In the plots with a history of K fertiliser application, higher amounts of K release was measured in trial 502b than 504. At the longest equilibration time (480 hours), an average of 1.95 mmol K kg^{-1} soil was released from trial 502b, while only 0.74 mmol K kg^{-1} soil was released from trial 504.

The effect of the different management zones on cumulative K release was related mostly to K fertiliser history of the soil (Table 18, Figure 17). As a result, K released from non-exchangeable form was more pronounced in the plots that received K fertiliser than those that did not receive any K fertiliser. In both trials, more K was released from the FP zones than the other zones, and K release in both trials increased in the order; HP<WC<BZ<FT<FP. Potassium fertiliser is normally applied in the BZ, FT and FP zones rather than the other two zones.

Table 18 Treatment effects on cumulative amount of K released (mmol K kg^{-1} soil) at different times. All treatments and interactions were significant at all measurement times ($p<0.001$)

Treatments			**Equilibration time (hours)**						
Trial	**K fert.**	**Zone**	**1**	**24**	**48**	**72**	**120**	**264**	**480**
502b	-K	HP	0.007	0.02	0.03	0.03	0.04	0.05	0.06
502b	-K	WC	0.009	0.03	0.04	0.05	0.07	0.08	0.09
502b	-K	BZ	0.004	0.01	0.02	0.03	0.03	0.04	0.05
502b	-K	FT	0.004	0.03	0.04	0.05	0.07	0.08	0.08
502b	-K	FP	0.005	0.02	0.03	0.04	0.05	0.07	0.07
502b	+K	HP	0.05	0.11	0.15	0.19	0.24	0.29	0.33
502b	+K	WC	0.15	0.28	0.39	0.50	0.61	0.72	0.81
502b	+K	BZ	0.31	0.58	0.83	1.06	1.29	1.46	1.63
502b	+K	FT	0.72	1.33	1.84	2.32	2.75	3.08	3.40
502b	+K	FP	0.72	1.35	1.91	2.42	2.90	3.25	3.60
502b –K mean			*0.01*	*0.02*	*0.03*	*0.04*	*0.05*	*0.06*	*0.07*
502b +K mean			*0.39*	*0.73*	*1.02*	*1.30*	*1.56*	*1.76*	*1.95*
502b mean			*0.20*	*0.38*	*0.53*	*0.67*	*0.81*	*0.91*	*1.01*
504	-K	HP	0.01	0.03	0.06	0.08	0.10	0.12	0.14
504	-K	WC	0.01	0.04	0.08	0.10	0.13	0.16	0.18
504	-K	BZ	0.02	0.04	0.06	0.08	0.10	0.12	0.14
504	-K	FT	0.02	0.04	0.07	0.09	0.11	0.14	0.16
504	-K	FP	0.02	0.04	0.07	0.09	0.12	0.16	0.18
504	+K	HP	0.06	0.14	0.23	0.31	0.53	0.60	0.14
504	+K	WC	0.12	0.28	0.42	0.53	0.65	0.76	0.18
504	+K	BZ	0.19	0.39	0.57	0.72	0.87	0.96	1.05
504	+K	FT	0.17	0.36	0.54	0.70	0.84	0.95	1.03
504	+K	FP	0.23	0.49	0.71	0.90	1.08	1.20	1.30
504 –K mean			*0.02*	*0.04*	*0.07*	*0.09*	*0.11*	*0.14*	*0.16*
504 +K mean			*0.15*	*0.33*	*0.49*	*0.63*	*0.79*	*0.89*	*0.74*
504 mean			*0.09*	*0.19*	*0.28*	*0.36*	*0.45*	*0.52*	*0.45*

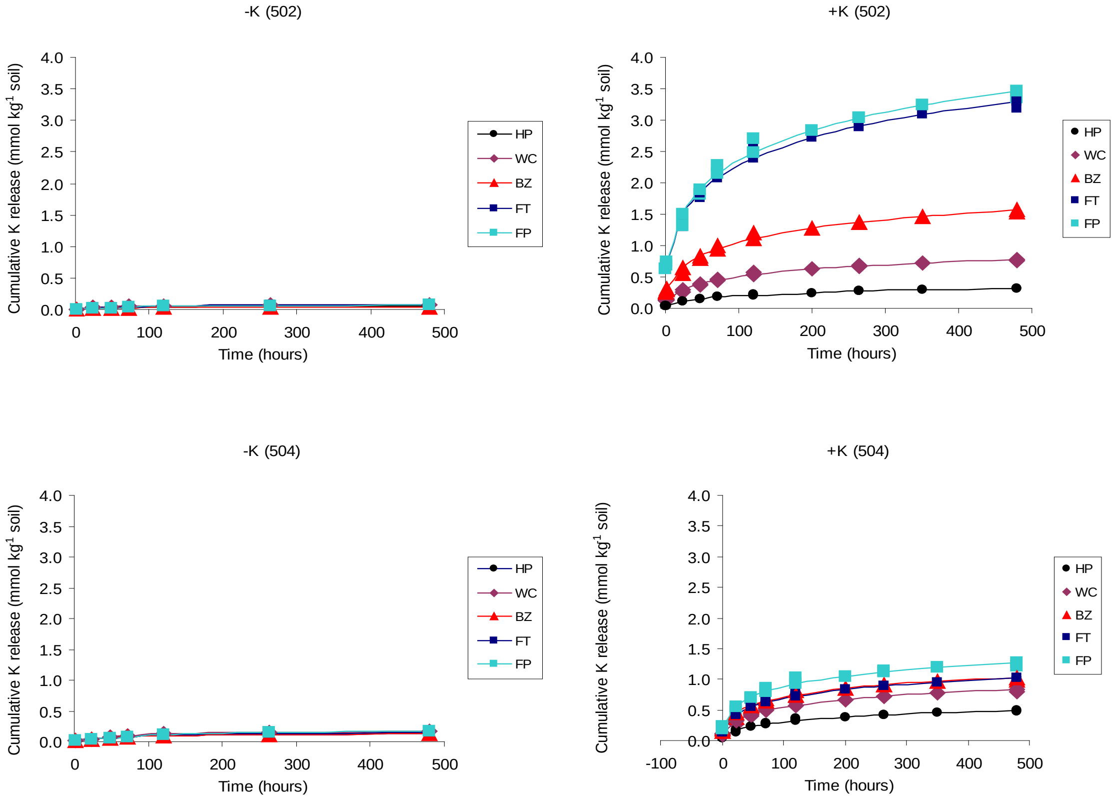

Figure 17. Release of non-exchangeable K into solution in trial 502b and 504. Points are data and lines are fitted curves (Equation 1). See Table 19 for fitted curve parameters. All treatment effects and all their interactions were significant ($p<0.001$).

5.3.2 Cumulative K release as a proportion of the non-exchangeable K

The proportion of non-exchangeable K that was released differed between the treatments. Irrespective of the K fertiliser history and the management zone, a higher proportion of K from the non-exchangeable K pool was released from trial 502b than trial 504 (Figure 18). The proportion of non-exchangeable K that was released was fairly constant above a threshold concentration (linear portion of curves in Figure 19). Based on the linear fit in Figure 19, the threshold concentrations were 1.61 and 3.76 mmol kg^{-1} in trial 502b and 504 respectively, and the proportion of non-exchangeable K above that value that was released was 9.6 % in trial 502b and 5.5 % in trial 504 (Figure 19).

There was a marked effect of K fertiliser treatments on K release as a proportion of the non-exchangeable K (Figure 18). In both trials, the proportion of non-exchangeable K released from the soils with a K fertiliser history was two times more than that from the soils that had received no K fertiliser.

The proportion of non-exchangeable K that was released differed between the zones, however the size of the difference was much greater in trial 502b than trial 504 (Figure 18). In trial 502b, irrespective of the K fertiliser history, a higher proportion of non-exchangeable K was released in the FT and FP compared to the other zones, with the least release of K from the HP zones. In trial 504 the proportion of the non-exchangeable K that was released followed similar trend but the differences between the different zones were less pronounced. Differences in release rate between the zones were explained by trial site and concentrations of non-exchangeable K (Figure 18).

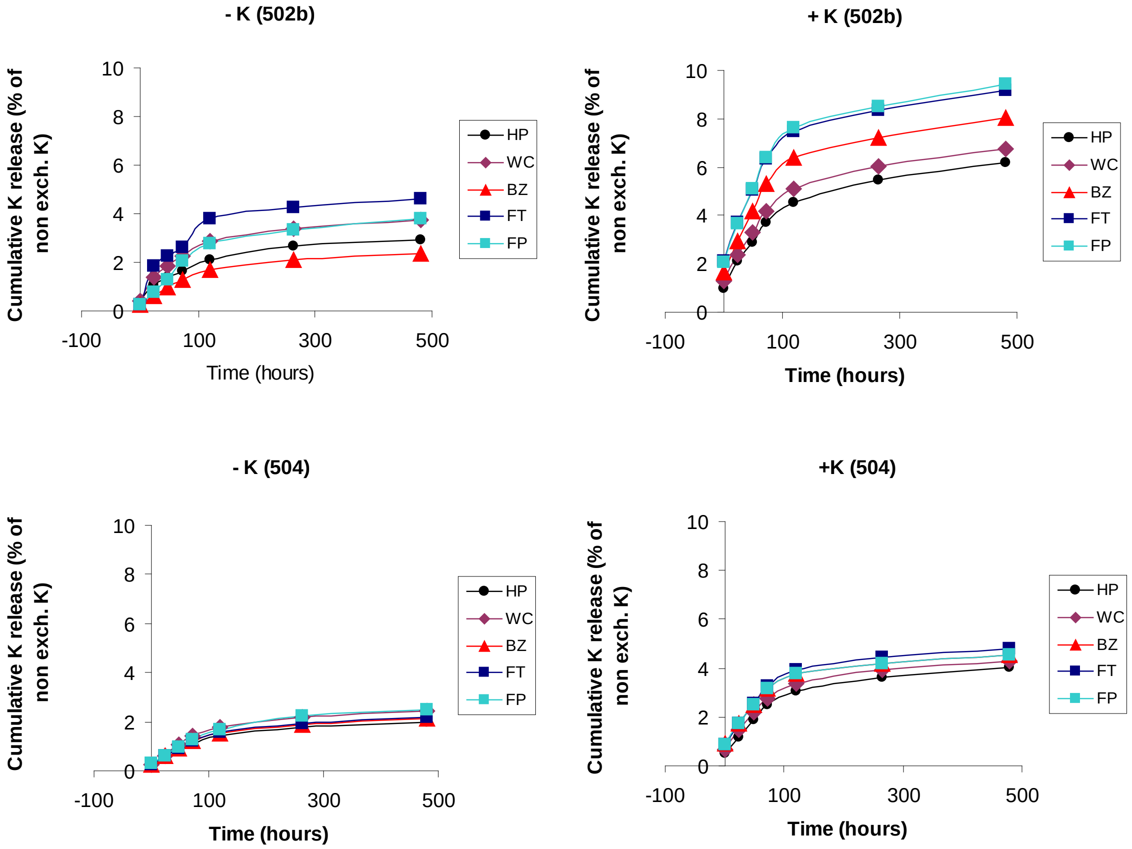

Figure 18. K release as a proportion of non-exchangeable K in trial 502b and 504.

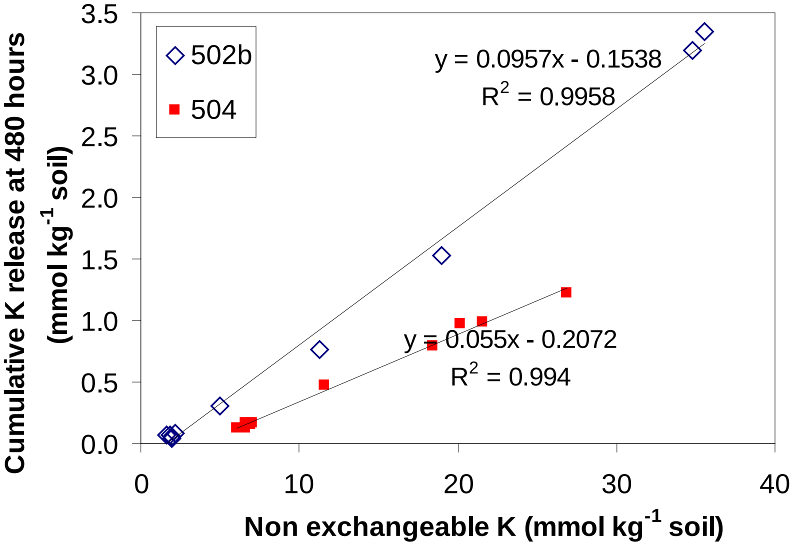

Figure 19. Relationship between cumulative release of non-exchangeable K and the amount initially present.

5.3.3 Kinetics of K release

The rate of K release decreased gradually with increasing time (Figure 17). This type of behaviour was observed in all the samples from the two trials but with different magnitudes. Release of K from the non-exchangeable K pool was rapid during the first 72 hours, and slowed thereafter.

The Elovich function fitted the data well (Table 19). This is evident from the high correlation coefficient values ($r^2 = 0.957\text{-}0.989$) and low standard errors (0.002-0.179). In the soils examined, t_0 ranged from 6 to 28 hours. The parameters α and $1/\beta$, which describe the shape of the curve, were closely related ($1/\beta = 4.0184\ \alpha + 0.0352$, $r^2 = 0.971$), and both were linearly related to the amount of non-exchangeable K measured in the soils at each site; i.e. the rate of release of non-exchangeable K was positively related to the amount present. The rate of release was greater for trial 502b than trial 504. The fit of data to the Elovich model from this experiment indicates that K release was a diffusion-controlled exchange reaction.

Non-exchangeable K content explained over 98% of the variation in release rate (Figure 20), so there was no effect of zones other than their content of non-exchangeable K. As described in Chapter 3, non-exchangeable K content was closely related to the amount of fertiliser K that each zone had received. Non-exchangeable K was released more rapidly from trial 502b soil than trial 504 soil.

Table 19. Elovich curve fitting to cumulative K release (mmol kg^{-1}), from Sigma Plot for each treatments.

Treatments							
Trial	K fert	Zone	α (mmol kg^{-1} h^{-1})	β (kg mmol $^{-1}$)	t_0 (h)	adjusted r^2	s.e. of estimate
502b	-K	HP	0.002	70.9	13.3	0.989	0.002
502b	-K	WC	0.003	51.4	9.1	0.987	0.003
502b	-K	BZ	0.001	74.3	19.2	0.985	0.002
502b	-K	FT	0.003	58.6	6.1	0.967	0.004
502b	-K	FP	0.001	45.0	21.6	0.955	0.005
502b	+K	HP	0.009	12.6	15.4	0.985	0.011
502b	+K	WC	0.023	5.2	15.9	0.979	0.032
502b	+K	BZ	0.061	2.8	12.1	0.967	0.081
502b	+K	FT	0.176	1.5	9.7	0.966	0.163
502b	+K	FP	0.164	1.4	10.5	0.964	0.179
502b –K mean			*0.002*	*60.0*	*13.9*	*0.977*	*0.003*
502b +K mean			*0.087*	*4.7*	*12.7*	*0.972*	*0.093*
502b mean			*0.044*	*32.4*	*13.3*	*0.974*	*0.048*
504	-K	HP	0.003	25.4	19.6	0.974	0.007
504	-K	WC	0.004	20.2	17.1	0.968	0.010
504	-K	BZ	0.003	26.8	19.0	0.981	0.006
504	-K	FT	0.003	23.1	19.3	0.980	0.007
504	-K	FP	0.003	18.5	27.7	0.984	0.007
504	+K	HP	0.013	8.2	12.6	0.965	0.028
504	+K	WC	0.029	5.2	10.7	0.969	0.043
504	+K	BZ	0.053	4.7	8.4	0.953	0.062
504	+K	FT	0.045	4.5	9.0	0.956	0.062
504	+K	FP	0.067	3.8	8.0	0.955	0.077
504 –K mean			*0.003*	*22.8*	*20.5*	*0.977*	*0.007*
504 +K mean			*0.041*	*5.3*	*9.7*	*0.960*	*0.054*
504 mean			*0.022*	*14.0*	*15.1*	*0.969*	*0.031*

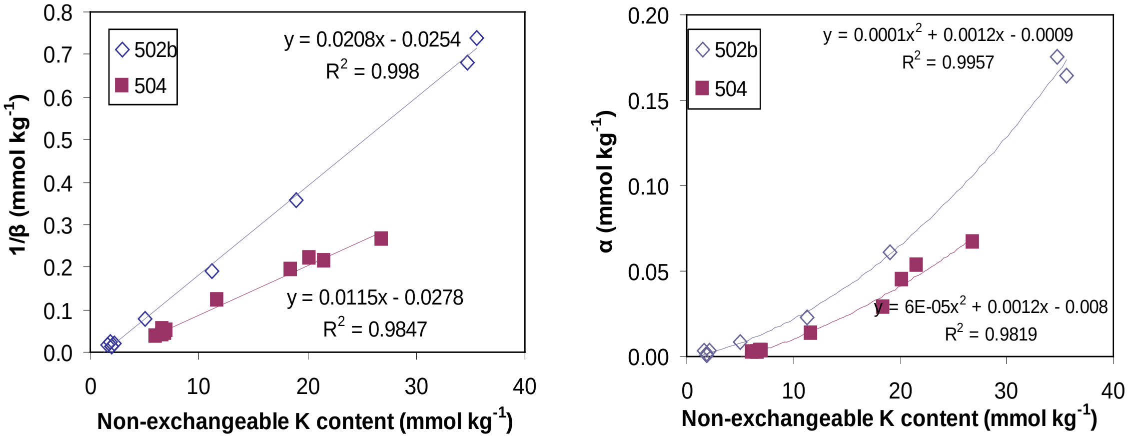

Figure 20. Release rate parameter for trial 502b and trial 504, as a function of the amount of non-exchangeable K measured prior to the release experiment.

5.4 Discussion

The results of this experiment showed that release was initially rapid at both sites, but then slowed with time. The rapid release of K in the earlier stages of reaction could be due to the fact that K was being released from easily accessible sites of the clay minerals. The later stage of slow release is from the interlayer sites of the clay minerals. Similar work by various researchers also showed similar trend (Cox and Joern 1997, Rao *et al.* 1999, Jalali 2005, Dhaliwal *et al.* 2006, Srinivasarao *et al.* 2006 and Li *et al.* 2010).

Clay content and mineralogy could have had an effect on K release in the two trial sites, by influencing the concentration of K in the K reserves, which is positively correlated to K release (Bhonsle *et al.* (1992). Trial 504 soil had higher clay+silt content than trial 502 soil and trial 504 was comprised predominantly of vermiculite whereas trial 502b soil was mostly smectite. However, surprisingly, trial 502b had higher ECEC than trial 504 (Chapter 3). Smectite is more weathered than vermiculite and when moving from vermiculite to smectite, some of the K ions are lost, resulting in a much lower K content in smectite than vermiculite (Brady and Weil, 2008). This could be another factor contributing to lower K release in trial 502b (with no K fertiliser applications). The higher proportion of fine clay in trial 504 may also have contributed to higher K release in the unfertilized soil. Cox and Joern (1997) found the release rates of K increased with a decrease in the particle size. The results from the three soils studied showed that the non-exchangeable K release in the fine clay was relatively fast and was almost completed in 8 hours. Dhaliwal *et al*. (2006) also reported difference in rate of K release between the benchmark soils studied was due to clay content.

Application of K fertiliser in trials 502b and 504 had a major effect on K release. Two observations were made in relation to the K fertiliser treatments: Firstly, K release was high in plots with a history of K fertiliser addition. Secondly, in the plots with a history of K fertiliser addition, a higher proportion of non-exchangeable K was released in trial 502b than 504. This is in contrast to the plots with a history of no K fertiliser which showed higher release in trial 504 than 502b. Prolonged application of K fertiliser since 1995 and 1994 in trial 502b and 504, respectively, had contributed to the high contents of K in the exchangeable and non-exchangeable pools compared to the plots with no K fertiliser application. The higher the content of K in the exchangeable and non-exchangeable pool, the higher the cumulative K release from the non-exchangeable pool. When considering the K fertiliser effects, the results from this study were similar to those reported by Rao *et al.* (1990) and Srivastava *et al.* (2002). Rao *et al.* (1990)

recorded the lowest K release from the non-exchangeable fraction of the soil in the 100% optimum nitrogen + phosphorus (NP) treatment (i.e. no K fertiliser applied), and the highest K release in the 100% optimum NPK + farmyard manure treatment. From their results, they concluded that continuous cropping without K inputs through fertilisers or manure caused a decline in non-exchangeable K reserves and release rate while application of recommended NPK plus farmyard manure maintained higher release rates. Similarly, Srivastava *et al.* (2002) measured the highest and lowest amount of K release in 100% NPK+farmyard manure and 100% NP (nil K) respectively. The release rate constants in their study were lowest in 100% NP (nil K) and highest in 100% NPK + farmyard manure treatment in the both surface and sub-surface soil.

The difference in K release rates between trial 502b and 504 may have been due to differences in their clay mineralogy. Release of K from non-exchangeable K pool in soils dominated by smectite and kaolinite minerals were quite rapid compared to vermiculite minerals (Eick *et al*. 1990). In smectite, the inner peripheral space is not held together by hydrogen bonds, but instead it is able to swell with adequate hydration thus allowing for rapid passage of K ions out of the interlayer. On the other hand, vermiculite has peripheral spaces that impede many ion exchange reactions such as the rate at which K ion is released from its interlayer (Sparks and Huang 1985). This could be the reason why the K release as a proportion of the non-exchangeable K in the native soil was higher in trial 502b than 504. Sparks and Jardine (1984) also found that the kinetic of K release on smectite and kaolinite were quite rapid compared to vermiculite minerals. Srinivasarao *et al.* (2006) studied release kinetics of non-exchangeable K on six soil series of India and also found that release rates of non-exchangeable K were greater in smectitic soils than in illitic soils.

The amounts and rates of K release from the non-exchangeable pool depend on the type of approach used. The K extraction methods used to estimate plant availability must access both exchangeable and non-exchangeable K forms or estimate the dynamic relationship between these two K pools. The amount of released K that was measured in this study was not the total amounts but only that which was in solution. More K was actually released, but was held as exchangeable K and not necessarily extracted by 0.01 M $CaCl_2$. In 0.01 M $CaCl_2$, the K ions on the surface of the clay mineral are replaced by Ca^{2+}. However, the Ca^{2+} ion does not exchange easily with the K in the interlayer of the clay minerals because of its larger size and hydration energy (Rao *et al*. 1999, Srinivasarao *et al*. 2006).

5.5 Conclusions

The rate and amount of K released from the non-exchangeable pool into solution was determined by the amount of non-exchangeable K present (determined mostly by K fertiliser history) and the trial site. K release from the non-exchangeable K was faster in trial 502b than in trial 504, presumably due to differences in the type of clay present. Surface management (zones) had no effect on the rate of K release, other than that due to their differences in non-exchangeable K content.

CHAPTER SIX

6 General discussion

6.1 Factors affecting forms of K, K fixation and K release

6.1.1 Effects of trial site

Clay content and type have been found to have a significant influence on the K balance of the soil, K fixation and release capacity of soils, particularly when smectite and vermiculite are present (Nabiollahy *et al.* 2006). In this study, the difference in native soil K contents between the two trials were related to clay type, whereas K fixation and release were more influenced by the concentration of K in the soil, which was mostly due to fertiliser history. Higher content of exchangeable and non-exchangeable K in trial 504 (in plots that had received no K fertiliser) was presumably related to the dominance of vermiculite in the soil mineralogy of that site. Vermiculite can hold more K ions in the exchangeable and non-exchangeable pools than smectite because it has higher CEC and negative charge. According to Brady and Weil (2008), the interlayer spaces of vermiculites contain strongly adsorbed water molecules, Al-hydroxy ions and cations like magnesium that act as bridges holding the units together rather than wedges driving them out. As a result of this, the degree of swelling and shrinkage is less than smectite clay mineral. Several studies have shown that soils with high contents of vermiculite and mica contain large amounts of exchangeable and non-exchangeable K (Martin and Sparks 1985; Shaviv *et al.* 1985). Surprisingly, the ECEC values for Trial 504, in which vermiculite dominates, were lower than trial 502b, in which the clay mineral component is dominated by smectite.

Potassium fixation capacity did not differ significantly between the two trials, despite their difference in mineralogy. Trial 504, having vermiculite as the dominant clay mineral, was expected to have higher fixation capacity than trial 502b, which is dominated by smectite. Vermiculite has a higher fixation capacity than smectite because it has a high tetrahedral negative surface charge, while smectite has mostly octahedral negative charge (Bouabid *et al.* 1991; Brady and Weil 2008). Studies have shown that soil chemical properties such as CEC, pH, organic C content, clay content and particle size distribution can have a major influence on K fixation capacity of soil (Brady and Weil 2008; Murashkina *et al*. 2007). Sardi and Csitari (1998) studied the K fixation of different soil types with different nutrient levels and found a positive relationship between exchangeable K content, dry K fixation and wet K fixation. They concluded that soil parameters in their study such as humus content, pH and CEC of clay gave a satisfactory explanation for the differences in dry and wet fixation. Conti *et al*. (2001) reported significant positive correlation between K fixation rate and soil organic C content. Fixation rates were increased with low organic C content. Even though vermiculite has the tendency to fix higher quantities of K than smectite, greater ECEC, lower organic C content, higher pH and higher clay content of the soil in trial 502b than 504 could have elevated the K fixation capacity of the soil in trial 502b to the same level as that found in trial 504.

Clay content may also have influenced K fixation capacity in this study. In a study on release of interlayer K in Norwegian soils, Øgaard and Krogstad (2005) found an increase in K fixation during 3 years of cropping without K fertiliser, which was positively related with the clay content. The effects of clay content or mineralogy on K fixation could not be determined definitively from my study because the clay content was only measured in the soils with a history of no K fertiliser application, and because the re was no way of separating the effects of the various soil properties that differed between the two trials.

The difference in the amount of K released from the non-exchangeable pool in the soils of the two trials was influenced mostly by the concentration of K in that pool. Similarly, Bhonsle *et al.* (1992) found K release to be the lowest in soils with low contents of exchangeable and non-exchangeable K. In addition, the amounts and rates of K release that they measured were positively and significantly correlated with the amount of K in the non-exchangeable pool. Dhaliwal *et al*. (2006) found differences in the amounts of K released in the five benchmark soil series they were studying. The soil series with the highest K release capacity contained the highest amount of exchangeable K initially, while the soil series with the lowest amounts of K released from the non-exchangeable pool had the lowest amount of exchangeable K initially.

Availability of non-exchangeable K depends primarily on the rate at which non-exchangeable K can be released into more labile forms (Sparks 1987). The rate of release should be rapid enough to support plant growth and to prevent K deficiency symptoms. The rate (kinetics) of K release differed between the trial sites and appeared to be related to the soil mineralogy at each site. The rate at which K was released from the non-exchangeable K pool was greater in trial 502b than 504. Previous studies had reported rapid K release from the smectite clay compared to other 2:1 clay minerals (Sparks and Huang 1985; Sparks and Jardine 1984; Eick *et al*. 1990; Srinivasarao *et al.* 2006). In smectite, the inner peripheral space is not held together by hydrogen bonds, but instead it is able to swell with adequate hydration thus allowing for rapid passage of K ions out of the interlayer. Vermiculite, on the other hand has peripheral spaces that impede many ion exchange reactions such as the rate at which K ion is released from its interlayer (Sparks and Huang 1985).

The layer edge and wedge zones and the swelling nature of the smectite clay could have facilitated the easier exchange.

6.1.2 Effects of K fertiliser application history

The results from Chapter 3, 4 and 5 have shown that K fertiliser application had the greatest influence on the three parameters measured (K amounts, K fixation and release capacity of the soils). Fertiliser application had increased exchangeable and non-exchangeable K contents in the soil by 23- and 8-fold respectively in trial 502b, and by 6- and 3-fold respectively in trial 504. The contents of these two forms of K were low in the soil that had received no K fertiliser, presumably at least partly due to mining of K by the palms since the trials started. Cope (1981) observed that the original exchangeable K content (54 mg kg^{-1}) of six surface soils (0-0.1m) in Alabama under a 2-year cotton/corn rotation receiving no K fertiliser, decreased by 26 % over a 50-year period, whereas application of 112 kg K ha^{-1} $year^{-1}$ over a 21-year period increased exchangeable K by an average of 240 %. Blake *et al.* (1999) studied the fate of K derived from mineral fertilisers and organic manures and the K balance in three European long-term field experiments and found that application of K fertiliser over a 30-year study period increased content of K in all extracts. They also found that the soils not treated with K but receiving N, P and Mg showed a decline in K content. The content of exchangeable and non-exchangeable K in plots with a history of K fertiliser could also have been naturally low as reported by Bleeker (1988).

Samadi *et al.* (2008) found a significant positive relationship between exchangeable K content, clay content, soil organic C content and CEC, indicating that as the size of the exchange complex increases, exchangeable K content increases. In my study, there was no difference in soil organic C content between plots that had received K fertiliser or not. The ECEC, however, was significantly higher in the fertilised plots compared to plots that had received no K fertiliser.

Fertiliser application had a pronounced effect on K fixation capacity of the soils in both trials. In plots that had received no fertiliser K, an average of 27 % of added K was fixed into non-exchangeable forms. In the plots that had received K fertiliser, substantial amounts of K were released from the non-exchangeable pool, although some K was still fixed in the WC zone in trial 504. The K pools (solution, exchangeable and non-exchangeable) are always in equilibrium with each other, thus a change in concentration in one will affect the other (Brady and Weil 2008). When K levels in the soil solution and exchangeable pools are heavily depleted through plant uptake or leaching, K is released from the non-exchangeable pool to buffer the falling K concentration in the two pools, thus the K in the non-exchangeable pool acts as a very important source of K for plant uptake in the absence of K fertiliser (Barre *et al*. 2007; Andrist-Rangel *et al*. 2007). Therefore, when K fertiliser is added to soil with low contents of exchangeable and non-exchangeable K, a proportion of the applied K will eventually move into the interlayer of the clay minerals where it is fixed. Dhaliwal *et al.* (2006) also reported high K fixation in soils with low K content under continuous cropping with little or no K fertiliser application. They measured K fixation values between 44.6 to 86.4 % of that added in the soil series with low K content, compared to 18 to 42 % in the K-rich soil series.

In soils with K fixing capacity, a significant relationship has been found between the amount of K fixed and the concentration of K ions in the exchangeable and non-exchangeable pools (Sparks and Huang 1985; Mittal *et al.* 1990; Conti 2001; Jalali 2007). The lower the concentration of K in exchangeable and non-exchangeable forms, the higher the K fixation capacity of the soil. Krishnakumari and Khera (1983) measured up to 80% fixation of added K in plots that had received high doses of N and P but no K fertiliser. Conti *et al*. (2001) measured up to 24 % fixation of added K in smectitic soil from plots that had received no K fertiliser.

Vermiculite normally has a higher fixing capacity than smectite because of its higher surface charge density and higher CEC (Brady and Weil 2008). Those characteristics were not apparent in this study as the soil from trial 504, which consists predominantly of vermiculite, had a lower ECEC than the smectitic soil from trial 502b. In addition, the vermiculitic soil in trial 504 had the same fixing capacity as the smectitic soil in trial 502b. Barre *et al.* (2008) found that the soil chemical environment can modify the interlayer site occupations, which implies that high level of K accumulation can occur without any modification of the clay structure sheet. Therefore other soil properties such as pH may have reduced the CEC and K fixation capacity of the vermiculite in trial 504 soil.

Previous researches on the effects of K fertiliser application history in long-term field trials have found that K release was influenced by the concentration of K ions in the soil (Rao *et al*. 1999; Sing *et al*. 2002; Srivastava *et al.* 2002; Simonsson *et al.* 2007). Similar results were observed in my study; faster K release was measured in plots that had received K fertiliser than plots that had not. Previous K fertiliser additions had increased the K releasing capacity of the soils by an average of 97% and 83 % in trial 502b and 504, respectively. Rao *et al.* (1999) found K release to be slowest in plots that had received either N alone or N and P, but no K fertiliser. They found the soil K contents to be largely depleted under optimum N and P supply.

6.1.3 Effects of surface management

The effect of the surface management zones on all the parameters measured in this study (concentration of different K forms, K fixation and K release) was more pronounced in soils that had received K fertiliser than in those that had not. For example, exchangeable and non-exchangeable K contents were higher in zones that received K fertiliser than in the plots and zones that had received no K fertiliser. The zones with high fixation capacity were the zones that had received little or no K fertiliser. The soil pH in each of the zones may also have also influenced differences in K fixation rates between the zones, because irrespective of the K fertiliser treatments (whether or not K was added) the pH values differed between zones. In general, the zones with higher K fixation capacity content also had higher pH values. Nelson *et al.* (2010) found differences in soil pH between zones (higher pH in the FP and BZ zone than the WC zone) in the absence of fertiliser application, as well as decreases in pH in all zones when fertiliser was applied. A positive relationship between K fixation and soil pH was shown by Huang (2005) and Brady and Weil (2009). In my study, the surface management zones that receive K fertiliser on a regular basis (which had higher soil pH) had high release of K from the non-exchangeable pool. The concentration of exchangeable and non-exchangeable K in these zones was much higher than in the zones that had received no K fertiliser. Therefore, the effects of surface management on the content of different K forms, K fixing capacity and K release from non-exchangeable K forms was mainly influenced by K fertiliser application and not the other soil properties measured within each of the zones (except perhaps pH and K fixation).

6.2 Yield response of oil palm in relation to forms of K, K fixation and K release characteristics of the soils

The yields in both trials (502b and 504) responded positively to the K fertiliser application 3-4 years after the initiation of the trials, and the yield response became consistent from 2003 afterwards (refer to yield trend in Chapter 2). In both trials, the yields from the plots that received K fertiliser were higher than the yields from the plots that received no K fertiliser. The difference can be related to the exchangeable and non-exchangeable K contents of those plots measured in this study (Chapter 3). The differences in soil K content and yield corresponded with leaf and rachis K contents, which indicates that more K was taken up from the soil in the plots that had received K fertiliser than in the plots that had not (refer to yield and rachis K concentration trend in Chapter 2).

Although both trials have the same fixation capacity, K was released more rapidly in trial 502b than 504. The difference in release rate between the soils at the two trial sites seems to be related to differences in response to K fertiliser between the sites. The response of yield and leaf K content was larger at trial 502 (with higher release rates) than trial 504 (Table 20). Due to the lower amount and faster release of native non-exchangeable K in trial 502, FFB yield in the -K plots could be expected to decline earlier in trial 502 than 504. However, yields in the -K plots have not declined over time in either trial (refer to yield trend in Chapter 2).

Table 20. Main effect of MOP on yield and leaf K content at the two trial sites over the 2005-2007 period (PNGOPRA Annual Report 2007).

Trial	Parameter	MOP (kg palm^{-1} year^{-1})		Difference	*% increase*
		0	7.5		
502b	FFB yield (t ha^{-1} year^{-1})	23.1	27.3	4.2	*18.2*
504	FFB yield (t ha^{-1} year^{-1})	26.3	29.6	3.3	*12.5*
502b	Leaf K content (% DM)	0.53	0.64	0.11	*20.7*
504	Leaf K content (% DM)	0.55	0.65	0.10	*18.2*

6.3 Implications for plantation management

The results of this study have implications for management of K fertiliser to oil palms grown on alluvial clay soils. When K fertiliser is applied in zones or soils low in K reserves, a considerable portion of that K will be fixed by the soil and may eventually become available for the oil palm to taken up. Whereas if K fertiliser is applied to areas with high K concentration from a prolonged history of K fertiliser application, then there will be no net fixation of K, but the added K will be immediately available. Therefore, judicious placement of K fertiliser might be used to considerably improve the agronomic efficiency and benefit:cost of current additions. From this study, the BZ, FT and FP zones have higher K reserves than the HP and WC zones, so continued placement of K fertiliser on those 3 zones will minimise the proportion that is fixed, thus improving K uptake by the oil palm. It would be possible to calculate the economics of various options for K fertiliser placement. Given the high cost of fertiliser, it may even be economic to continue placing fertiliser in the same zones after the palms in the current crop have been felled and replanted.

A K budget done by Webb *et al*. (2009) on the same soil used this study, showed about 40% of the total amount of K fertiliser applied to the soil over 13 years was taken up by the oil palms while the remainder had accumulated in the top 60 cm of the soil. Virtually no K had been lost by leaching (Berthelsen *et al.* 2010). Most of the K that had accumulated in the soil will still be available for uptake at some stage when the exchangeable concentration declines sufficiently for release of fixed K to occur. The fixation results from this study suggest that when K fertiliser was added initially, about 30% would have been fixed, but after 13 years of K fertiliser application the non-exchangeable K sites in the zones where fertiliser was added have been saturated and no net fixation occurs.

6.4 Conclusions

This study showed that the fixation and release of K in alluvial soils of PNG under oil palm cultivation was largely influenced by management. K fixation and release were related more to the K fertiliser treatments than the other two treatments (trial site and management zones). Irrespective of the presence of different clay minerals at each site, approximately 20-30% of the K added to the soil (in the laboratory) was fixed in the plots and zones with a history of no K fertiliser in both trials. K release from the non-exchangeable pool was mainly influenced by the amount of non-exchangeable K (which is determined mostly by the K fertiliser history) and the trial site. K release from the non-exchangeable K pool was faster in trial 502b than in trial 504, due to differences in the type of clay present. Surface management (zones) had no effect on the rate of K release.

When K fertiliser is applied in zones or soils low in K reserves, a considerable portion of that K will be fixed by the soil and becomes temporarily unavailable for uptake by the palms. Whereas if K fertiliser is applied to zones or plots with a prolonged history of K fertiliser application, there will be no net fixation of K, instead the added K will be immediately available. From this study, the BZ, FT and FP zones have higher K reserves than the HP and WC zones, so continued placement of K fertiliser on those 3 zones to will minimise the proportion that is fixed, thus improving K uptake by the oil palm.

7 Bibliography

Aharoni C, Sparks DL, Levinson S, Ravina I (1991) Kinetics of soil chemical reactions: Relationships between empirical equations and diffusion models. *Soil Science Society of America Journal* 55, 1307-1312.

Andrist-Rangel, Edwards AC, Hillier S, Oborn I (2007) Long term dynamic in organic and conventional mixed cropping systems as related to management and soil properties. *Agriculture, Ecosystems and Environment* **122**, 413 – 426

Barre P, Velde B, Catel N (2007) Soil-plant potassium transfer: impact of plant activity on clay minerals as seen from X-ray diffraction. *Plant Soil*. doi: 10.1007/s11104-007-9208-6

Beckett PHT (1970) Fixed K and the residual effects of k fertiliser. Potash Review Subject 16, 52th Suite:1-12

Berthelsen S, Webb MJ, Nelson PN. 2010. Limited movement of fertiliser-derived Mg and K through volcanic ash and alluvial clay soils of Papua New Guinea. In: Gilkes RJ, Prakongkep N, editors. *Proceedings of the 19th World Congress of Soil Science; Soil Solutions for a Changing World; ISBN 978-0-646-53783-2; Published on DVD; http://www.iuss.org; Division Symposium 3.2; Nutrient best management practices; 1-6 August 2010.* Brisbane, Australia: International Union of Soil Science. p 140-143.

Best EK (1977) A study of potassium in a Papuan alluvial soil. Masters of Science Thesis submitted to the Chemistry Department, University of Papua New Guinea.

Bhonsle NS, Pal SK, Sekhon GS (1992) Relationship of K forms and release characteristics with clay mineralogy. *Geoderma* **54**, 285 - 293

Bleeker P (1983) Soils of Papua New Guinea. Australian University Press. Canberra, Australia, Australia, London, England and Miami, Fla., USA.

Bleeker P (1988) Report on Soils of Milne Bay Estates, Gumini – Sagarai. Report No. 518. Department of Agriculture and Fisheries, Port Moresby, PNG.

Blevins, GD (1985) Role of Potassium in Protein Metabolism in Plants. In 'Potassium in Agriculture'. (Eds RD Munson). Pp 413-424. Madison, Wisconsin USA.

Bolt GH, Sumner ME, Kamphorst A (1963) A study of equilibria between three categories of potassium in an illitic soil. *Soil Science Society of America Proceedings* **27**, 294-299.

Bouabid R, Badraoui M, Bloom PR (1991) Potassium fixation and charge characteristics of soil clays. *Soil Science Society of America Journal* **55**, 1493 – 1498

Brady, CN, Weil RR. (2008) The Nature and Properties of Soils. 15 edn. Prentice Hall, Upper Saddle River, New Jersey 07458.

Carey PL, Metherell AK (2003) Rates of release of non-exchangeable potassium in New Zealand soils measured by a modified sodium tetraphenyl-boron method. *New Zealand Journal of Agricultural Research* **46 (3)**, 185-197

Carter MA, Singh B (2006) Response of maize and potassium dynamics in Vertisols following potassium fertilization. 3rd Australian New Zealand Soils Conference, 5-9 December 2004, University of Sydney, Australia.

Claassen N, Dessougi EH, Trehan SP (1990) Crop Growth and Potassium Uptake as related to Plant and Soil Properties. Central Potato Research Station Publication, India.

Conklin, AR (2005) Introduction to Soil Chemistry: Analysis and Instrumentation. John Wiley and Sons Inc., Hoboken, New Jersey.

Conti ME, Horra de la AM, Effron D, Zourarakis (2001) Factors affecting potassium fixation in Argentine Agricultural Soils. *Communication in Soil Science and Plant Analysis* **32 (17 & 18)**, 2679-2690

Cope JT (1981) Effects of 50 years of fertilization with phosphorus and potassium on soil test evels and yields at six locations. *Soil Science Society of America Journal* **45**, 342–347.

Cox AE, Joern BC (1997) Release kinetics of non-exchangeable potassium in soils using sodium tetraphenylboron. *Soil Science* **162** (8), 588-598

Cox AE, Joern BC, Roth CB (1996) Non exchangeable ammonium and potassium determination in soils with a modified sodium tetraphenylboron method. *Soil Science Society of America Journal* **60**, 114-120

Dhaliwal AK, Gupta RK, Yadvinder S, Bijay S (2006) Potassium fixation and release characteristics of some Benchmark Soil Series under Rice-Wheat Cropping System in the Indo-Gangetic Plains of Northwestern India. *Communications in Soil Science and Plant Analysis* **37**, 827-845.

Dhillon SK, Dhillon KS (1992) Kinetics of release of potassium by sodium tetraphenyl boron from some top soil samples of Red (Alfisols), Black (Vertisols) and Alluvial (Inceptisols and Entisols) soils of India. *Fertiliser Research* **32**, 135 – 138

Dhillon SK, Sidhu PS, Bansal RC (1989). Release of potassium from some bench mark soils of India. *Journal of Soil Science* **40**, 783-797.

Drew MC (1975) Comparison of the effects of a Localised Supply of Phosphate, Nitrate, Ammonium and Potassium on the Growth of the Seminal Root System and the Shoot, in Barley. *New Phytologist* **75**, 479-490.

Eick JM, Bar-Tal A, Sparks LD, Feigenbaum (1990) Analysis of Adsorption Kinetics Using a Stirred-Flow Chamber: II. Potassium-Calcium Exchange on Clay Minerals. *Soil Science Society of American Journal* **54**, 1278 – 1282.

Etchevers JD, Hidalgo CM (2005) Dynamics of Soil K Release. *Communications in Soil Science and Plant Analysis* **36**, 341-354

Evans, HJ, Wildes, RA (1971). Potassium and its role in enzyme activation. In 'Potassium in biochemistry and physiology'. Pp 13-39. International Potash Institute, Berne, Switzerland.

Filep G (1999) Soil Chemistry. Processes and Constituents. Akademiai Kiado, Hungary

Foth DH (1990) Fundamentals of Soil Science. 8th Edn. John Wiley & Sons Inc. United States.

Gil-Sotres F, Rubio B (1992). Kinetics and structural effects of the extraction of nonexchangeable potassium from the clay fractions of soils of Galicia (N. W. Spain). *Communications in Soil Science and Plant Analysis* **23**, 143-156.

Gillman GP, Skjemstad JO, Bruce RC (1982) A comparison of methods used in Queensland for determining cation exchange properties. Division of Soils Technical Paper No. 44, CSIRO Australia.

Gillman GP, Sumpter EA (1986) Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Australian Journal of Soil Research* **24**, 61-66

Goulding KTW (1987) Potassium fixation and release. *Proceedings of the Colloquium of the Internation Potash Insitute* **20**, 137-154

Gourley CJP (1999) Potassium. In 'Soil Analysis – an Interpretation Manual'. (Eds. Peverill KI, Sparrow LA and Reuter DJ) pp. 229-243. CSIRO Publishing, Collinwood, VIC 3066, Australia.

Grimme, H (1974) Potassium release in relation to crop production. In 'Potassium Research and Agricultural Production'. pp 131-136. International Potash Institute, Basel, Switzerland.

Guzel N, Buyuk G, Ibrikci H (2001) Non exchangeable and exchangeable potassium status of soils in relation to clay mineralogy and other soil properties in Hilvan area of upper Mesopotamia in Southeastern Anatolia. *Communication in Soil Science and Plant Analysis* **32** (17 & 18), 2877-2892

Haby VA, Russel MP, Skogley E O (1990) Testing soils for potassium, calcium and magnesium. Pp. 181-227 in: 'Soil testing and plant analysis' (3rd edition), SSSA book series 3, (Eds Westerman, R L) pp Wisconsin, Madison, USA., Soil Science Society of America.

Harding PE, Hombunaka P (1998). A review of coffee nutrition research in Papua New Guinea. *Papua New Guinea Journal of Agriculture, Forestry and Fisheries* **41**, 44-64.

Hartemink AE (1998) Soil chemical and physical properties as indicators of sustainable land management under sugarcane in Papua New Guinea. *Geoderma* **85**, 283-306.

Hartemink AE, Bourke RM (2000) Nutrient deficiencies of agricultural crops in Papua New Guinea. *Outlook on Agriculture* **29** (2), 97-108.

Hartley CWS (1988) The Oil Palm, 3rd Edition. Longman Scientific and Technical Publication, New York. Longman.

Hartley A (2005) Crop-Soil Relationships- Hagita Plantation. Report No. 121. Department of Agriculture and Fisheries, Port Moresby, PNG.

Havlin JL, Westfall DG, Olsen SR (1985) Mathematical models for potassium release kinetics in calcareous soils. *Soil Science of American Journal* **49**, 371-376.

Huber SC (1985) Role of Potassium in Photosynthesis and Respiration. In 'Potassium in Agriculture'. (Eds RD Munson). Pp 369-391. Madison, Wisconsin USA.

Jackson ML (1979) Soil Mineralogy. In 'The encyclopedia of soil science, Part 1.'(Eds RW Fairbridge and CW Finkl, Jr). pp 475-482. Stroudsburg, PA.

Jackson RB, Caldwell MM (1989) The timing and degree of root proliferation in fertile-soil microsites for three cold-desert perennial. *Oecologia* **81**, 149-153.

Jalali M (2005) Release Kinetics of Non-exchangeable Potassium in Calcareous Soils. *Communications in Soil Science and Plant Analysis,* **36**, 1903 – 1917

Jalali M (2006) Kinetics of non-exchangeable potassium release and availability in some calcareous soils of western Iran. *Geoderma* **135**, 63 – 71

Jalali M (2007) A study of quantity/intensity relationships of potassiumin some calcareous soils of Iran. *Arid Land Res. Management* **21** (2), 133 - 141

Jungk A (2001) Root hairs and the acquisition of plant nutrients from soil. *Journal of Plant Nutrition and Soil Science* **164**, 121-129

Kafkafi U (1990) The functions of plant K in overcoming environmental stress situations. In 'Proceedings of the 22nd colloquium of IPI'. Pp 81-83, Soligorsk, USSR, IPI, Bern.

Kafkafi U (1991) Root growth under stress. Pp. 375 – 391. In 'Plant Roots, The Hidden Half'. (Eds Waisel, Y, A. Eshel and U. Kafkafi) pp. 375 - 391. Marcel Dekker, Inc. New York.

Kirkman JH (1981) Morphology and structure of halloysite in New Zealand Tephras. *Clays and Clay minerals* **29**, 1-9.

Kirkman JH, Basker A, Surapaneni A, MacGregor (1994) Potassium in the soils of New Zealand – a review. *New Zealand Journal of Agricultural Research* **37**, 207-227.

Koch K, Mengel K (1974) The influence of the level of potassium supply to young tobacco plants (Nicotiana tabacum L.) on short term uptake and utilization of nitrate nitrogen (15N). *Journal of Science, Food and Agriculture* **25,** 465-471

Krishnakumari MK, Khera MS (1984) Effect of long term N and P fertiliser application in an intensive cropping system on K fixing characteristics of an Inceptisol. *Fertiliser News* **28 (10)**, 27-30

Li X, Lu J, Wu L, Chen F, Malhi S (2010) Potassium Fixation and Release Charateristics in Rhizosphere and Nonrhizosphere Soils for a Rapeseed-Rice Cropping Sequence. *Communication in Soil Science and Plant Analysis* **41**, 865-877

Lopez-Pineiro A, Garcia NA (1997). Potassium release kinetics and availability in unfertilized Vertisols of south western Spain. *Soil Science* **162**, 912-918.

Mackay AD, Barber SA (1985) Soil moisture effects on potassium uptake by corn. *Agronomy Journal* **77**, 524-527.

Magnus S, Stefan A, Ylva A, Stephen H, Lennart M, Ingrid O (2007) Potassium release and fixation as a function of fertilizer application rate and soil parent material. *Geoderma* **140**, 188 - 198.

Malavolta E (1985) Potassium status of tropical and subtropical region soils. In 'Potassium in Agriculture'. (Ed. RD Munson). pp 163-200. ASA and SSSA, Madison, WI USA.

Malla PB (2002) Vermiculites. In 'Soil mineralogy with environmental applications' (Eds JB Dixon & DG Schulze) pp 501-529 (Soil Science Society of America Madison, WI).

Marschner H (1995) Mineral nutrition of higher plants, 2nd edition. Academic Press Inc. London and New York 889 pp.

Martin HW, Sparks DL (1985) On behaviour of non exchangeable potassium in soils. *Communication for Soil Science and Plant Analysis* **16**, 133 – 162

Martin HW, Sparks DL. (1983). Kinetics of nonexchangeable potassium release from two coastal plain soils. *Soil Science Society of America Journal* **47**, 883-887.

McAlpine JR, Keig G, Falls R (1983). Climate of Papua New Guinea. Australian University Press. Canberra, Australia.

McLean EO, Watson ME (1985) Soil Measurements of Plant-Available Potassium. In 'Potassium in Agriculture'. (Eds RD Munson). Pp 277 - 308. Madison, Wisconsin USA.

Mehdi SM, Ranja AM (1997) Potassium fixation and release in some alluvial soils of Pakistan. *Journal of Potassium Research* **13**, 297 – 301

Mengel K (1985) Dynamics and availability of major nutrients in soils. *Advances in Soil Science* **2**, 65 – 131

Mengel K (2006). Potassium. In 'Handbook of Plant Nutrition' (Eds AV Barker, DJ Pilbeam) pp 91 – 120. CRC, Taylor & Francis Group, Boca Raton, London, New York.

Mengel K, Kirkby EA, Kosegarten H, Apple T (2001) Principles of Plant Nutrition, 5th Edition. Kluwer Academic Publishers Dordrecht Netherlands 849pp.

Mengel K, Uhlenbecker K (1993) Determination of available interlayer potassium and its uptake by ryegrass. *Soil Science Society of America Journal* **57**, 761 – 766

Menzies NW, Bell LC (1988) Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Australian Journal of Soil Research* **26**, 451-464.

Mittal SB, Singh R, Mehta SC, Singh M (1990) Potassium depletion under long-term fertiliser in a semi-arid soil in India. *Journal of Agriculture Science (Cambridge)* **101**, 115 – 173

Moody PW, Bell MJ (2006) Availability of soil potassium and diagnostic soil tests. *Australian Journal of Soil Research* **44**, 265 – 275

Munn DA, Wilding LP, McLean EO (1976) Potassium release from Sand, Silt and Clay Soil Separates. *Soil Science Society of America Journal* **40**, 364 – 366

Nelson LW (1985) Plant factors affecting Potassium Availability and Uptake. In ‘Potassium in Agriculture’. (Eds RD Munson). Pp 355-383. Madison, Wisconsin USA.

Nelson PN, Banabas M, Scotter DR, Webb MJ (2006) Using soil water depletion to measure spatial distribution of root activity in oil palm (*Elaeis guineensis* Jacq.) plantations. *Plant Soil* **286**, 109 – 121

Nelson PN, Berthelsen S, Webb MJ, Banabas M. 2010. Acidification of volcanic ash soils under oil palm in Papua New Guinea: effects of fertiliser type and placement. In: Gilkes RJ, Prakongkep N, editors. *Proceedings of the 19th World Congress of Soil Science; Soil Solutions for a Changing World; ISBN 978-0-646-53783-2; Published on DVD; http://www.iuss.org; Division Symposium 3.2; Nutrient best management practices; 1-6 August 2010.* Brisbane, Australia: International Union of Soil Science. p 8-11.

Øgaard AF, Krogstad (2005) Release of interlayer potassium in Norwegian grassland soils. *Journal of Plant Nutrition and Soil Science* **168**, 80 – 88

Olsen CG, Thompson ML, Wilson MA (2000) Phyllosilicates. In ‘Handbook of Soil Science’. (Ed. ME Sumner). Pp F77 – F123, WI USA.

Papua New Guinea Oil Palm Research Association Annual Report 2007. Dami West New Britain, Papua New Guinea.

Peoples TR, Koch DW (1987) Role of potassium in carbon dioxide assimilation in *Medicago sativa* L. *Plant Physiology* **63,** 878-881

Parfitt RL (1992) Potassium-Calcium exchange in some New Zealand soils. *Australian Journal of Soil Research* **30**, 145-158

Qifu M, Zed R, Bill B (2007) Heterogeneous distribution of phosphorus and potassium in soil influences wheat growth and nutrient uptake. *Plant and Soil* **297**, 301-309.

Rao S, Swarup A, Rao SA, Gopal RV (1999) Kinetics of nonexchangeable potassium release from a Tropaquept as influenced by long-term cropping, fertilisation and manuring. *Australian Journal of Soil Research* **37**, 317 – 328

Regmi AP, Ladha JK, Pathak H, Pasuquin E, Bueno C, Dawe D, Hobbs PR, Joshy D, Maskey SL, Pandey SP (2002b) Yield and soil fertility trends in a 20-year rice-rice-wheat experiment in Nepal. *Soil Science Society of America Journal* **66**, 857-867.

Rich CI (1964) Effect of cation size and pH on potassium exchange in Nason soil. *Soil Science* **98**, 100-106

Robinson D (2001) Root proliferation, nitrate inflow and their carbon costs during nitrogen capture by competing plants in patchy soil. *Plant and Soil* **232,** 41-50

Rubio B, Gil-Sotres F (1996). Determination of K forms in K fertilized soils by electroultrafiltration. *Plant and Soil* **180**, 303-310.

Sachdev CB, Khera MS (1980) Utilisation of potassium from non exchangeable sources in soil under intensive wheat-bajra cropping system. *Fertiliser News* **25**, 6-10

Sardi K, Csitari (1998) Potassium Fixation of Different Soil Types and Nutrient Levels

Schultze DG (2002) An introduction to soil mineralogy. P 1-35 In Dixon JB and Schultze DG (Eds.) 'Soil Mineralogy with Environmental Applications'. Soil Science Society of America Inc. Madison, WI, USA.

Shaviv AM, Mohsin M, Pratt PF, Mattigod SV (1985) Potassium fixation characteristics of five southern California soils. *Soil Science Society of American Journal* **49**, 1105 – 1109

Singh M, Singh VP, Reddy DD (2002) Potassium balance and release kinetics under continuous rice-wheat cropping system in Vertisol. *Field Crops Research* **77**, 81 – 91

Sharpley AN (1990) Reaction of fertilizer potassium in soils of differing Mineralogy. *Soil Science* **149**, 44-51

Sharma VK, Mishra MK (1991) Potassium adsorption kinetics in soil differing in clay content and mineralogy. *Journal of Potassium Research* **7**, 176 – 181

Sheldrick, WF (1985) World Potassium Reserves. In 'Potassium in Agriculture'. (Eds RD Munson). Pp 3-28. Madison, Wisconsin USA.

Simonsson M, Anderson S, Andrist-Rangel Y, Hillier S, Mattsson L, Oborn I (2007 Potassium release and fixation as a function of fertiliser application rate and soil parent material. *Geoderma* **140**, 188-198

Singh M, Singh VP, Reddy DD (2002) Potassium balance and release kinetics under continuous rice-wheat cropping system in Vertisol. *Field Crop Research* **77**, 81-91.

Song SK, Huang PM. (1988). Dynamics of potassium release from potassium bearing minerals as influenced by oxalic and citric acids. *Soil Science Society of America Journal* **52**, 383-390.

Sparks, DL (1980) Chemistry of Soil Potassium in Atlantic Coastal Plain Soils. A Review. Commun. *Soil Science and Plant Analysis* **11**, 435-449

Sparks DL (1987) Potassium dynamics in soils. *Advance in Soil Science* **6**, 1-63

Sparks DL (2000) Bioavailability of Soil Potassium. In ‘Handbook of Soil Science’. (Ed. ME Sumner). Pp D38 – D53, WI USA.

Sparks DL, Jardine PM (1981). Themodynamics of potassium exchange in soil using soil kinetics approach. *Soil Science Society of America Journal* **45**, 1090 – 1099.

Sparks DL, Jardine PM (1984) Comparison of kinetic equations to describe K-Ca exchange in pure and in mixed systems. *Soil Science* **138**, 115 – 122

Sparks DL, Huang PM (1985) Physical Chemistry of Soil Potassium. In ‘Potassium in Agriculture’. (Eds RD Munson). Pp 202-265. Madison, Wisconsin USA.

Srinivasarao C, Rupa RT, Rao SA, Ramesh G, Bansal KS (2006) Release Kinetics of Nonexchangeable potassium by Different Extractants from Soils of Varying Mineralogy and Depth. *Communication in Soil Science and Plant Analysis* **37**, 347 – 491

Srivastava S, Rupa RT, Swarup A, Singh D (2002) Effect of long-term fertilisation and manuring on potassium release properties in a Typic Ustochrept. *Journal of Plant Nutrition and Soil Science* **165**, 352 - 356

Steffens D, Mengel K (1985) Potassium uptake of rye grass (*Lolium perenne* L.) and red clover (*Trifolium pretense* L.) as related to root parameters. *Biology and Fertility of Soils* **1**, 53-58.

Steffens D, Sparks DL (1997) Kinetics of non exchangeable ammonium release from soils. *Soil Science Society of American Journal* **61,** 455-462

Stucki WJ, Huo D (1997) Continued Studies on the Behavior of Potassium in Soils. Illinois Fertiliser Conference Proceedings, January 27-29, 1997.

Sumner ME, Naidu R (1998) Sodic Soils. Distribution, Properties, Management and Environmental Consequences. Oxford University Press.

Surapaneni A, Palmer AS, Tilman RW, Kirkman JH, Gregg PEH (2002) The Mineralogy and Potasssium Supplying Power of Some Loessial and Related Soils of New Zealand. *Geoderma* **110**, *191-204*

Tan KH (1994) Environmental Soil Science. Marcel Dekker, Inc. 270 Madison Avenue, New York

Tisdale LS, Nelson LW, Werner LN, Beaton D J, Havlin LJ (1993) Soil Fertility and Fertilisers (Fifth Edn). Macmillan Publishing Company, 866 Third Avenue, New York, New York.

Tributh H, Boguslawski von E, Liers von A, Steffens S, Mengel K (1987) Effect of potassium removal by crops on transformation of illitic clay minerals. *Soil Science* **143**, 404-409

Troeh RF, Thompson ML (2005) Soils and Soil Fertility (Sixth Edn). Blackwell Publishing Ltd, 9600 Garsington Road, Oxford OX4 2DQ, UK.

Webb M, Berthelsen S, Nelson P, van Rees H (2009) Overcoming magnesium deficiency in oil palm crops on volcanic soils of Papua New Guinea. ACIAR Final Report Number FR 2009-11. Canberra, ACT, Australia

Zeng Q, Brown HP (2000) Soil Potassium Mobility and uptake by corn under differential soil moisture regimes. *Plant and Soil* **221**, 121-134.

Zhu YG, Luo JX (1993). Release of nonexchangeable soil K by organic acids.
Pedosphere **3**, 269-276.