# KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

## COLLEGE OF SCIENCE

# INORGANIC PHOSPHORUS FRACTIONATION IN SOME SELECTED SOILS FROM THE EASTERN REGION OF GHANA

BY

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## DECLARATION

I hereby declare that this thesis is my own towards the MPhil and that, to the best of my knowledge and belief, it contains no material that has been accepted for the award of any other degree in any educational institution nor material previously published or written by another person, except where due acknowledgement has been made in the text.

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# DEDICATION

I dedicate this book to my mother, may her soul rest in peace, my son, Tijani Abdul Rahman Junior, my father, my wife and my siblings as well as generation to come; you truly are the catalyst for all my effort and achievement in all my work.

### ABSTRACT

Amounts of phosphorus (P) in inorganic form was determined for twelve top soils (0-10)cm), sub-surface soils (10 - 20 cm) and sub soil (20 - 30 cm) which had been cultivated for at least 20 years, and their virgin analogues, to ascertain if relative pool sizes or soil P fertility are being changed by cultivation and associated fertilizer application. The soils were representative of major agricultural areas of the New Juaben and Yilo Krobo Districts of Eastern Region, with total P concentrations ranging from 11.60  $\mu$ g/g to 31.82 µg/g (inorganic P). P forms in the pools and extractants used were as follows: looselybound (1.0M NH<sub>4</sub>Cl), nonoccluded (0.5M NH<sub>4</sub>F + 0.1M NaOH), occluded (citratedithionite-bicarbonate + 0.5M NH<sub>4</sub>F + 0.1M NaOH), and Ca bound (1.0M HCl). Loosely-bound P was not analysed in this work because of its small concentration in the soils. Akwadum fertilized cultivated soils had higher distributions of P-fractions (Al-P, Fe-P and Ca-P) and all found in the surface soil (0 - 10 cm). Inorganic P-fractions were greatly influenced by soil properties such as soil pH, soil electrical conductivity (EC), % organic carbon (% OC) and soil particle sizes. Cultivation resulted in an increase in nonoccluded and decrease in occluded P. Average distribution of P-fractions as a percentage of total fraction in the Huhunya virgin soils was 57.53 % Ca-P, 18.68% Al-P and 18.15% Fe-bound. Huhunya cultivated soils recorded 50.27% Ca-P, 20.43% Al-P and 20.02% Fe-P. Akwadum fertilized cultivated soil had 62.29% Ca-P, 14.07 Al-P and 13.86% Fe-P. Correlation analysis showed significant relationship among inorganic P fractions themselves and some soil physical properties. The conversion of organic to inorganic P may be reversed by management practices allowing a build up of soil organic matter. Since little change in amounts of loosely-bound inorganic P was observed during cultivation, the more stable pools may represent a better estimate of long-term soil fertility.

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# LIST OF ABBREVIATIONS

CDB: CITRATE DITHIONITE BICARBONATE

TOT: TOTAL

E C: ELECTRICAL CONDUCTIVITY

O C: ORGANIC CARBON

#### **CHAPTER ONE**

Soil phosphorus (P) exists in inorganic and organic forms. Each form is a continuum of many P compounds, existing in equilibrium with each other and ranging from solution P (taken up by plants) to very stable or unavailable compounds (the most typical). In most soils, 50 % to 75 % of the P is inorganic.

Although the total amount of P in the soil may be high, it is often present in unavailable forms or in forms that are only available outside of the rhizosphere. Few unfertilized soils release P fast enough to support the high growth rates of crop plant species. In many agricultural systems in which the application of P to the soil is necessary to ensure plant productivity, the recovery of applied P by crop plants in a growing season is very low, because in the soil more than 80% of the P becomes immobile and unavailable for plant uptake because of adsorption, precipitation, or conversion to the organic form (Holford, 1997).

Inorganic P is usually associated with aluminium (Al), iron (Fe), and calcium (Ca) compounds of varying solubility and availability to plants. Phosphorus has to be added to most soils so that adequate levels are available for optimum crop growth and yield. However, P can be rapidly fixed (also referred to as sorption) in forms unavailable to plants, depending on soil pH and type (Al, Fe, and Ca content). Conversion of unavailable to available forms of soil P usually occurs too slowly to meet crop P requirements. As a result, soil P tests were developed to determine the amount of plant-available P in soil, and from this, how much P should be added as fertilizer or manure to meet desired crop yield goals. The estimated amount of plant-available soil P is subsequently referred to as soil test P.

Organic P compounds range from readily available undecomposed plant residues and microbes within the soil to stable compounds that have become part of soil organic matter. Biological processes in the soil, such as microbial activity, tend to control the mineralization and immobilization of organic P.

Mineralization, the breakdown or conversion of readily available organic P to inorganic solution P, occurs in most soils, but it is usually too slow to provide enough P for crop growth. Immobilization is the formation of more stable organic P, which is resistant to breakdown. In most soils, the P content of surface horizons is greater than subsoil. Except in special situations, added P tends to be fixed by the soil where it is applied, allowing for little movement down through the soil.

In reduced tillage systems, fertilizers and manures are surface applied with little or no mechanical incorporation, thus increasing P build up in the top 2 to 5 inches of soil.

Overall, soil pH is the main property controlling inorganic P forms, although Al, Fe, and Ca contents determine the amounts of these forms. In acidic soils, Al and Fe dominate P fixation, while Ca compounds fix P in alkaline soils. As a result, P availability is greatest at soil pH between 6 and 7. Immobilization of inorganic P by these processes renders a portion of the added P unavailable for plant uptake.

In the United States, an average 29% of P added in fertilizer and manures is removed by harvested crops, ranging from < 1% in Hawaii to 71% in Wyoming (National Research Council, 1993). The low recovery reflects the predominance of high P-fixing soils in Hawaii.

Chemical fractionation of soil inorganic phosphorus(P) provides a method for identifying the predominant individual forms of inorganic P in soils, most commonly soluble P, aluminium P (Al-P), iron P (Fe-P), occluded P and calcium P (Ca-P) (Chang and Jackson,1957).

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Fractionation of inorganic P is commonly carried out to characterize the effects of soil types and P sources on the fate and potential availability and mobility of P in soils (Tekaign and Haque, 1991).

Inorganic P fractionations have been widely used to interpret native inorganic P status and the applied P to soils (Sui et al., 1999).

Jiang and Gu, (1989) suggested their fractionation sequence based on the ability of extractant such as NaHCO<sub>3</sub>, NH<sub>4</sub>F, NaOH-Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to extract CaHPO<sub>4</sub>.2H<sub>2</sub>O,  $Ca_8H_2(PO_4)_3$  AlPO<sub>4</sub>.nH<sub>2</sub>O, FePO<sub>4</sub>.2H<sub>2</sub>O and  $Ca_{10}(PO4)_6F_2$ , respectively.

Some researchers found that occluded P (O-P), extracted with citrate dithionate bicarbonate (CDB), was related to CDB-extractable Fe and concluded that O-P was associated with the crystal lattice of Fe-P minerals. Some studies performed on calcareous soils have shown that P behavior is controlled mainly by the presence of small amounts of iron or aluminum oxides (Townsend *et al.*, 2002).

Other researchers have demonstrated that Al-P and Fe-P are among the most important forms of P in virgin and fertilized calcareous soils from Western Australia (Samadi and Gilkes,1999).

The P release characteristics of soils and soil components have been studied extensively (Barrow, 1979; Chien and Clayton, 1980; Kuo and Lotse, 1974;Sharpley *et al.*, 1981). Factors that influence the extent of P release to solution include: soil pH, solution composition, (e.g., ionic strength and concentration of competing inorganic and organic anions, temperature and duration of contact with added P) (Barrow, 1983; Lopez-Hernandez *et al.*, 1986; Ryden *et al.*, 1977; 1987).

Ecosystems worldwide are undergoing unprecedented rates of land conversion and land use change (Meyer and Turner, 1992).

Land management practices such as fire, grazing, tillage, and fertilizer application, among others, affect ecosystem composition, the distribution of organic matter, and a variety of nutrient cycling processes, including losses of limiting and essential elements to atmospheric and aquatic realms (Ewel *et al.*, 1981). The most dramatic recent land use changes have been centred in tropical and subtropical forested ecosystems (Skole and Tucker, 1993), where deforestation now removes roughly 2 % of the remaining forest cover per year (Williams and Chartres, 1991; Nepstad, 1999), most of which becomes cattle pasture (Fearnside, 1996).

The biogeochemical consequences of land use change in the tropics are potentially quite different from those in temperate regions, in large part because tropical ecosystems frequently occur on extremely old soils. The combination of greater soil age along with a warm, often wet climate, leads to highly weathered soils that are typically depleted in phosphorus (P) and base cations (Ca, Mg, K), rich in iron and aluminum oxides, and of variable charge (Uehara and Gillman, 1981); these are the Oxisols and Ultisols that dominate many tropical regions.

Carbon uptake and storage in ecosystems on such soils are often limited by P and/or base cation supply (Vitousek and Sanford, 1986; Herbert and Fownes, 1995). Thus any land use driven changes in P and/or base cation availability may be central to predicting the sustainability of cleared land, as well as land-atmosphere exchanges of carbon and trace gases following forest conversion. P limitation, in particular, is believed to be common in tropical forests on old soils, and the constraints imposed by low P availability are a widely recognized problem in tropical agriculture (Sanchez *et al.*, 1982). Not only are many tropical soils relatively low in total soil P, but their high iron and aluminium oxide contents cause strong "fixation" of plant available inorganic P into more occluded forms that are thought to be largely unavailable to biota (Sanchez *et al.*, 1982; Uehara and Gillman, 1981).

Identification of soil P compounds can provide valuable information for P management. Soil P forms are often investigated by sequential chemical fractionation procedures (Chang *et al.*, 1957; Hedley *et al.*, 1982). Sequential extraction procedures utilize the ability of various chemical reagents to selectively solubilize the Al, Fe, or Ca phosphate phases contained in the soil. Although imperfect separation may exist, it has been shown that with careful design and interpretation, chemical fractionation procedures can be very useful in revealing the controlling phases of soil P dynamics (Sui *et al.*, 1999; Delgado and Torrent, 2000). In addition to chemical fractionation, sorption characteristics have also been widely studied in order to understand P retention in soils (Agbenin and Tiessen, 1995).

The coupling of chemical fractionation and sorption indices has been successively employed to explain the chemical changes associated with P retention and loss in biosolids-amended soils (Maguire, 2000). While exact reaction mechanisms may not be eluded from sorption isotherm data, statistically significant correlations can provide insight about the P retention characteristics in calcareous soils (Olsen *et al.*, 1954).

Identification and quantification of individual soil and sediment phosphorus (P) compounds can provide valuable information on P chemical dynamics. Direct identification and quantification of P species in soils by physical methods such as x-ray diffraction is difficult due to the overall low concentration of P in soils.

Instead, chemical fractionation procedures (Kuo, 1996) that partition P contained in soils and sediments into associated P groups or pools are used. For calcareous soils, sequential chemical fractionation schemes attempt to separate soil inorganic P into discrete groups of (i) Fe /Al-phosphates (ii) P occluded within coatings of Fe oxide and hydrated oxides and (iii) Ca associated phosphates (Olsen and Sommers, 1982). Sequential extraction procedures use various chemical reagents to selectively solubilize the Al, Fe, or Ca phosphate phases but separation of P into the broad range of detailed Al-, Fe-, and Ca phosphate associated groups is imperfect. Even so, chemical fractionation procedures have provided valuable information in numerous soil P studies (Sui *et al.*, 1999; Delgado and Torrent, 2000; Maguire, 2000). Phosphorus fractionation procedures were first used a hundred years ago (Fraps, 1906) and have been modified over the years (Dean, 1938; Chang and Jackson, 1957; Williams *et al.*, 1980; Hedley *et al.*, 1982). One of the most recent changes is the addition of an initial extraction intended to estimate plant-labile P.

Labile P in inorganic and organic P fractionation procedures has been estimated using several different extractions. The most common extractants for labile P are water (Dou *et al.*, 2000), resin, NaHCO<sub>3</sub> (Zhang *et al.*, 2004; Sharpley and Smith, 1984; Samadi and Gilkes, 1999), or a combination of resin and NaHCO<sub>3</sub> (Hedley *et al.*, 1982; Sharpley *et al.*, 1986; Beauchemin *et al.*, 2003). Another change to the P fractionation schemes is the addition of the sodium citrate-sodium bicarbonate extraction (CB-P). This extraction is often inserted after the NaOH-P extraction for Ca-P and before the CBD-P fraction for reductant P (Olsen and Sommers, 1982). The purpose of the CB-P extractions is to desorb P that sorbed to CaCO<sub>3</sub> during the NaOH-P extraction (Williams *et al.*, 1971). However, little is known about the impact of these additional steps on subsequent fractions.

Analysis of solution P has been traditionally analyzed by the molybdenum blue or ascorbic acid colorimetric methods (Murphy *et al.*, 1962; Olsen and Dean, 1965).

For the last two decades, inductively coupled plasma argon emission spectroscopy (ICPAES, ICP for short) has gradually replaced colorimetric methods due to its speed and ability to measure many elements simultaneously. Phosphorus chemical fractionation techniques were originally created for use with colorimetric analysis. Today P fractionation results are reported using both ICP as well as colorimetric analytical analyses. However, it has not been fully evaluated if the various background solutions yield consistent results especially in lieu of high salt matrix encountered in P fractionation procedures (Chang and Jackson, 1957; Olsen and Sommers, 1982).

It has been reported that available P (P extracted by Olsen method) was significantly correlated with dicalcium phosphates (Ca<sub>2</sub> –P), octacalcium phosphates (Ca<sub>8</sub> –P), Al-P, calcium phosphates (Ca<sub>2</sub> -P+ Ca<sub>8</sub> -P+ Ca<sub>10</sub> -P) and aluminum iron oxides (Al-Fe-P). This result indicates that these fractions probably can be used by plants. Their unavailability could lead to reduction in crop yield (Samavati and Hossinpur, 2006). Huhunya located in the Yilo Krobo district in Eastern Region is one of the major producers of maize in Ghana and so is Akwadum in New Juaben district where cocoa is mostly cultivated. These two crops are among the crops that are of economic importance to Ghana. However the yield of these crops has been in decline inspite of application of fertilizers and the values are as follows: 2004- 2.2 mt/ha, 2005- 2.1 mt/ha, 2006- 2.3 mt/ha, 2007- 2.1mt/ha, 2008- 1.6 mt/ha, and 2009- 1.46 mt/ha. This could be due to unavailability of the required fraction in the applied fertilizer. It could also be due to the chemistry of the soil making them unavailable. This research work thus seeks to study the P status in the soils.

## **1.1 OBJECTIVES**

The main objectives of this research are:

- to chemically speciate and compare inorganic P forms in some Akwadum and Huhunya soils.
- to measure the physico-chemical properties of the soil sample.
- to evaluate relationships between inorganic P fractions and soil characteristics in order to provide insight into the proper management of the cultivated soil from Akwadum and Huhunya.
- to determine the phosphorus status of the virgin soil.
- to compare the status of the cultivated soils to that of the virgin soil.

#### **CHAPTER TWO**

#### LITERATURE REVIEW

## **2.1 GENERAL BACKGROUND**

Phosphorus (P) is a nutrient essential for plant growth. It stimulates root and shoot growth (Hedley *et al.*, 1982), promoting vigorous seedling growth and advancing maturity (Sanchez and Buol, 1975). Phosphorus management and nutrition have both economic and environmental implications (Condron *et al.*, 1990; Buresh *et al.*, 1997).

Phosphorus (P) has long been recognized as an essential input for plant and animal production. Dramatic improvements in the economic efficiency of grain and animal protein production during the last 50 years have been coupled with an increasing incidence and severity of freshwater eutrophication (Dorich *et al.*, 1980). Eutrophication is the process of increasing organic enrichment or biological productivity of a water body and is generally accelerated by greater inputs of P. In most cases, eutrophication restricts water use for fisheries, recreation, and industry due to the increased growth of undesirable algae and aquatic weeds followed by oxygen shortages resulting from their death and decomposition. Moreover, an increasing number of surface waters have experienced periodic and massive harmful algal blooms (e.g., *cyanobacteria* and *Pfiesteria*), which contribute to summer fish kills, unpalatability of drinking water, formation of carcinogens during water chlorination, and links to neurological impairment in humans (Huettl *et al.*, 1979).

As freshwater eutrophication is usually accelerated by P, much political and research attention has been directed to developing strategies to reduce the risk of P loss from agricultural nonpoint sources. To a large extent, these strategies depend on the accurate measurement of forms of P in soil, water, and residual materials, often seen as a source of surface water P (Logan et al., 1979). In comparison with point sources of P, such as wastewater treatment plants and industrial facilities, there has been less success in decreasing nonpoint sources of P, primarily because they are difficult to identify and thus control (Lajtha and Harrison, 1995).

Also, recent advances in analytical equipment used in soil P testing have improved recommendations for land application of P (as fertilizer and manure) and contributed to increased cost-effective grain and forage production (Qian *et al.*, 1992). In the last decade, there has been increased use of soil test P as an indicator of potential environmental risk for P enrichment of runoff and possible acceleration of eutrophication (Saggar *et al.*, 1992).

## **2.2 NOMENCLATURE OF PHOSPHORUS**

Nomenclature for forms of P in soil, water, or residual materials varies in the literature, particularly for operationally-defined forms of P in water samples (Bray and Kurtz, 1945). Phosphorus forms in soils are also difficult to standardize with any reasonable consensus, due to the number of different disciplines involved (e.g., soil scientists, agronomists, ecologists, biologists, limnologists, hydrologists). Thus, beyond using total soil P, it is strongly encouraged to use the specific chemical terminology (e.g., water-extractable,  $CaCl_2$ -extractable, 0.1 M NaOH-extractable, Mehlich-extractable P, etc.), which have been clearly defined. Any other terminology, which may be used in conclusions and interpretations (e.g., desorbable, available, bioavailable, sorbed P etc.), must also be clearly defined (Fixen and Grove, 1990).

Traditionally, extractable P has been used by soil testing laboratories to describe the amount of P in soil available for crop uptake and to determine the probability of crop response to added P, and thereby fertilizer P requirements. Bioavailable P is often used to describe P in soil or sediment that is available for uptake by algae or macrophytes in

surface waters. To some extent, bioavailable P is also used to describe the availability of soil P to plants (Barber, 1995). There are also a large number of soil P extraction methods that have been designed to account for various soil types and mechanisms controlling the chemistry of soil P. For example, numerous soil extractants are available for acid soils, where Al and Fe dominate P chemistry, and basic or calcareous soils, where Ca dominates soil P reactions (Sanchez and Uehara, 1980).

## 2.3 FORMS OF PHOSPHORUS IN SOILS

In soils P may exist in many different forms. In practical terms, however, P in soils can be thought of existing in3 "pools":

- solution P
- active P
- fixed P

The solution P pool is very small and will usually contain only a fraction of a pound of P per acre. The solution P will usually be in the orthophosphate form, but small amounts of organic P may exist as well. Plants will only take up P in the orthophosphate form. The solution P pool is important because it is the pool from which plants take up P and is the only pool that has any measurable mobility. Most of the P taken up by a crop during a growing season will probably have moved only an inch or less through the soil to the roots. A growing crop would quickly deplete the P in the soluble P pool if the pool was not being continuously replenished.

The active P pool is P in the solid phase which is relatively easily released to the soil solution, the water surrounding soil particles. As plants take up phosphate, the concentration of phosphate

in solution is decreased and some phosphate from the active P pool is released. Because the solution P pool is very small, the active P pool is the main source of available P for crops. The ability of the active P pool to replenish the soil solution P pool in a soil is what makes a soil fertile with respect to phosphate. An acre of land may contain several pounds to a few hundred pounds of P in the active P pool. The active P pool will contain inorganic phosphate that is attached (or adsorbed) to small particles in the soil and phosphate that reacted with elements such as calcium or aluminium to form somewhat soluble solids, and organic P that is easily mineralized. Adsorbed phosphate ions are held on active sites on the surfaces of soil particles. The amount of phosphate adsorbed by soil increases as the amount of phosphate in solution increases and vice versa.

Soil particles can act either as a source or a sink of phosphate to the surrounding water depending on conditions. Soil particles with low levels of adsorbed P that are eroded into a body of water with relatively high levels of dissolved phosphate may adsorb phosphate from the water, and vice versa.

The fixed P pool of phosphate will contain inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization by microorganisms in the soil. Phosphate in this pool may remain in soils for years without being made available to plants and may have very little impact on the fertility of a soil. The inorganic phosphate compounds in this fixed P pool are more crystalline in their structure and less soluble than those compounds considered being in the active P pool. Some slow conversion between the fixed P pool and the active P pool does occur in soils.

## 2.4 THE PHOSPHORUS CYCLE

The P cycle is similar to several other mineral nutrient cycles in that P exists in soils and minerals, living organisms, and water. Although P is widely distributed in nature, P is not found by itself in elemental form.

Elemental P is extremely reactive and will combine with oxygen when exposed to the air. In natural systems like soil and water, P will exist as phosphate, a chemical form in which each P atom is surrounded by 4 oxygen (O) atoms. Orthophosphate, the simplest phosphate, has the chemical formula  $PO_4^{3^-}$ . In water, orthophosphate mostly exists as  $H_2PO_4^{-}$  in acidic conditions or as  $HPO_4^{2^-}$  in alkaline conditions. Phosphate is taken up by plants from soils, utilized by animals that consume plants, and returned to soils as organic residues decay in soils (Figure2.1). Much of the phosphate used by living organisms becomes incorporated into organic compounds. When plant materials are returned to the soil, this organic phosphate will slowly be released as inorganic phosphate or be incorporated into more stable organic materials and become part of the soil organic matter.

The release of inorganic phosphate from organic phosphates is called mineralization and is caused by microorganisms breaking down organic compounds.



FIGURE 2.1: PHOSPHORUS CYCLE

The activity of microorganisms is highly influenced by soil temperature and soil moisture. The process is most rapid when soils are warm and moist but well drained. Phosphate can potentially be lost through soil erosion and to a less extent to water running over or through the soil.

Many phosphate compounds are not very soluble in water; therefore, most of the phosphate in natural systems exists in the solid form. However, soil water and surface water (rivers and lakes) usually contain relatively low concentrations of dissolved (or soluble) phosphorus. Depending on the types of minerals in the area, bodies of water usually contain about 10 ppb or more of dissolved P as orthophosphate. Water bodies may also contain organic P and phosphate attached to small particles of sediment.

Total phosphorus in water is all of the phosphorus in solution regardless of its form and is often the form reported in water quality studies.

Algal available or bioavailable phosphorus is P that is estimated to be available to organisms like algae that are present in a lake or river. This is usually estimated by a

chemical test which is designed to measure the dissolved P and the particulate P that are easily available. This is a measure of the P that is of immediate concern to water quality. The word phosphorus or P refers to the element and is also used as a general term when a particular chemical form of P is not being designated. For example, the total P content of a soil or plant material is usually expressed as percent P. However, fertilizer analyses are usually reported as percent  $P_2O_5$ . The phosphate form ( $P_2O_5$ ) is a chemical produced during fertilizer analysis, but does not exist in either fertilizers or soils.

## 2.5 FATE OF PHOSPHORUS ADDED TO SOILS

The phosphate in fertilizers and manure is initially quite soluble and available. Most phosphate fertilizers have been manufactured by treating rock phosphate (the phosphatebearing mineral that is mined) with acid to make it more soluble. Manure contains soluble phosphate, organic phosphate, and inorganic phosphate compounds that are quite available. When the fertilizer or manure phosphate comes in contact with the soil, various reactions begin occurring that make the phosphate less soluble and less available. The rates and products of these reactions are dependent on such soil conditions as pH, moisture content, temperature, and the minerals already present in the soil.

As a particle of fertilizer comes in contact with the soil, moisture from the soil will begin dissolving the particle.

Dissolving of the fertilizer increases the soluble phosphate in the soil solution around the particle and allows the dissolved phosphate to move a short distance away from the fertilizer particle. Movement is slow but may be increased by rainfall or irrigation water flowing through the soil. As phosphate ions in solution slowly migrate away from the fertilizer particle, most of the phosphate will react with the minerals within the soil.

Phosphate ions generally react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe), and forming compounds that are solids. The adsorbed phosphate and the newly formed solids are relatively available to meet crop needs.

Gradually reactions occur in which the adsorbed phosphate and the easily dissolved compounds of phosphate form more insoluble compounds that cause the phosphate to be become fixed and unavailable. Over time this results in a decrease in soil test P. The mechanisms for the changes in phosphate are complex and involve a variety of compounds. In alkaline soils (soil pH greater than 7) Ca is the dominant cation (positive ion) that will react with phosphate. A general sequence of reactions in alkaline soils is the formation of dibasic calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite. The formation of each product results in a decrease in solubility and availability of phosphate. In acidic soils (especially with soil pH less than 5.5) Al is the dominant ion that will react with phosphate. In these soils the first products formed would be amorphous Al and Fe phosphates, as well as some Ca phosphates.

The amorphous Al and Fe phosphates gradually change into compounds that resemble crystalline variscite (an Al phosphate) and strengite (an Fe phosphate). Each of these reactions will result in very insoluble compounds of phosphate that are generally not available to plants. Reactions that reduce P availability occur in all ranges of soil pH but can be very pronounced in alkaline soils (pH > 7.3) and in acidic soils (pH < 5.5). Maintaining soil pH between 6 and 7 will generally result in the most efficient use of phosphate (Figure 2.2). Adding to the active P pool through fertilization will also increase the amount of fixed P. Depleting the active pool through crop uptake may cause

some of the fixed P to slowly become active P. The conversion of available P to fixed P is partially the reason for the low efficiency of P fertilizers.

Most of the P fertilizer applied to the soil will not be utilized by the crop in the first season. Continued application of more P than the crops utilize increases the fertility of the soil, but much of the added P becomes fixed and unavailable.

Most fine-to medium-textured soils have large capacities to hold phosphate by adsorption and precipitation. Occasionally the question of how much phosphate a soil can hold is asked, especially when high loading rates of P are expected or have occurred. Soils differ in their phosphate holding capacity. Fine-textured soils can generally hold hundreds of pounds of phosphate per acre while coarse-textured soils can generally hold much less phosphate due to the more inert character of sand particles as compared to clay particles.

In addition, the subsoil of many soils often has an even greater capacity to hold phosphate than does the corresponding surface soil. However, an important aspect of the ability of a soil to hold phosphate is that a soil cannot hold increasing amounts of phosphate in the solid phase without also increasing soil solution phosphate.

Increased amounts of phosphate in solution will potentially cause more phosphate to be lost to water running over the soil surface or leaching through the soil.

Loading soils with very high levels of phosphate will generally not hurt crops but may result in increased phosphate movement to nearby bodies of water.

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FIGURE 2.2: Phosphorus Availability against Soil pH

## 2.6 PREDICTING THE AVAILABILITY OF PHOSPHORUS IN SOILS

Soils may contain several hundred to several thousand pounds of phosphate per acre. However, much of the phosphate in soils is not available to growing plants. Phosphates found in the soil solution P pool are immediately available, but their amounts are very small in compared to the total P in soils. The active P pool is phosphorus that can be released into solution but is generally small in comparison to the fixed P.

To determine the need for supplemental P, soil tests are often used to estimate how much phosphate will be available for a crop. The most common way of determining P availability is to mix a small amount of soil with an extracting solution that contains an acid and/or complexing agent that will remove some of the phosphate from the soil particles.

The extracting solution and soil are separated by filtration and the amount of P extracted is determined. In alkaline soils, a basic solution may be used as the extractant because an acidic solution will be neutralized by the alkaline soil and be less effective in extracting P. Calibration studies have been done to correlate crop response to fertilizer additions in soils with various soil test levels of P. Using the calibration data, recommendations can be made as to the amounts of phosphate fertilizer that will most likely give optimum yields.

## 2.7THE RELEASE OF P IN SOIL

The P release characteristics of soils and soil components have been studied extensively (Barrow, 1979; Chien and Clayton, 1980; Kuo and Lotse, 1974;Sharpley *et al.*, 1981). Factors that influence the extentof P release to solution include: soil pH; solution composition, e.g., ionic strength and concentration of competing inorganic and organic anions; temperature; and duration of contact with added P (Barrow, 1983; Lopez-Hernandez *et al.*, 1986; Ryden *et al.*, 1977).

Recent studies (Curtin *et al.*, 1987; Smillie *et al.*, 1987) have produced evidence that the equilibrium between surface P and P in solution is influenced toa considerable degree by the nature of the exchangeable cation suite. For example, Curtin et al. (1987) found that when a group of New Zealand soils were Na-saturated, an average 2.6 times more P was released to distilled water (10 consecutive extractions),than from the original soils, where Ca was the dominant exchangeable cation. This effect may have an important bearing on the availability of P in soils that have become saline or receive saline irrigation water. It has been suggested (Curtin *et al.*, 1987) that Prelease induced by Na-saturation could be due to release of P associated with oxide surfaces or to dissolution of Ca-P phases. The relative importance of P desorption and Ca-P dissolution was not established, although such information is essential to understanding the role of exchangeable cations in the chemistry of soil P.

Sequential chemical extraction procedures have been widely used to characterize soil P and offer a means of quantifying changes in sorbed P and Ca-P. Hedley *et al.* (1982) have developed a modification of the Chang and Jackson (1957) inorganic P fractionation procedure, which enabled the P fractions, depleted as a result of plant uptake, to be identified (Hedley *et al.*,1982) and the transformations of soil P during long-term cultivation to be traced (Sharpley *et al.*,1985).

Because previous studies of the effect of Na saturation on P release (Curtin *et al.*, 1987; Smillie *et al.*, 1987) were confined to seven soil types with a narrow range of pH values, it is not known if the results are applicable to soils in general.

## **2.8SHORTAGE OF P IN SOIL**

In many tropical soils, shortage of phosphorus (P) is a major constraint for crop production (Buresh *et al.*, 1997). This deficiency is primarily a result of inherent poverty of the soil in P, depletion of soil P by cropping, and sorption and precipitation involving Fe and Al oxides and hydroxides. The availability of P in soil is regulated by both geochemical and biochemical processes.

In most natural ecosystems, geochemical processes determine the long-term distribution of P in the soil, whereas in the short term, biochemical processes influence the distribution since most of the P available to plants is derived from the soil organic matter.

Natural forest, which relies on nutrient cycling, has developed the necessary mechanisms to obtain its requirements for rapid nutrient cycling (Lal, 1986). However, clearing and cultivation without fertilizer causes significant decrease in soil organic matter and depletion of P (Buresh *et al.*, 1997). In the semi-arid part of northern Tanzania, the indigenous tropical woodland is rapidly being replaced by low input agriculture. In

addition, large areas of acacia (Acacia tortilis Forsk. Hayne) stands are selectively deforested for charcoal production. This unprecedented rate of deforestation has resulted in environmental degradation in the region and it was found that 56% and 51% reduction of C and N contents in the soil of cultivated fields (Solomon *et al.*, 2000).

However, almost no quantitative information exists about the impact of land use changes on the amount and structural composition of P in this soil. The rational choice of cropping systems and supplementary fertilization with P should be based on the understanding of nutrient transformations, and if we do not understand these we are likely to manage the land poorly for agriculture.

## 2.9HISTORY OF CHEMICAL P FRACTIONATION

Chemical fractionation of soil inorganic P dates from the early 1900's (Fraps, 1906; Dean, 1938). Today, the most commonly used procedure is that of Chang and Jackson (1957).

The discovery that neutral NH<sub>4</sub>F selectively dissolves Al-P without dissolving Fe-P (Olsen *et al.*, 1954), prompted Chang and Jackson (1957) to include NH<sub>4</sub>F for P extraction. Briefly, their procedure uses 1 N NH<sub>4</sub>Cl to remove water soluble and loosely bound P, followed by neutral 0.5 N NH<sub>4</sub>F to remove aluminium phosphate. Iron phosphate is then removed by 0.1 N NaOH, followed by Ca phosphate with 0.5 N H<sub>2</sub>SO<sub>4</sub>.

Reductant soluble Fe phosphate is extracted last by  $0.3 M \text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  and 1 g.  $\text{Na}_2\text{S}_2\text{O}_4$ . This procedure has been used to fractionate both acid and calcareous soils and sediments (Williams *et al.*, 1971a). It is the basis for several improved procedures (Williams *et al.*, 1980; Hedley *et al.*, 1982).

One early change to the Chang and Jackson fractionation procedure was increasing the buffer pH of the 0.5 N NH<sub>4</sub>F extractions from 7 to 8.2 (Pratt and Garber, 1964). Further

changes were proposed due to complications with the NH<sub>4</sub>F extraction, leading to its underestimation in both acid and calcareous soils. In a study of acid soils, it was found that all of the sorbed P lost in the NH<sub>4</sub>F extraction due to resorption by ferric compounds was recovered in the following NaOH extraction and proposed a mathematical factor of the NH<sub>4</sub>F extracted P to correct for this discrepancy (Williams *et al.*, 1967).

They also proposed replacement of 0.5 N H<sub>2</sub>SO<sub>4</sub> extraction (used to estimate acid extractable Ca-P) with 0.5 N HCl to facilitate the use of the extract with the colorimetric procedure. In addition, a Na<sub>2</sub>CO<sub>3</sub> fusion step was added at the end of the procedure to estimate residual inorganic P (Williams *et al.*, 1967).

In calcareous soils, the NH<sub>4</sub>F extractable P fraction was also compromised due to the probable formation of CaF<sub>2</sub> compounds during the extraction (Fife, 1959; Williams *et al.*, 1971;Syers *et al.*, 1972).

The P dissolved during the NH<sub>4</sub>F extraction was believed to be resorbed by both the newly formed CaF<sub>2</sub> and CaCO<sub>3</sub> (Williams *et al.*, 1971) resulting in the underestimation of NH<sub>4</sub>F and NaOH extractable P (estimates of Al and Fe bound P, respectively) and the overestimation of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>- NaHCO<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (CBD) extractable P (reductant soluble P) and the HCl extractable Ca- P. For this reason, the NH<sub>4</sub>F extraction was removed from the fractionation procedure for calcareous soils and sediments, leaving only the NaOH, CBD, and HCl extractions.

Although, removing  $NH_4F$  from the procedure did eliminate the formation of  $CaF_2$ , it did not prevent resorption of P by  $CaCO_3$  during the NaOH extraction since  $CaCO_3$  still existed. Generally, the NaOH extraction was found to be associated with Fe and Al bound P but not with Ca bound P. The bulk of the CBD extractable P was believed to be related to the recovery of P that was resorbed during the previous NaOH extraction while only a smaller portion was related to P occluded in Fe oxides (Williams *et al.*, 1971).

After the removal of the  $NH_4F$  extraction from the P fractionation procedure for calcareous soils, the revised procedure was tested on several phosphate minerals to verify the P forms extracted by the procedure (Williams *et al.*, 1980).

In their experiment, the P fractionation procedure began with the CDB followed by the NaOH, HCl, and Na<sub>2</sub>CO<sub>3</sub> fusion extraction procedures.

It was found that the scheme was able to reasonably separate Al and Fe bound P (CDB plus NaOH extractable) from that of the apatite associated P (HCl extractable).

In addition, they also noted that other findings were also very important to the interpretation of the extractable P fractions. First they found that vivianite  $(Fe_3(PO_4)_2$ .H<sub>2</sub>O) was extracted almost entirely by the CDB extraction (>99%).

However when the vivianite was added to a sediment sample, its recovery was incomplete until the subsequent NaOH extraction. This was attributed to the resorption of CDB extractable P by other sediment components. Williams et al. (1980) hypothesized that this resorption of CBD-P may occur to some degree during the CDB extraction in any sediment containing CDB extractable P components. The second striking finding of their study was that variscite (AlPO<sub>4</sub> .2H<sub>2</sub>O) was the only mineral investigated in the study that was highly extractable by NaOH. This was attributed to the fact that the variscite is highly insoluble at a pH of <2 but are highly susceptible to hydrolysis in the presence of NaOH. Finally, they noted that the Na<sub>2</sub>CO<sub>3</sub> fusion

extractable P, an estimate of the residual P fraction, was the only extraction which was able to solubilize the monazite (CePO<sub>4</sub>) and xenotime (YPO<sub>4</sub>) minerals.

Since these minerals have been found in soils (Quereshi *et al.*, 1978), but are considered to be quite rare, it was concluded that mineral P phases such as these are the dominant components in the generally small residual P fraction.

More recent adjustments to the P fractionation procedure include introducing additional P extractions at the beginning of the procedure to estimate plant available or labile P forms and also the separation of inorganic P from organic P within each extraction (Hedley *et al.*, 1982).

Both of these adjustments were originally made to evaluate differences in inorganic and organic P fractions between soils of different ecosystems. In the procedure described by Hedley *et al.* (1982), two extractions were added to estimate the more labile P forms.

The first was a resin exchangeable P (resin-P) which was believed to be the most "biologically available" inorganic P (Amer *et al.*, 1955).

The next extraction, applied to the first resin-P residue, was a NaHCO<sub>3</sub> extractable P (NaHCO<sub>3</sub>-P) which was believed to include both inorganic P (*Pi*) and organic P (*Po*) sorbed on the soil surface and also some microbial P. In addition, the duplicate resin-P was pretreated with CHCl<sub>3</sub> followed by the NaHCO<sub>3</sub> extraction for removing P from lysed microbial cells. Subsequent fractionations included NaOH, HCl, and H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> digestion (Hedley *et al*, 1982).

Separation of Pi from Po was accomplished by treating a portion of the extract from each sequential extraction (with the exception of the resin-P and HCl-P) with acidified (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. This fractionation scheme which utilizes the separation of Pi and Po and

includes initial labile P fractions is often referred to as the Hedley P fractionation scheme. To meet specific research needs the Hedley procedure has also been modified by others. For example, in a study focused on the transformations of P fractions due to the application of biosolids, Sui *et al.* (1999) used a H<sub>2</sub>O extractable P instead of resin-P in the Hedley procedure because they believed that H<sub>2</sub>O soluble P better related to bioavailable P in surface runoff than did the resin-P (Sui *et al.*, 1999).

While all these procedures have been employed to elucidate P chemistry for various soil systems, the most commonly used fractionation scheme of P for calcareous and non calcerous soils includes three fundamental steps: NaOH extraction for Fe-/Al-P, CBD extraction for reductant-P, and HCl extraction for Ca-P (Kuo, 1996), with or without a total digestion for residual-P.

## 2.10 P ANALYSIS

The mainstay of P analysis for all solution types has been the use of colorimetric procedures, most notably (Murphy and Riley, 1962).

Colorimetric procedures are sensitive, reproducible, and lend themselves to automated analysis. In addition, the methods can accommodate water samples, digest solutions, and extracts. Variations in the procedure are incorporated into other sections, despite the appearance of redundancy. Modifications to the procedures are often method-specific.

Inductively coupled plasma (ICP) spectrophotometry is also now commonly used for P determination, particularly in routine soil P tests offered by public (Land Grant University) and commercial laboratories. The use of ICP has increased as the use of multi-element soil extractants becomes more popular. Results from colorimetric analyses are not always directly comparable to those from ICP, because ICP estimates the total amount of P in a solution, while the colorimetric procedures measure P that can react
with the colour developing reagent. Moreover, there are certain limitations that must be considered when data generated by ICP are compared (de Boer *et al.*, 1998). For example, there are matrix effects, so that the type of extract has to be taken into account. Other elements in the water or extract can also interfere with the number generated. Even the type of instrument (axial versus radial view) and the wavelength (178 nm versus 213 nm) used for determination can cause variation in the data generated.

The use of solution <sup>31</sup>P NMR spectroscopy of P in soil and residual materials has allowed identification of P forms in animal manures and confirmed P forms estimated by commonly used chemical extractants, such as sequential fractionation schemes.

Use of the procedure has enabled more accurate determination of organic forms of P in soil and residual materials. In addition, the use of synchrotron-based techniques has provided insight into both organic and inorganic forms of P in soil and residual materials. Clearly, synchrotron-based techniques will play an increasing role in the study of P in natural systems. These analytical advances have been critical in gaining a more detailed understanding of soil P transformations and reaction products following land application of residual materials. This information has helped assess the fate, reactivity, and behaviour of specific forms of P and their implications on land when applying certain materials during environmental risk response.

## 2.11EFFECT OF pH ON SOIL P

In nature, phosphorus is always found in combination with oxygen in the phosphate form.

This chemical form allows the molecule to react with up to three single positive ions such as hydrogen ( $H^+$ ), potassium ( $K^+$ ), or ammonium ( $NH_4^+$ ) or with other positive ions with +2 or even +3 charges. Phosphorus is absorbed by plants in the orthophosphate

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form, generally as  $H_2PO_4^-$  or  $HPO_4^{2-}$ . The amounts of these ions in the soil solution are determined by soil pH.

At pH 7.2, there are approximately equal amounts of these two forms in solution. Maximum solubility of calcium phosphate minerals occurs at about the same pH, therefore maximum plant available P occurs at approximately pH 7. As pH changes in either direction, P availability is decreased. It may be noticed that other forms of phosphate are equally prevalent at the extreme ends of the pH scale, but this occurs outside the range of normal soil pH. While the portion of P in these forms is high, plants cannot survive the other conditions resulting from these extreme pH levels.

At normal soil pH (5.0-8.0), the concentration of  $H^+$  available for reactions is so low that the phosphate forms mentioned earlier are only a small and transient component of the total soil P reserve. This means that phosphates react with other positively charged ions to form stable components that can both bind and release P.

Most soils can bind much more P than plants can use. This explains the concept of P sufficiency and the reason why P may not be required for many years on some sites. The soil can be viewed as a giant warehouse for P. The resupply of P comes from the P bound to the soil and only refills the warehouse at a slow rate. Some warehouses start out full (high P soils) and some start out almost empty (low P soils). Those that are full have more P supplying potential than those that start out almost empty. The good news is that P fertilizer can be used to fill the warehouse to provide sufficient P for plant growth. It is important to note that while soil test P levels increase with P fertilizer applications, it takes about 15 pounds of  $P_2O_5$  applied per acre to increase soil test P by one point. This makes it impractical to attempt to raise soil test P levels over a short time; it would just take too much fertilizer.

It is possible, however, to satisfy the crops immediate needs with reasonable rates of fertilizer. It is crucial that P fertilizer be applied annually at reasonable rates to satisfy plant needs if soil tests levels indicate a deficiency.

At a soil pH above 5.5 most of the phosphates react with calcium to form calcium phosphates. Below pH 5.5, aluminium  $(Al^{3+})$  is abundant and will react more readily with the phosphates. Calcium phosphates are relatively more water-soluble than aluminium phosphates. The lack of water solubility of aluminium phosphates means that these compounds are not readily available for plant use. In other words, in strongly acid soils, most of the P is bound and not released. This means the warehouse is locked and no P can get out. Lime application to raise pH will open the warehouse and reverse this reaction by supplying carbonates to neutralize acidity and calcium to react with phosphorus.

Calcium, when supplied at adequate rates, "knocks off" the aluminium and replaces it with calcium, rendering the phosphate water soluble once again.

The nuts and bolts are that: When the P soil test index indicates a deficiency, then the likelihood of response to P fertilizer is high. Choosing not to test soil sample or to ignore soil test recommendations for P means missing out on potential yields. If your soil test P level is only 50 % sufficient then you can only achieve 50 % of the maximum potential yield. This is before any other yield-limiting factors are encountered. Lack of rainfall only exploits deficiencies. In drier years, it is important to apply fertilizer so as to eliminate deficiencies and to take full advantage of the moisture that is present.

The highest solubility for calcium phosphates occurs around pH 7.2. The highest level of plant available phosphorus parallels this solubility range. Letting pH fall below 5.5

"locks the warehouse" and severely reduces the amount of water-soluble P components in the soil and increases the amount of insoluble aluminium phosphates. This in turn directly reduces plant available P.

There are really only two solutions to this problem.

- 1. Apply lime to acceptable pH.
- 2. Band P with the seed at planting. This reduces the amount of soil the phosphorus must react with and hopefully creates an area of concentrated P that doesn't react with aluminium.

# 2.12 COLLECTION AND SAMPLING TECHNIQUE FOR P ANALYSIS

The collection of a representative and reliable soil sample for phosphorus (P) analysis requires predetermination of sampling depth, position relative to nutrient application patterns, and sampling intensity within the field.

The appropriate soil sampling depth is dependent upon the planned interpretation of the analytical data. If investigation of P distribution or concentration with depth is a specified research objective, three factors must be considered when determining the appropriate sampling depth: 1) influence of changes in soil morphology with depth (i.e., horizonation); 2) influence of surface soil management (e.g., tillage); and 3) necessity to maintain sample collection depth uniformity across numerous sites.

Sample collection depth based on observed morphological horizon depths is quite useful when attempting to associate soil P measurements with soil physical properties.

This technique may generate very reliable data for a particular, well-defined location, but this laborious task is not very practical when a research project focuses on more than a few soils or when the data will be subjected to broader, perhaps watershed-scale, interpretation. Depth of tillage will dramatically impact soil P distribution with depth. Tillage depth is seldom constant across a given field. Sampling depths should include soil collected from a depth confidently within the tillage zone and excluding soil from below the tillage zone. A second transitional depth should be collected that is expected to be variably affected by tillage and includes the lower tillage boundary. Deeper sampling depths should not be directly impacted by physical tillage activity.

Relating soil physical and chemical properties to the potential for P transport with surface runoff water requires a different approach to soil sample collection. Sharpley (1985) studied five soils of varying physical and chemical properties and found that effective depth of interaction between surface soil and runoff ranged from 2 to 40 mm. The effective depth of interaction varied with soil type, surface slope, rainfall intensity, and crop residue. For most agricultural soils, samples collected to a depth of 20 mm would accurately define the effective depth of runoff interaction generated by moderate to high rainfall intensity (< 50 mm/h).

For medium to coarse textured soils on steeper slopes (>12 %) that are subjected to high intensity rainfall (> 100 mm /h), soils should be sampled to a depth of 40 mm in order to more accurately relate the potential for P transport with surface runoff to soil physical and chemical properties.

Recommended soil sampling intensity is usually between 10 and 30 subsamples per composite sample (Whitney *et al.*, 1985; Kitchen *et al.*, 1990; Coale, 1998). A single composite sample may represent a single research plot or an entire production field, but generally not more than 10 ha.

Discrete nutrient application patterns in a field can increase the complexity of appropriate soil sample collection procedures. In a review of positional P availability

resulting from band application of fertilizer P, it was stated that collection of 15 (Ward and Leikam, 1986; Shapiro, 1988) to 30 random samples (Hooker, 1976) were adequate to reflect crop P availability in conventionally tilled fields where previous P fertilizer bands exist. For no-till or minimum-till soils containing residual P fertilizer bands in which the location of the P bands is known, sampling to include one "in-the-band" soil sample for every 20 "between-the-band" samples for 76 cm band spacing, and one "in-the-band" sample for every 8 "between-the-band" samples for 30 cm band spacing, will accurately reflect the mean soil P status of the field (Kitchen *et al.*, 1990). Twenty to 30 subsamples per composite are adequate. When the location of the P bands is not known, collection of 20 to 30 subsamples per composite is also adequate but paired subsamples should be collected where the location of the first subsample of the pair is completely random and the second subsample of the pair is located 50% of the band-spacing distance from the first, perpendicular to the band direction (Kitchen *et al.*, 1990).

### 2.12.1 DRYING SOIL SAMPLES FOR P ANALYSIS

Air-drying should be satisfactory for investigations into relative changes in soil P concentrations in response to imposed treatments or for routine comparative P analyses. Soil samples should be air-dried (25 to  $30^{\circ}$ C) and crushed to pass a 2 mm sieve.

Air-dried and crushed soil samples are stable at room temperature. Air-drying may not be suitable for determination of the absolute quantity of the various P fractions in soils. Air-drying may artificially elevate the quantity of soluble reactive P above *in situ* conditions. Bartlett and James (1980) studied P solubility in the surface soil of a loamy fine sand and found water-soluble P concentrations to be five times higher in air-dried samples (~30 mg P L-1) than in samples stored at field moisture (~5 mg P/ L). The effect of air-drying was only partially reversed by rewetting and incubating the air-dried soil for one month (~20 mg P L-1). Water-soluble P in rewetted soil samples that had previously been air-dried was shown to decrease during three months of storage at 20°C (Bartlett and James, 1980). For quantitative characterization studies, soil and sediment samples should be stored at field moisture content under refrigeration, between 0 and 4°C. Soil and sediment samples should not be stored frozen (<0°C), because the watersoluble proportion of total P increases after freezing (Mack and Barber, 1960). Mixing moist soil samples to achieve homogeneity is difficult, and careful attention should be paid to ensure thorough mixing prior to sub sampling. Moist soils are also difficult to sieve, but large particles (> 2mm) should be removed from the sample prior to analysis.

## 2.13EFFECT OF SHIFTING CULTIVATION ON P DYNAMICS

Ecological and economic constraints on agricultural intensification in the tropics compel the scientific community to re-examine the effects of traditional shifting cultivation on phosphorus dynamics. Particularly in the tropics, phosphorus often limits agricultural production (Sanchez and Buol, 1975). Past research has focused on a single cycle of slash-and-burn cultivation followed by regrowth (Nye and Greenland, 1960; Sanchez, 1976; Ewel *et al.*, 1981; Uhl and Jordan, 1984). Little is known about the long-term effects of shifting cultivation, including its potential to sustain rural populations.

Soil phosphorus availability may limit productivity in lowland tropical forests, especially on Oxisols and Ultisols, which occupy up to 40% of the land area of the tropics (Sanchez, 1976; Richter and Barber, 1991).

Phosphorus availability in these soils is often controlled by the high adsorption capacity of soil minerals and by the tendency of adsorbed P to be occluded in the interior of iron (Fe) and aluminum (Al) minerals (Sollins *et al.*, 1988; Frossard *et al.*, 1995; Lajtha and

Harrison, 1995). Rapid sorption of P on the abundant Fe and Al minerals in tropical soils precludes its free movement through the soil solution to plant roots.

In addition to long-term P losses via leaching, rapid sorption may be responsible for phosphorus limitation of plant growth in tropical forests (Vitousek, 1984; Vitousek and Sanford, 1986). At a highly weathered tierrefirme site in Venezuela, 40–80% of all phosphorus was in resistant forms (Tiessen*et al.*, 1994).

In a global analysis of soils, research found that organic forms are often associated with the availability of soil P. Tiessen and coworkers (1994) found that the amount of organic phosphorus determined P availability in Ultisols.

In many tropical forests, nutrient limitations, especially by phosphorus, have resulted in the evolution of nutrient-conserving mechanisms that can be lost upon forest clearing (e.g., root mats, sclerophylly, mycorrhizal infection, and nutrient retranslocation.( Jordan and Herrera,1981). Shifting cultivation has developed over thousands of years to address the problems of short-term fertility decline as well as weed and pest proliferation (Ewel, 1986). With rising human population and economic development, however, shifting cultivation has intensified in many areas through either continuous cropping or shortened fallow periods. Yields, initially low, often decline with continuous cropping (Driessen *et al.*, 1977).

A better understanding of how shifting cultivation affects long-term phosphorus dynamics will aid the development of sustainable agricultural methods in the tropics. It will also indicate the constraints on potential alternative land uses, including the restoration of mature forest.

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#### 2.13.1 PHOSPHORUS DYNAMICS FOLLOWING SLASH AND BURN

In the wet tropics, primary forest biomass contains from 30 to 301 kg P/ha, whereas secondary forest contains from 17 to 137 kg P/ha (Lawrence, 1998). Shifting cultivation begins with the slash and burn of a patch of primary or secondary forest; in West Kalimantan mean patch size was just over 1 ha (Lawrence *et al.*, 1998). The fire transfers nutrients from vegetation and surficial organic detritus to the soil.

It is also likely to affect nutrients stored in the surface soil (0-2.5 cm deep) where temperatures may rise as high as  $250^{\circ}$ C (Sanchez 1976). Pyromineralization of organically bound soil P may occur, and the heat may also cause the transformation of more resistant forms into plant-available forms (Saa *et al.*, 1993). Not all of the biomass phosphorus enters the soil as ash. In many areas of the moist tropics, much of the organic matter is not consumed in the fire (Sanchez, 1976).

Also, depending on the intensity of the slash fire, 3–55% of total P stocks can be lost to the atmosphere in smoke (Raison *et al.*, 1985; Kauffman *et al.*, 1993; Romanya *et al.*, 1994).

Much of this phosphorus may be redistributed within the landscape, rather than lost entirely from it (Menaut*et al.*, 1993).

Up to 50% of the phosphorus that is deposited during the fire may be lost from the site through erosion by wind and water (Ewel *et al.*, 1981; Kauffman *et al.*, 1993). While the site is unvegetated, P can be lost due to leaching (Palm *et al.*, 1996). In addition to losses of P during slash-and-burn, fixation of P in resistant forms may further reduce the availability of P that remains on site. Measured increases in plant-available soil phosphorus after a slash fire are often 10 times lower than the estimated stock in burned vegetation, ranging from 6 to 25 kg/ha (Sanchez, 1976;Juo and Manu, 1996). This

amount is adequate to support one to several crops, but it may not provide adequate P for secondary forest regrowth. A final constraint on P supply early in the cycle of shifting cultivation is that much of the P taken up by the crop is removed in the harvest (;6 kg/ha per 1000 kg of rice; 1000 kg/ha is a typical yield) (Sanchez, 1976). These findings highlight the importance of additional phosphorus pools, beyond those considered readily available, for plant production during both crop and fallow periods (Hedley *et al.*, 1994). In West Kalimantan, typically one or two crops of upland rice (*Oryzasativa*) are farmed during the swidden period (one crop per year); then the patch is abandoned to natural forest regeneration for 8 to 30 years (Dove, 1985). For secondary forest cleared between 1990 and 1995 in Kembera, the mean fallow period was 20 years (Lawrence *et al.*, 1998). In a chronosequence of fallow succession in Kembera, research found that nutrients accumulated in secondary forest biomass for 3 to 11 years before soil stocks began to increase. They suggested that the current fallow length was adequate to restore fertility in surface soils, but data on soil phosphorus availability were limited.

To assess the impact of repeated shifting cultivation on soil phosphorus, a series of sites varying in cultivation history was sampled, ranging from sites that have never been cleared to those cultivated ten or more times.

## 2.14 ESSENTIAL ROLE OF PHOSPHORUS (P) IN PLANTS

Phosphorus is an essential nutrient both as a part of several key plant structure compounds and as a catalyst in the conversion of numerous key biochemical reactions in plants. Phosphorus is noted especially for its role in capturing and converting the sun's energy into useful plant compounds.

Phosphorus is a vital component of DNA, the genetic "memory unit" of all living things. It is also a component of RNA, the compound that reads the DNA genetic code to build proteins and other compounds essential for plant structure, seed yield, and genetic transfer. The structures of both DNA and RNA are linked together by phosphorus bonds. Phosphorus is a vital component of ATP, the "energy unit" of plants.

ATP forms during photosynthesis and has phosphorus in its structure, and processes from the beginning of seedling growth through to the formation of grain and maturity. Thus phosphorus is essential for the general health and vigour of all plants. Some specific growth factors that have been associated with phosphorus are: stimulated root development, increased stalk and stem strength, improved flower formation and seed production, more uniform and earlier crop maturity, increased nitrogen N-fixing capacity of legumes, improvements in crop quality, and increased resistance to plant diseases.

Phosphorus deficiency is more difficult to diagnose than a deficiency of nitrogen or potassium. Crops usually display no obvious symptoms of phosphorus deficiency, other than a general stunting of the plant during early growth, and by the time a visual deficiency is recognized it may be too late to correct in annual crops. Some crops, such as corn, tend to show an abnormal discoloration when phosphorus is deficient.

The plants are usually dark bluish-green in colour with leaves and stem becoming purplish. The degree of purple is influenced by the genetic makeup of the plant, some hybrids showing much greater discoloration than others.

The purplish colour is due to accumulation of sugars which favour the synthesis of anthocyanin (a purplish coloured pigment) that occurs in the leaves of the plant.

Phosphorus is highly mobile in plants and when deficient it may be translocated from old plant tissue to young actively growing areas. Consequently, early vegetative responses to phosphorus are often observed. As a plant matures, phosphorus is translocated into the fruiting areas of the plant where high energy requirements are needed for the formation of seeds and fruit.

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Phosphorus deficiencies late in the growing season affect both seed development and normal crop maturity. The percentage of the total amount of each nutrient taken up is higher for phosphorus late in the growing season than for either nitrogen or potassium.

### 2.15 ENVIRONMENTAL CONCERNS OF P IN SOILS

Phosphorus movement off agricultural land to surface waters may speed algal growth in water bodies. These algae ultimately die and decay in the water. This process may reduce oxygen levels and ultimately reduce higher-order aquatic populations. Research has shown 50 to 95 percent of P movement within a landscape is attached to moving sediment. Since P is closely attached to solid soil materials, erosion control limits P movement to surface waters. Best management practices (BMP's) are simple, low cost, common sense ways to minimize P movement. Some BMP's for P management in agriculture are listed below.

- Use soil test-based recommendations for P fertilizer application rates.
- Maintain and calibrate applicators and spreaders for more efficient fertilizer applications.
- Base animal wastes application rates on nutrient analysis of the material to be used.
- Do not apply fertilizers too close to surface waters.
- Apply fertilizers when growing crops will utilize them.
- Control erosion to keep sediment from entering surface waters.
- Use risk assessment tools such as the Phosphorus Index to evaluate your situation.
- Use the best combination of these for your situation.

Some situations may require more extensive nutrient management planning, such as animal feeding operations. This may include the Mississippi Phosphorus Index Risk Assessment Tool to evaluate the potential for P to move in the landscape.

The risk assessment tool incorporates site-specific soil conditions and applied management practices in the evaluation. Soil test phosphorus levels, soil permeability, field slopes, animal by product application rates, distance to surface water, and other factors are used to determine the probability of nutrient movement in the landscape. Evaluations are done on a field-by-field basis, usually by county Natural Resource Conservation Service offices and private technical service providers.

### 2.16 SOIL PHOSPHORUS AND WATER QUALITY

Phosphorus is a somewhat unique pollutant in that it is an essential element, has low solubility, and is not toxic itself, but may have detrimental effects on water quality at quite low concentrations. There is considerable concern about P being lost from soils and transported to nearby streams and lakes. Several chemical properties of soil P have important implications for the potential loss of P to surface water.

Phosphorus in soils is almost entirely associated with soil particles. When soil particles are carried to a river or lake, P will be contained in this sediment. When the sediment reaches a body of water it may act as a sink or a source of P in solution. In either case, it is a potential source of P that may eventually be released.

Most soils have a large capacity to retain P. Even large additions of P will be mostly retained by soils provided there is adequate contact with the soil.

Increasing the amounts of phosphate in soils results in increased levels of phosphate in soil solutions. This will generally result in small but potentially important increases in the amounts of phosphate in water that passes over or through soils.

Phosphate in soils is associated more with fine particles than coarse particles. When soil erosion occurs, more fine particles are removed than coarse particles, causing sediment leaving a soil through erosion to be enriched in P.

### 2.17 TOTAL PHOSPHORUS IN SOIL

There have been many methods developed to extract and analyze total phosphorus (P) in soil (Bray and Kurtz, 1945; Jackson, 1958; Syers *et al.*, 1969; Sommers and Nelson, 1972; Dick and Tabatabai, 1977; Olsen and Sommers, 1982; Bowman and Cole, 1978). Four methods have been more commonly used: sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) fusion (Jackson, 1958), perchloric acid (HClO<sub>4</sub>) digestion (Jackson, 1958), sulphuric acid-hydrogen peroxide-hydrofluoric acid (H2SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> -HF) digestion (Bowman and Cole, 1988), and sodium hypobromite (NaOBr) oxidation followed by H<sub>2</sub>SO<sub>4</sub> dissolution (Dick *et al.*, 1977). These four methods convert soil organic P to inorganic P to allow total P determination (Kuo, 1996). Of these methods, Na<sub>2</sub>CO<sub>3</sub> fusion is thought to give more reliable results (Syers *et al.*, 1969; Sommers *et al.*, 1972).

Underestimation of total P by acid digestion is thought to be due to inability of these methods to extract P from apatite inclusions or imbedded in the matrix of silicate minerals (Syers *et al.*, 1969).

The ability of an acid digestion to extract P from inclusions depends upon the acid or combination of acids used.

Syers *et al.* (1967) showed that the effectiveness of extraction generally followed the order:  $Na_2CO_3$  fusion > HF digestion > HClO<sub>4</sub> digestion > H<sub>2</sub>SO<sub>4</sub> digestion > ignition. Methods developed by Sommers and Nelson (1972) and Bowman (1988) are variations of standard HClO<sub>4</sub> and HF digestion methods.

These methods were shown to give a similar degree of underestimation of total P as standard HClO<sub>4</sub> digestion methods. Dick *et al.*, (1977) proposed an alkaline oxidation method using NaOBr. This method was shown to give results 1% higher than those found by HClO<sub>4</sub> digestion. However, the method still underestimated total P by 4% when compared to results from Na<sub>2</sub>CO<sub>3</sub> fusion.

### 2.18 BIOLOGICALLY AVAILABLE PHOSPHORUS

Biologically available P (BAP) has been operationally defined as "the amount of inorganic P, a P-deficient algal population can utilize over a period of 24 h or longer" (Sonzogni *et al.*, 1982). The amount of P in soil, sediment, and water that is potentially available for algal uptake (bioavailable P) can be quantified by algal assays, which require up to 100 days incubations (Miller *et al.*, 1978). Thus, more rapid chemical extractions, such as those using NaOH (Butkus, *et al.*, 1988; Dorich *et al.*, 1980), NH<sub>4</sub>F (Porcella *et al.*, 1970), ion exchange resin (Huettl *et al.*, 1979) and citrate-dithionite-bicarbonate (Logan *et al.*, 1979), have been used routinely to estimate bioavailable P.

The weaker extractants ( $NH_4F$  and NaOH) and short-term resin extractions may represent P that could be utilized by algae in the photic zone of lakes under aerobic conditions.

In contrast, the more severe extractants (citrate-dithionite-bicarbonate) represent P that may become bioavailable under the reducing conditions found in the anoxic hypolimnion of stratified lakes.

Sharpley *et al.* (1991) showed that when using a wide solution:soil ratio (500:1), 0.1 *M* NaOH extractable P (NaOH-P) was closely related to the growth of several algal species.

However, the complexity of algal assay and chemical extraction methods often limit their use by soil testing laboratories. For example, long assay incubation (7 to 100 days) and

chemical extraction times (> 16 hr), as well as large solution volumes (> 500 mL) are particularly inconvenient. As the amount of P extracted depends on ionic strength, cationic species, pH, and volume of the extractant used (Hope and Syers, 1976; Sharpley *et al.*, 1981), these limitations will be difficult to overcome. Questions also have been raised as to the validity of relating the form or availability of P extracted by chemical solutions to P bioavailability in the aquatic environment. As a result, P sink approaches have been developed to estimate BAP in soil, sediment, and water.

## 2.19PHOSPHORUS SORPTION INDEX

The phosphorus (P) sorption capacity of soils is typically determined by the use of batch equilibrium experiments that are used to generate sorption isotherms. These isotherms are plots of the amount of P adsorbed from several solutions of known initial concentration vs. the P concentration at equilibrium for each solution.

For example, Nair *et al.* (1984) proposed, based on an inter laboratory comparison study, a standard approach to construct P sorption isotherms, using a soil: solution ratio of 1:25 (w: v), six initial P concentrations (as  $KH_2PO_4$  in a 0.01*M* CaCl<sub>2</sub> matrix), and a 24 h equilibration period. Results from sorption isotherms can be used to calculate P sorption maxima and P bonding energies for soils with different properties and/or as influenced by cultural practices, such as crop rotation, tillage, and manure addition.

While useful for agronomic and environmental characterization of the P sorption capacity of soils, P sorption isotherms are too time-consuming, complicated, and expensive for routine use. To overcome these obstacles, Bache and Williams (1971) developed a "P Sorption Index" (PSI) that could rapidly determine soil P sorption capacity. They evaluated 12 approaches and found that a PSI derived from a single-point isotherm (P sorbed from a single solution containing 50 µmol P/g soil) was easy to use

and well correlated with the P sorption capacity of 42 acid and calcareous soils from Scotland (r=0.97). Other researchers have used the PSI, or modified versions, and shown it to be well correlated with soil P sorption capacity determined from complete sorption isotherms for soils of widely varying chemical and physical properties (Mozaffari and Sim, 1994; Sharpley *et al.*, 1984). In most cases these researchers have maintained the original ratio of added P to soil (1.5 g/kg), but have slightly changed the soil: solution ratio, background electrolyte, and/or shaking time. Most of these modifications have not affected the correlations between P sorption capacity estimated from the PSI and that determined by a full sorption isotherm.

### **CHAPTER THREE**

# MATERIALS AND METHOD

# **3.1 STUDY AREA**

The areas for this study were selected based on their contribution towards the production of food and cash crops in the Eastern Region. The areas are Akwadum in New Juaben and Huhunya in Yilo-Krobo districts.

A cocoa farm was selected in Akwadum, and a maize farm and a virgin land were selected in Huhunnya. The cocoa farm was cultivated with fertilizer while maize farm was cultivated without fertilizer.

# **3.2 GLASSWARE CLEANING**

All glassware used were soaked in detergent solution, rinsed and soaked in 5 % (v/v)  $HNO_3$  overnight. They were rinsed with distilled water followed by 0.5 % (w/v)  $KMnO_4$ , rinsed with distilled water and dried before used.

### **3.3GLASSWARE**

Pyrex glass bottles

50 ml, 100 ml, 250 ml, 500 ml, 1000 ml, 2000 ml pyrex volumetric flasks

5 ml micro pipette

- 25 ml and 50 ml burettes
- 50 ml centrifuge tubes

#### **3.4 EQUIPMENT USED**

1. Shaker

2. KontronInstruments Centrifuge (CENTRIKON T- 42K)

- 3. Hot water bath
- 4. Shimadzu UV- Visible Spectrophotometer (UV mini- 1240).

- 5. Hanna Instruments pH meter (pH 209)
- 6. WTW Conductivity Meter (LF 538)

### APPARATUS USED

- 1. 2 mm sieve
- 2. Whatman No. 41 filter paper

# **3.5 REAGENTS USED**

Ammonium chloride (1*M* NH<sub>4</sub>Cl): 53.3 g of NH<sub>4</sub>Cl was dissolved in 1 L deionized water.

Ammonium fluoride (0.5 M NH<sub>4</sub>F, pH 8.2): 18.5 g of NH<sub>4</sub>F was dissolved in 1 L deionized water and the pH was adjusted to 8.2 with 4 M NH<sub>4</sub>OH.

Sodium hydroxide (2 M and 0.1 M NaOH): 80 g and 4.0 g, respectively, of NaOH were dissolved in 1 L deionized water.

Sodium chloride (Sat. NaCl): 400 g of NaCl was added to 1 L deionized water.

Sulfuric acid (0.25 M  $H_2SO_4$ ): 14 mL of concentrated  $H_2SO_4$  was diluted to 1 L with deionized water.

Hydrochloric acid (2 M HCl): 168 mL of concentrated HCl was diluted to 1 L with deionized water.

Sodium citrate (0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>•2H<sub>2</sub>O): 88.2 g of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>•2H<sub>2</sub>O was dissolved in 1 L deionized water.

Sodium bicarbonate (1 M NaHCO<sub>3</sub>): 84 g of NaHCO<sub>3</sub>was dissolved in 1L deionized water.

Boric acid ( $0.8 \text{ M H}_3\text{BO}_3$ ): 50 g of  $\text{H}_3\text{BO}_3$  was dissolved in 1 L deionized water. Sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), reagent grade.

p-nitrophenol indicator: 0.25 g of p-nitrophenol was dissolved in 100 mL deionized water.

Potassium dichromate (1M  $K_2Cr_2O_7$ ): 49.024 g of dry  $K_2Cr_2O_7$  was dissolved in 800 ml deionized water and diluted to 1000 ml.

Ferrous ammonium sulphate solution (1M): 78.390 g of ferrous ammonium sulphate was dissolved in 50 ml  $H_2SO_4$  and diluted to 1000 ml with distilled water.

Indicator solution: 1, 10- phenanthroline monohydrate- ferrous sulphate  $[(C_{12}H_{18}N_2)_3FeSO_4]$ 

: 1.845 g of 1, 10 ortho- phenanthroline monohydrate ( $C_{12}H_{18}N_2$  .H<sub>2</sub>O) was dissolved in 100 ml of 0.025 M ferrous sulphate (0.695 g of ferrous sulphate in 100ml of distilled water).

## 3.5.1 REAGENT A

Phospho-molybdate reagent. 12g of ammonium paramolybdate  $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$  was dissolved in 250 mL of deionized water and 0.2908 g of potassium antimony tartrate (KSbO•C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) was dissolved in 100 mL of deionized water.

These solutions were added to 1 L of 2.5 M  $H_2SO_4$  (141 mL of concentrated  $H_2SO_4$  diluted to 1 L), mixed thoroughly, and after cooling, diluted to 2 L with deionized water. The solution (Reagent A) was stored in a dark, cool place.

#### **3.5.2 REAGENT B**

1.056 g of L-ascorbic acid ( $C_6H_8O_6$ ) was dissolved in 200 mL of Reagent A, and mixed. Reagent B was prepared as needed, because it was used within 24 hour.

# **3.6 SAMPLING METHOD**

The sample sites used for this research were maize plantation farm in Huhunya (HC), cocoa farm in Akwadum (AC) and uncultivated virgin land in Huhunya (HV).Twelve soil samples per site were collected from three land utilization sites. Samples from three soil depths were taken from each sample site which comprises topsoil (0–10 cm), sub surface soil (10-20 cm) and subsoil (20-30 cm). In total 36 samples were obtained. Table 3.1 shows soil sample, depths and their various codes.

	Sample Location						
Depth/cm	Huhunya maize	Akwadum Cocoa	Huhunya Virgin				
	cultivation	farm	land				
0-10 (Top soil)	HC1	AC1	HV1				
10-20 (Sub surface)	HC2	AC2	HV2				
20-30 (subsoil)	HC3	AC3	HV3				

Table 3.1 Soil sample, depths and their code names

With the use of a push-tube coring device, samples were taken and placed in polyethene bags. Soils were air dried at room temperature, finely powdered and sieved through 2 mm mesh size sieve.

#### 3.7 SOIL pH AND ELECTRICAL CONDUCTIVITY DETERMINATION

20 g of the soil sample was added to 50 ml of deionised water. The mixture was stirred for 10 minutes, allowed to stand for 30 minutes and it was stirred again for 2 minutes. The pH of the soil suspension was measured.

The suspension was allowed to settle for 1 hour and the conductivity of the supernatant liquid was measured.

# **3.8 ORGANIC CARBON CONTENT OF SOIL DETERMINATION**

In a 50 ml digestion tube, 0.4 g of finely ground soil was mixed with 5 ml of potassium dichromate solution and 7.5 ml sulphuric acid.

The tube was placed in a preheated block at 145-155°C for 30 minutes. The tube was then removed and allowed to cool.

The digest was quantitatively transferred to 100 ml volumetric flask and 0.3 ml of the indicator solution was added. The mixture was mixed thoroughly and was titrated with ferrous ammonium sulphate solution. The end point colour change was from greenish to brown.

The titre was recorded and was corrected for the mean of reagent blanks (X).

# **3.8.1 CALCULATION**

% Organic Carbon= X \* 0.2 \* 0.3 where X = Vb - Vs; Sample weight

Vb= volume of ferrous ammonium sulphate used to titrate reagent blank solution Vs= volume of ferrous ammonium sulphate used to titrate reagent sample solution

### **3.9 FRACTIONATION PROCEDURE**

#### **3.9.1 LOOSELY BOUND PHOSPHATE**

1.0 g (<2 mm) of soil and 25 mL of 1*M* NH<sub>4</sub>Cl were added together in a 50 mL centrifuge tube and shaken for 30 min to extract the soluble and loosely bound P.

The mixture was centrifuged and the supernatant was decanted into a 50-mL volumetric flask and brought to volume with deionized water.

## **3.9.2 ALUMINIUM BOUND PHOSPHATE**

25 mL of 0.5 M NH<sub>4</sub>F (pH 8.2) was added to the residue and the suspension was shaken for 1 h to extract aluminum phosphates. The mixture was centrifuged and the supernatant was decanted into a 50-mL volumetric flask (extract B). The soil sample was washed twice with 25-mL portions of saturated NaCl and centrifuged. The washings were combined with extract B and brought to volume.

## **3.9.3 IRON BOUND PHOSPHATE**

25 mL of 0.1 M NaOHwas added to the soil residues and shaken for 17 h to extract iron phosphates. The mixture was centrifuged and the supernatant solution was decanted into a 50-mL volumetric flask (extract C).

The soil was washed twice with 25-mL portions of saturated NaCl and centrifuged. The washings were combined with extract C and brought to volume.

# **3.9.4 REDUCTANT SOLUBLE PHOSPHATE**

A 20 mL volume of 0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>•2H<sub>2</sub>O and 5 mL of 1 M NaHCO<sub>3</sub>was added to the residue, and the suspension was heated for 15 min in a water bath at 85°C. A 1.0 g mass of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (sodium dithionate) was added and stirred rapidly to extract reductant-soluble P. The heating was continued for 15 min and then centrifuged. The supernatant solution was decanted into a 50-mL volumetric flask (extract D).

The soil was washed twice with 25-mL portions of saturated NaCl and centrifuged. The washings were combined with extract D, and diluted to volume. Extract D was exposed to air to oxidize  $Na_2S_2O_4$ .

## **3.9.5 CALCIUM BOUND PHOSPHATE**

A 25 ml volume of 0.25 M  $H_2SO_4$  was added to the soil residue and shaken for 1 hr. The suspension was centrifuged for 10 min and the supernatant was decanted into a 50-mL volumetric flask (extract E). The soil was washed twice with 25-mL portions of saturated NaCl, and centrifuged. The washings were combined with the extract E and diluted to volume.

# **3.10 ANALYZING THE EXTRACTED P FRACTIONS**

Aliquot containing 2 to 40 µg P were transferred from each of extracts A, B, C, D, and E to separate 50-mL volumetric flasks. Five to ten mL deionized water and five drops of p-nitrophenol indicator was added to the volumetric flasks containing extracts C and E, and the pH was adjusted with 2 M HCl or 2 M NaOH until the indicator colour just changed. The indicator colour changes from yellow to colourless for extract C, and from colourless to yellow for extract E.

A 15 mL volume of 0.8 M H<sub>3</sub>BO<sub>3</sub> was added to the volumetric flask containing extract B. Phosphorus concentrations in the various solutions were determined using the phospho-molybdate method (Murphy and Riley, 1962). The heteropoly blue colour was developed by adding 4 mL of the reagent B to the suitable aliquotes, the contents of the flask were mixed well, and the volume was diluted to 50 ml mark with deionized water, and mixed thoroughly. The absorbances were measured at 880 nm, when the maximum colour intensity developed in 10 min, and the colour was stable for 24 hours.

### **3.10.1 CALCULATIONS**

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

P concentration in given fraction (mg kg-1) =

[Conc. of P (mg  $L^{-1}$ ) x Volume of extractant (L)]  $\div$  mass of soil (kg)

# **3.11 CALIBRATION CURVE**

Calibration curve was prepared by taking 0 ml, 2 ml, 4 ml, 8 ml, 10 ml and 12 ml of 2 ppm phosphate standard solution into 25 ml volumetric flask. A 4 ml volume of reagent B was added to each standard and diluted to volume. The absorbances were measured at 882 nm. The concentration of phosphorus was extrapolated from the calibration curve.

## **3.12 PROCEDURE FOR DETERMINING TOTAL PHOSPHORUS**

In a 50 mL digestion tube, 1.0 g of finely ground soil (<0.5 mm) was mixed with 15 mL of 70% HClO<sub>4</sub>. The contents of the flask were digested on a preheated sand bath on a hot plate at 130°C in a well-ventilated, perchloric acid hood until the dark colour from organic matter disappears. The heating at 203°C continued for 20 min.

Heavy white fumes appeared, and the insoluble material became like white sand. When digestion was complete, the mixture was cooled before bringing the volume to 50 mL with deionized water. The contents of the flask were mixed, and the sediment was then allowed to settle.

To analyze for total P, the aliquot was transferred into a 50-mL volumetric flask (for samples containing 2 to 40  $\mu$ g P). Five drops of *p*-nitrophenol indicator was added, the contents of the flask mixed, and the pH of the solution was adjusted (colour changes from colourless to yellow) by adding dropwise 5 M NaOH.

The heteropoly blue colour was developed by adding 4 mL of the reagent B, the contents of the flask were mixed well, the volume was brought to 50 mL with deionized water,

and mixed thoroughly. The absorbance was measured at 880 nm; when the maximum colour intensity developed in 10 min, and the colour was stable for 24 hours.

### **3.12.1 CALCULATIONS**

Total P, mg/kg =

[Concentration of P in initial 250 mL dilution, mg  $L^{-1}$ ] x [0.25 ÷ mass of soil, kg]

#### **3.13 PARTICLE SIZE ANALYSIS**

A 51 g mass of soil sample was weighed into a 'milkshake' mixed cup. To this 50.0 ml of 10 % sodium hexaminephosphate along with 100 ml distilled water were added. The mixture was shaken for 15 minutes after the suspension was transferred from the cup into 1000 ml measuring cylinder. With a hydrometer in the suspension, distilled water was added to reach the 1000 ml mark. The mixture was inverted several times until the soil was in suspension. The cylinder was placed on a flat surface and time was noted. Immediately the soil hydrometer was placed into the suspension and the first reading on the hydrometer was taken at 40 seconds. The temperature of the suspension was allowed to stand for three hours and the second hydrometer and temperature reading were taken. The first reading indicates the percentage of sand and second reading indicates the percentage of clay. The percentage silt was determined by the difference.

# **3.13.1 CALCULATIONS**

% SAND = 100- [H1 + 0.2 (T1- 20) – 2.0]  $\times$  2

%CLAY = [H2 + 0.2 (T2 - 20) - 2.0]  $\times$  2

%SILT = 100 - (% sand + % clay)

H1= Hydrometer reading at 40 seconds

T1 = Temperature reading at 40 seconds

- H2 = Hydrometer reading at 3 hours
- T2 = temperature reading at 3 hours
- 0.2(T 20) = Temperature correction to be added to hydrometer reading
- -2.0 = Salt correction to be added to hydrometer reading

#### **CHAPTER FOUR**

#### **RESULTS AND DISCUSSION**

Proper understanding of the distribution of the different forms of P and their relations with soil physico-chemical properties will give a greater insight into the dynamics of P in the soil. This study was conducted to ascertain the dynamics of phosphorus in the soil. A total of thirty six soil samples were obtained from three sites in Eastern Region of Ghana. The sample sites were cocoa farm in Akwadum (AC), cultivated soil in Huhunya (HC) and Huhunya virgin soil (HV). The soil sample depths comprising top soil (0-10 cm), subsurface soil (10-20 cm) and subsoil (20-30 cm) were taken from four locations on each sample site. The fractionation of soil phosphorus and total phosphorus as well as soil physico-chemical parameters (pH, % organic carbon, electrical conductivity and soil particle size) were measured.

### 4.1 Soil physical and chemical properties

Results for all soil physicochemical properties are presented in Table 4.1. Particle size analysis indicated that the soil samples obtained from fertilized Akwadum cultivated soils and Huhunya unfertilized cultivated and virgin soils were sand, clay and silt with most of the soil being sandy. All the soils were classified as sandy, clay and loamy. The low level of organic carbon in soils observed in this study may be attributed to low vegetative cover, poor farming practices and the annual bush fires which destroy the accumulated plant debris and organic matter.

There was no significant difference between the values of the soil pH across all the sites. The higher values of electrical conductivity in Akwadum fertilized cultivated soils is as a result of minerals added to the soils due to fertilizer application.

SAMPLE	DEPTH/cm	pН	EC (mS/min)	% OC	SAND (%)	SILT(%)	CLAY(%)	SOIL TYPE
	(0-10)	6.93	83.75	1.10	82.38	13.23	4.40	LOAMY SAND
	(10-20)	6.79	56.75	0.76	83.88	11.73	4.43	LOAMY SAND
НС	(20-30)	6.75	52.00	0.63	84.80	9.80	5.40	LOAMY SAND
	(0-10)	7.59	123.50	1.88	69.10	8.35	22.55	SANDY CLAY LOAMY
	(10-20)	7.55	80.25	1.09	75.00	4.88	20.13	SANDY CLAY LOAMY
AC	(20-30)	7.53	73.75	1.12	72.53	4.48	23.00	SANDY CLAY LOAMY
	(0-10)	7.52	72.25	1.47	84.38	7.38	7.35	LOAMY SAND
	(10-20)	7.49	43.75	1.66	82.30	8.85	8.80	LOAMY SAND
HV	(20-30)	7.51	42.00	1.48	83.35	6.88	9.80	LOAMY SAND

Table 4.1: Soil physical and chemical properties.

# 4.2 Inorganic phosphorus fractions and total phosphorus

Phosphorus fractionations and total-P data for Huhunya unfertilized cultivated soil samples, Akwadum fertilized cultivated soil samples and Huhunya virgin soil samples are presented in table 4.2. The P fractions obtained in this study were P-Al, Fe-P and Ca-P. Overall, Ca-P concentrations were higher for all the samples. The dominance of Ca-bound fractions is likely due to the minimal weathering of P-bearing minerals (apatite and basalt).

SAMPLE	DEPTH/cm	tot-P (µg/g)	Al-P (µg/g)	Fe-P (µg/g)	Ca-P (µg/g)
	(0-10)	13.08	2.90	3.04	6.19
	(10-20)	11.60	2.31	2.29	6.87
НС	(20-30)	12.53	2.16	1.90	5.52
	(0-10)	31.82	4.98	5.08	15.75
	(10-20)	28.58	3.86	2.42	21.25
AC	(20-30)	26.70	3.54	3.67	17.87
	(0-10)	15.99	1.88	2.20	11.17
	(10-20)	14.28	3.41	2.23	7.71
HV	(20-30)	13.77	2.94	3.39	6.33

Table 4.2: Amount of inorganic phosphorus fractions and total phosphorus

### 4.3 Physicochemical parameters for virgin and cultivated soil

pH ranged from 6.7 to 7.05 for Huhunya cultivated soils (HC), from 7.33 to 7.90 for Akwadum cultivated soils (AC) and from 7.37 to 7.72 for Huhunya virgin soils (HV) (Table A.11).

The soil pH values obtained in this study for HV soils and AC soils are similar to soil pH obtained by Samadi *et al.* (1998) which was 7.9 in Australian oxisols. In oxisols soil solution forms weak bond with phosphate which implies a decrease in P sorption. Thus AC and HV soils will have more available P than HC due to their high pH values.

Electrical conductivity (EC) ranged from 24 to 135 mS/min for HC soils, from 50 to 143 mS/min for AC soils and from 30 to 82 mS/min for HV soils respectively. Measurement of EC by Mostashari *et al.* (2008) in Iranian soils gave a conductivity value of 20.25 mS/cm which is quite lower than the results of the current studies. Higher values of EC suggest high clay content in the current studies compared to Iranian soils and these results in increase in other soil properties such as cation exchange capacity (CEC), porosity, salinity and medium water holding capacity. Increase in these properties increases yield production because P is available.

Percentage organic carbon (%OC) ranged from 0.50 to 1.19 (mean=  $0.83\pm0.24$ ) for HC soils, from 0.82 to 2.15 (mean=  $1.36\pm0.46$ ) for AC soils and from 0.86 to 1.96 (mean=  $1.53\pm0.34$ ) for HV soils (Table A.11). Results elsewhere show that the mean % OC obtained in twenty eight oxisols in Western Australia range from 8 to 12 (Samadi *et al.*, 1998). The results in this study suggest that the % OC for the selected soils from eastern region is low. The lower % OC might be due to low vegetative cover, poor farming practices and the annual bush fires which destroy the accumulated plant debris and organic matter.

Percentage sand ranged from 80.40 to 86.30 (mean=  $83.68\pm2.10$ ) for HC, from 62.87 to 86.30 (mean=  $72.21\pm6.64$ ) for AC soils and from 72.50 to 90.20 (mean=  $83.36\pm5.60$ ) for HV soils.

Percentage silt ranged from 2.00 to 11.70 (mean=  $5.9\pm2.63$ ) for AC soils, from 9.80 to 15.87 (mean=  $11.58\pm2.42$ ) for HC and from 2.00 to 13.80 (mean=  $7.70\pm3.08$ ) for HV soils respectively.

Percentage clay ranged from 9.80 to 29.40 (mean=  $21.89\pm5.08$ ) for AC soils, from 2.00 to 5.90 (mean=  $4.74\pm1.32$ ) for HC soils and from 3.90 to 15.70 (mean=  $8.65\pm3.49$ ) for HV soils (Table A.11).

The high percentage of sandy soil in all the three sites suggests that total P as well as the various fractions of P are less tightly bound to the soil particle because of small surface area of sandy soil. Also sandy soils are most susceptible to phosphorus leaching and the consequence of phosphorus leaching is the contamination of ground water reserves.

The soil type in all the three sites classified as sandy clay loam suggests the presence of organic matter. Organic matter increases phosphate uptake by plant, displace sorbed phosphate, source of P through mineralization reaction and the humus coats of Al and Fe oxides which reduces P sorption.

## 4.4 P fractions in the soils

Soil P exists in various chemical forms including inorganic P (Pi) and organic P (Po). These P forms differ in their behavior and fate in soils (Hansen *et al.*, 2004; Turner *et al.*, 2007).

Pi usually accounts for 35% to 70% of total P in soil (calculation from Harrison, 1987). Primary P minerals including apatites, strengite, and variscite are very stable, and the release of available P from these minerals by weathering is generally too slow to meet the crop demand though direct application of phosphate rocks (i.e. apatites) has proved relatively efficient for crop growth in acidic soils. In contrast, secondary P minerals including calcium (Ca), iron (Fe), and aluminum (Al) phosphates vary in their dissolution rates, depending on size of mineral particles and soil pH (Pierzynski *et al.*, 2005;Oelkers *et al.*, 2008). With increasing soil pH, solubility of Fe and Al phosphates increase but solubility of Ca phosphate decreases, except for pH values above 8 (Hinsinger, 2001). The P adsorbed on various clays and Al/Fe oxides can be released by desorption reactions. All these P forms exist in complex equilibria with each other, representing from very stable, sparingly available, to plant-available P pools such as labile P and solution P.

Aluminium-P ranged from 1.094 to 8.809  $\mu$ g/g (mean= 2.743  $\mu$ g/g±2.309) for Huhunya virgin soils, from 1.537 to 4.044  $\mu$ g/g (mean= 2.457  $\mu$ g/g±0.780) for Huhunya cultivated soils and from 1.787 to 6.87  $\mu$ g/g (mean= 4.126  $\mu$ g/g±1.881) for Akwadum cultivated soils.

Iron-P ranged from 2.133 to 6.343  $\mu$ g/g (mean= 3.724  $\mu$ g/g±1.475) for Akwadum cultivated soils, from 1.330 to 3.837  $\mu$ g/g (mean= 2.411  $\mu$ g/g±0.869) for Huhunya cultivated soils and from 0.845 to 5.042  $\mu$ g/g (mean= 2.608  $\mu$ g/g±1.196) for Huhunya virgin soils.

Calcium-P ranged from 3.587 to 12.465  $\mu$ g/g (mean= 6.193  $\mu$ g/g±2.304) for Huhunya cultivated soils, from 3.816 to 16.620  $\mu$ g/g (mean= 8.404  $\mu$ g/g±3.723) for Huhunya virgin soils and from 8.740 to 30.512  $\mu$ g/g (mean= 18.289  $\mu$ g/g±7.472) for Akwadum cultivated soils.

Total- P ranged from 8.601 to 19.044  $\mu$ g/g (mean= 12.403  $\mu$ g/g±2.898) for Huhunya cultivated soils, from 17.341 to 44.252  $\mu$ g/g (mean= 29.033  $\mu$ g/g±9.093) for Akwadum cultivated soils and from 9.321 to 22.271  $\mu$ g/g (mean= 14.680  $\mu$ g/g±4.037) for Huhunya virgin soils.

A study by Mostashari *et al.* (2008) on phosphorus fractions of selected soils of Qazvin Province showed that Ca-P which was 21.95  $\mu$ g/g was predominant in the P fractions and their value is higher than the total mean value of Ca-P of 18.29  $\mu$ g/g in this study for all the three sites.

A study on fractionation of inorganic phosphorus in virgin and cultivated soils in the USA also obtained Ca-P with value of 545 mg/kg dominating the remaining fractions (Sharpley *et al.*, 1985). Thus, the values of Ca-P obtained in this study compared to other research works is quite lower which might be due to lower pH of the soils and high amount of clay mineral and Fe/Al oxides. Ca-P in the soil is less soluble at lower pH to which most of the total-P is bound and not released. Clay minerals and Fe/Al oxides have large specific surface areas, which provide large number of adsorption sites, thus their abundance can bind the P and make it unavailable.

#### 4.5 Total-P in the soils

Total phosphorus (Pt) content of soils is of little importance for soil fertility, but it has been used as weathering index to differentiate between highly weathered and less weathered soils (Walker *et al.*, 1976). It is also used as a check on P balance when soil P is fractionated.

Generally the amount of inorganic total phosphorus decreases with increase in depth of soil, but this was not the case for Huhunya cultivated soils where the subsoil (20-30 cm)

recorded higher amount of 12.53  $\mu$ g/g than sub-surface soil (10-20 cm) with an amount of 11.60  $\mu$ g/g. Furthermore the amount of inorganic total phosphorus in Akwadum cultivated soils were the highest in all the three soil depths (fig 4.1). This might be due to increase in soil nutrient due to frequent fertilizer application to the soil. The amounts of total-P in Huhunya cultivated soils recorded the lowest in all the three soil samples which could be due to erosion, crop removal and precipitation of phosphorus from soil solution which decreases P availability. However the amount of total-P in Huhunya virgin soils recorded the intermediate distribution in all the three soil samples. In general the total P obtained in this study is quite lower than results from other studies and this might be due to lower phosphorus fertilization and difference in climatic condition.



Fig4.1: Total-P distribution in virgin and cultivated soils

# 4.6: Aluminium-P distribution in the soils

All the three depths of soil recorded the high levels of Al-P in Akwadum cultivated soils with the surface soil (0-10 cm) being the highest of the three having 4.976  $\mu$ g/g. But the least amount of Al-P was found in Huhunya virgin surface soil with 1.88  $\mu$ g/g. (Fig 4.2)

Amount of Al-P decreases with increase in depth of soil for Huhunya cultivated soils. Meanwhile the sub-surface soil recorded the highest level of Al-P for the three depths of virgin soils. The higher values of Al-P in AC soils might be due to P sorption by Al oxide. Its presence in the surface soil might be due to minimal leaching given the aridity of the soil. Lower value of Al-P in the virgin soil might be as a result of minimal weathering of P bearing mineral and also this lower concentration might be due to precipitation under higher pH.



Fig 4.2: Aluminium-P distribution in virgin and cultivated soils
#### 4.7: Iron- P distribution in the soils

The distribution of iron-P in both cultivated and virgin soil samples does not follow any pattern with Akwadum surface cultivated soils which recorded highest amount of Fe-P (5.08  $\mu$ g/g) while Huhunya cultivated surface soils recorded the lowest (2.20  $\mu$ g/g). But on the other hand the amount of Fe-P in Huhunya virgin soils decrease with depth of soil (Fig 4.3). A study by Campbell *et al.* (1987) showed that the absence of significant leaching, ions (i.e., Al and Fe) released from rock minerals tend to remain in the surface soil. Thus, the weathering of P containing parent materials can promote the accumulation of secondary mineral precipitates such as Al and Fe phosphates. This thus conforms to the current research.



Fig 4.3: Fe- P distribution in virgin and cultivated soils

#### 4.8: Calcium- P distribution in virgin and cultivated soils

Huhunya cultivated soils showed a pattern of decrease in amount of Ca-P with decrease in the depth of the soil. The other two soils showed no pattern of Ca-P amount with depth of soil. Huhunya virgin subsoil recorded the lowest amount of Ca-P (5.52  $\mu$ g/g) while sub-surface soil in Akwadum recorded the highest (21.25  $\mu$ g/g) (Fig 4.4).

The high value of Ca-P in sub-surface soil might be due to the presence of significant leaching given the aridity of the soil and also this might be due to the absence of chemical weathering.



Fig 4.4: Calcium- P distribution in virgin and cultivated soils

#### 4.9: Inorganic phosphorus fractions in Huhunya unfertilized cultivated soils

Ca-P has dominated P fraction in all the three soil depths of Huhunya cultivated soil samples with a total amount of 18.58  $\mu$ g/g with Al-P constituting 7.57  $\mu$ g/g while the total amount of Fe-P in all the three soil depths recorded the lowest 7.23  $\mu$ g/g (Fig 4.5). There was no significant difference in terms of total amount between Al-P and Fe-P. Total fraction of P decreases with increase in soil depth. Many studies performed on calcareous soils have shown that P behaviour is controlled mainly by the presence of small amounts of iron or aluminum oxides. For example, Ryan *et al.* (1985) showed that P sorption in 20 Lebanese most commonly calcareous soils was related to oxalate-extractable Fe, i.e. amorphous forms of iron oxides.

The percentage of inorganic P fractions obtained by the various extractants in Huhunya unfertilized cultivated soil when added together is not equal to the total P determined by the perchloric acid digestion. However the total percentage of the fractions is always quite close to 100 % and is reasonably consistent for the various depths of soil. Soil depth HC2 was the closest which recorded 97.50 % while HC3 was the least with 81.73 %. Ca-P had the highest percentage of 57.64 % while Fe-P recorded the lowest of 16.73 % in all the depths (Fig 4.6). For all depths the average values of P fractions when expressed as a percentage of total P deceases in the order:

Ca-P (50.27 %) > Al-P (20.43 %) > Fe-P (20.02 %).



Fig 4.5: P fractions in Huhunya cultivated soils



Fig 4.6: Distribution of P fractions as a % total-P in Huhunya cultivated soils

#### 4.10: Inorganic phosphorus fractions in Akwadum fertilized cultivated soils

Ca-P has dominated P fraction in all the three soil depths of Akwadum cultivated soil samples with a total amount of 54.868  $\mu$ g/g. Al-P constituted 12.38  $\mu$ g/g while the total amount of Fe-P in all the three soil depths recorded the lowest of 11.17  $\mu$ g/g (Fig 4.7). There was no significant difference in terms of total amount between Al-P and Fe-P. Total fraction of P does not show any pattern with increase in soil depth.

A study by Acquaye *et al.* (1989) in the savannah zone of Ghana showed that Ca-P constituted 75 % of the inorganic P fractions and Ca being the predominant cation on the exchange complex of that soil means most of the fertilizer P was transformed into Ca-P. The percentage of Ca-P is high compared to the current studies.

Generally, the total inorganic P factions as a percentage of total P in Akwadum fertilized cultivated soil is reasonably close to 100 % considering the various soil depths involved. AC2 dominated the closeness with a total percentage of 95.50 %, AC1 recorded the least with a total percentage of 82.48 %. (Fig 4.8)

Considering the percentage of P fractions in all the three soil depths Ca-P (72.52 %) recorded the highest while Fe-P (9.07 %) had the lowest. The average values of P fractions when expressed as a percentage of total P in various soil depth deceases in the order:

Ca-P (62.29 %) > Al-P (14.07 %) > Fe-P (13.86 %)



Fig 4.7: P fractions in Akwadum cultivated soils



Fig 4.8: Distribution of P fractions as a % total-P in Akwadum cultivated soils

#### 4.11: Inorganic phosphorus fractions in Huhunya virgin soils

Ca-P has dominated P fraction in all the three soil depths of Huhunya cultivated soil samples with a total amount of 25.21  $\mu$ g/g which constitute 61.10 %. Al-P constituted 19.94 % representing 8.23  $\mu$ g/g while the total amount of Fe-P in all the three soil depths recorded the lowest 7.83 $\mu$ g/g constituting 18.96 % (Fig 4.9). There was no significant difference in terms of total amount between Al-P and Fe-P. There was a slight decrease in total fraction of P with increase in soil depth. Similar trend of Ca-P dominance was shown in research conducted by Sharpley et al. (1985) in unfertilized cultivated soils. Samadi *et al.* (1998) demonstrated that Al-P and Fe-P were amongst the most important forms of P in virgin and fertilized cultivated soils from Western Australia.

All the soil depth in Huhunya Virgin soil have total inorganic P fractions expressed as percentage of total P reasonably close to 100%.

The closeness to 100 % was dominated by soil depth HV1 (95.44 %) with HV2 (93.01 %) being the least. On the other hand Ca-P (69.11 %) was the highest of the P fractions while Al-P was the lowest (12.26 %) at all the soil depths (Fig 4.10).For all depths the average values of P fractions when expressed as a percentage of total P deceases in the order:

Ca-P(57.53 %) > Al-P(18.68 %) > Fe-P(18.15 %)



Fig 4.9: P fractions in Huhunya virgin soils



Fig 4.10: Distribution of P fractions as a % total-P in Huhunya virgin soils

#### 4.12: Distribution of P fractions as a Percentage total-P in various sample locations

Ca-P (62.29 %) in Akwadum cultivated soils dominated the P fractions in all the sample locations with Fe-P (13.86 %) in Akwadum cultivated soils being the least. Generally all the sample locations had total inorganic P fractions expressed as percentage of total P reasonably close to 100% and they increase in the order:

AC (90.22 %) < HP (90.72 %) < HV (94.36 %)

The average values of P fractions at all the sample locations when expressed as a % of total P deceases in the order:

Ca-P (56.69 %) > Al-P (17.73 %) > Fe-P (17.35 %)

#### 4.13: Correlation Analysis

Pearson's correlation was used to determine any correlation between P fractions and soil physicochemical parameters for each site. The results are presented in tables 4.3 to 4.5.

# 4.13.1: Pearson's correlation between phosphorus fractions and physicochemical properties (Huhunya cultivated soils)

The results of correlation studies on Huhunya cultivated soils showed a positive significant correlation of Al-P with Fe-P (r= 0.669), with pH (r= 0.766) and with electrical conductivity (r= 0.799).

Also, pH showed positive correlation with Fe-P (r= 0.656), with electrical conductivity (r= 0.909) and with percentage organic carbon (r= 0.806).

Electrical conductivity correlated positively with percentage organic carbon (r= 0.650) and lastly, percentage organic carbon correlated positively with silt % (r= 0.727). There

was, however a negative significant correlation between silt % and sand % (r= -0.839). (Table 4.3)

Correlation studies above showed that pH and the other physicochemical parameters influence the formation of Al-P and Fe-P fractions of P. Also the correlation between Al-P and Fe-P might be due to the increase in chemical weathering of P containing parent materials which will precipitate Al and Fe.

	Variables									
			Fe-P			E.C				
	tot-P µg/g	Al-P µg/g	Hµg/g	Ca-P µg/g	pН	mS/cm	% OC	sand%	silt%	clay%
tot-P µg/g	1	0.112	0.083	0.508	0.104	-0.169	0.087	-0.263	0.128	0.186
Al-P µg/g	0.112	1	0.669*	-0.075	0.766**	0.799**	0.467	0.018	0.057	-0.133
$Fe\text{-}P\;\mu g/g$	0.083	0.669*	1	-0.165	0.656*	0.500	0.434	-0.252	0.224	-0.009
Ca-P µg/g	0.508	-0.075	-0.165	1	-0.033	-0.124	0.055	-0.433	0.254	0.225
рН	0.104	0.766**	0.656*	-0.033	1	0.909**	0.806**	-0.240	0.361	-0.280
E.C mS/cm	-0.169	0.799**	0.500	-0.124	0.909**	1	$0.650^{*}$	-0.093	0.237	-0.286
% OC	0.087	0.467	0.434	0.055	0.806**	0.650*	1	-0.504	0.727***	-0.530
sand%	-0.263	0.018	-0.252	-0.433	-0.240	-0.093	-0.504	1	-0.839***	-0.055
silt%	0.128	0.057	0.224	0.254	0.361	0.237	0.727**	-0.839**	1	-0.497
clay%	0.186	-0.133	-0.009	0.225	-0.280	-0.286	-0.530	-0.055	-0.497	1

 Table 4.3: Pearson's correlation between phosphorus fractions and physicochemical properties and the fractions (Huhunya)

\*. Correlation is significant at the 0.05 level.

\*\*. Correlation is significant at the 0.01 level.

a. Listwise N=12

## 4.13.2: Pearson's correlation between phosphorus fractions and physicochemical properties ( Akwadum soils)

The results of correlation studies on Akwadum cultivated soils showed a positive significant correlation of total-P with Al-P (r=0.834), with Ca-P (r=0.828), with pH (r=0.770), with electrical conductivity (r=0.792) and with percentage organic carbon (r=0.605). Al-P showed positive significant correlation with pH (r=0.819), with electrical conductivity (r=0.867) and with % organic carbon (r=0.601) and it showed a negative significant correlation with % clay (r=-0.578). Ca-P correlated significantly with pH (r=0.639). The pH showed positive correlation with electrical conductivity (r=0.672), with % sand (r=0.699) and negative significant correlation with % clay (r=-0.771). (Table 4.4)

Electrical conductivity showed significant positive correlation with % organic carbon (r=0.813). Percentage organic carbon showed significant positive correlation with Fe-P (r=0.599) and with % silt (r=0.616). Percentage sand showed negative correlation with % silt (r=-0.721) and with % clay (r=0.933).

The correlation studies showed that Al and Ca fractions of the total-P contribute significantly to P uptake by plants. Also the physicochemical parameters have significant effects on the total-P and P fractions concentrations. The effect of silt on Fe-P might be due to chemical weathering of P bearing Fe mineral.

		Al-P	Fe-P	Ca-P		E.C				
	tot-P µg/g	µg/g	µg/g	µg/g	pН	mS/cm	% OC	sand%	silt%	clay%
tot-P µg/g	1	0.834**	0.002	0.828**	$0.770^{**}$	0.792**	$0.605^{*}$	0.365	-0.029	-0.462
Al-P µg/g	0.834**	1	0.153	0.526	0.819**	0.867**	0.601*	0.418	0.063	$-0.578^{*}$
Fe-P µg/g	0.002	0.153	1	-0.310	-0.188	0.457	$0.599^{*}$	-0.449	$0.675^{*}$	0.237
Ca-P µg/g	$0.828^{**}$	0.526	-0.310	1	0.639*	0.455	0.137	0.557	-0.345	-0.550
рН	$0.770^{**}$	0.819**	-0.188	0.639*	1	$0.672^{*}$	0.283	0.699*	-0.275	-0.771**
E.C mS/cm	$0.792^{**}$	$0.867^{**}$	0.457	0.455	$0.672^{*}$	1	0.813***	0.211	0.375	-0.470
% OC	$0.605^{*}$	$0.601^*$	$0.599^{*}$	0.137	0.283	0.813**	1	-0.274	$0.616^{*}$	0.039
sand%	0.365	0.418	-0.449	0.557	0.699*	0.211	-0.274	1	-0.721**	-0.933**
silt%	-0.029	0.063	$0.675^{*}$	-0.345	-0.275	0.375	$0.616^{*}$	-0.721**	1	0.424
clay%	-0.462	$-0.578^{*}$	0.237	-0.550	-0.771**	-0.470	0.039	-0.933**	0.424	1

Table 4.4:Pearson's correlation between phosphorus fractions and physicochemical properties and the fractions (Akwadum soils)

\*\*. Correlation is significant at the 0.01 level.

\*. Correlation is significant at the 0.05 level.

a. Listwise N=12

## 4.13.3: Pearson's correlation between phosphorus fractions and physicochemical

#### (Huhunya Virgin soils)

The results of correlation studies on Huhunya virgin soils showed a positive significant correlation of total-P with Ca-P (r=0.675), with % clay (r=0.632) and negative correlation with % sand (r=-0.697).

Fe-P correlated significantly positive with % clay (r=0.616). There was also a significant positive correlation of Ca-P with electrical conductivity (r=0.639) and Ca-P also correlated significantly negative with % sand (r=-0.592). Percentage sand correlated significantly negative with % silt (r=-0.782) and with % clay (r=-0.808). (Table 4.5)

The correlation studies showed that Ca fractions of the total-P contribute significantly to P uptake by plants. Physicochemical parameters like electrical conductivity contribute significantly to Ca-P concentration and also influence of clay on Fe-P might be due to the adsorption of high amount of Fe-P by clay which has a large surface area.

		Al-P	Fe-P	Ca-P						
	tot-P $\mu g/g$	µg/g	µg/g	µg/g	рН	E.C mS/cm	% O C	sand%	silt%	clay%
tot-P µg/g	1	0.227	0.379	0.675*	-0.363	0.379	0.506	-0.697*	0.352	0.632*
Al-P µg/g	0.227	1	-0.135	-0.384	-0.214	-0.202	0.254	0.165	-0.052	-0.169
Fe-P µg/g	0.379	-0.135	1	-0.026	-0.309	-0.315	0.056	-0.557	0.291	0.616 <sup>*</sup>
Ca-P µg/g	$0.675^{*}$	-0.384	-0.026	1	-0.129	0.639*	0.262	-0.592*	0.295	0.482
рН	-0.363	-0.214	-0.309	-0.129	1	0.337	-0.436	0.371	-0.145	-0.428
E.C mS/cm	0.379	-0.202	-0.315	0.639*	0.337	1	0.024	0.059	-0.082	-0.192
% O C	0.506	0.254	0.056	0.262	-0.436	0.024	1	-0.278	-0.122	0.455
sand%	-0.697*	0.165	-0.557	-0.592*	0.371	0.059	-0.278	1	-0.742**	-0.808**
silt%	0.352	-0.052	0.291	0.295	-0.145	-0.082	-0.122	-0.742**	1	0.244
clay%	0.632*	-0.169	0.616*	0.482	-0.428	-0.192	0.455	-0.808**	0.244	1

 Table 4.5: Pearson's correlation between phosphorus fractions and physicochemical properties and the fractions (Huhunya Virgin soils)

\*. Correlation is significant at the 0.05 level.

\*\*. Correlation is significant at the 0.01 level.

a. Listwise N=12

#### **CHAPTER FIVE**

#### **CONCLUSIONS AND RECOMMENDATION**

#### **5.1 CONCLUSION**

The following conclusions may be deduced from the study.

The fractions of phosphorus present in the soil samples were aluminium- phosphate (Al-P), iron phosphate (Fe-P) and calcium phosphate (Ca-P). Inorganic phosphorus content in the soil samples are very low in this study compared to soils from elsewhere in the world. It was also found out from the study that P fractions in Akwadum soils are higher than those of Huhunya soils which may be due to fertilizer application in the former.

From correlation studies, significant correlation was observed between the P forms and soil characteristics which is presumably a reflection of the existence of a dynamic relation between the chemical forms of an element in soil and physicochemical parameters. Dependency of P forms on soil characteristics can provide insight into proper management of soil.

The study also revealed that level of inorganic P in virgin soils decreases with increase in depth and Ca-P dominated at all the depths. Cultivated soils in Huhunya exhibited similar pattern to that of the virgin soil but Akwadum cultivated soils did not follow any pattern in terms of soil depth, though, Ca-P dominate at all the depths while Fe-P recorded lowest amount in all the three sites.

The trend for P fractions at the sample sites are as follows:

Huhunya unfertilized cultivated soil: Ca-P > Al-P > Fe-P,

Huhunya virgin soil: Ca-P > Al-P > Fe-P and

Akwadum fertilized cultivated soil: Ca-P > Al-P > Fe-P.

## RECOMMENDATION

In future works, fractionation should involve organic phosphate determination in order to provide adequate understanding of P status in the soils.

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## APPENDICES

## APPENDIX A

## **CALIBRATION CURVE**



### **APPENDIX B**

## TABLES OF VALUES OF PHYSICOCHEMICAL PARAMETERS AND AMOUNTS OF P FRACTIONS

## Table B.1: Some physicochemical properties of soil samplesfromHuhunyacultivated soils

Soil	Donth (orm)	Sampled areas per site					
parameters	Depin(cm)	1	2	3	4		
	HC1(0-10)	6.92	7.05	6.80	6.94		
pH	HC2(10-20)	6.83	6.76	6.76	6.82		
	HC3(20-30)	6.78	6.70	6.75	6.78		
ELECTRICAL	HC1(0-10)	67	135	48	85		
CONDUCTIVITY	HC2(10-20)	79	55	32	61		
	HC3(20-30)	60	76	24	48		
PERCENTAGE	HC1(0-10)	1.19	1.06	0.98	1.15		
ORGANIC CARBON	HC2(10-20)	0.98	0.69	0.65	0.70		
	HC3(20-30)	0.57	0.50	0.58	0.87		
% SAND	HC1(0-10)	80.40	86.30	82.40	80.40		
	HC2(10-20)	82.40	84.30	86.40	82.40		
	HC3(20-30)	84.30	84.30	84.30	86.30		
% SILT	HC1(0-10)	15.70	9.80	13.70	13.70		
	HC2(10-20)	15.60	9.80	9.80	11.70		
	HC3(20-30)	9.80	9.80	9.80	9.80		
% CLAY	HC1(0-10)	3.90	3.90	3.90	5.90		
	HC2(10-20)	2.00	5.90	3.90	5.90		
	HC3(20-30)	5.90	5.90	5.90	3.90		
SOIL TYPE	HC1(0-10)	LOAMY SAND	LOAMY SAND	LOAMY SAND	LOAMY SAND		
	H2(10-20)	LOAMY	LOAMY	LOAMY	LOAMY		
	LIC2(20, 20)	SAND	SAND	SAND	SAND		
	ПС3(20-30)	SAND	SAND	SAND	SAND		

Soil		Sampled areas per site					
physicochemical	Depth(cm)						
parameters		1	2	3	4		
рН	AC1(0-10)	7.56	7.81	7.47	7.53		
P	AC2(10-20)	7.47	7.86	7.41	7.45		
	AC3(20-30)	7.53	7.90	7.33	7.35		
ELECTRICAL	AC1(0-10)	84	135	132	143		
	AC2(10-20)	65	120	67	69		
	AC3(20-30)	50	130	60	55		
PERCENTAGE	AC1(0-10)	1.29	2.15	2.10	1.99		
CARBON	AC2(10-20)	0.82	1.16	1.29	1.08		
	AC3(20-30)	1.01	1.34	1.00	1.13		
% SAND	AC1(0-10)	72.50	68.60	68.60	66.70		
	AC2(10-20)	72.50	86.30	66.70	74.50		
	AC3(20-30)	72.50	82.40	62.70	72.50		
% SILT	AC1(0-10)	5.90	7.90	7.90	11.70		
	AC2(10-20)	5.90	3.90	5.80	3.90		
	AC3(20-30)	4.00	2.00	7.90	4.00		
% CLAY	AC1(0-10)	21.60	23.50	23.50	21.60		
	AC2(10-20)	21.60	9.80	27.50	21.60		
	AC3(20-30)	23.50	15.60	29.40	23.50		
SOIL TYPE	AC1(0-10)	SANDY CLAY LOAMY	SANDY CLAY LOAMY	SANDY CLAY LOAMY	SANDY CLAY LOAMY		
	AC2(10-20)	SANDY CLAY LOAMY	LOAMY SAND	SANDY CLAY LOAMY	SANDY LOAM		
	AC3(20-30)	SANDY CLAY LOAMY	LOAMY SAND	SANDY CLAY LOAMY	SANDY LOAM		

 Table B.2: Some physicochemical properties of soil samples from Akwadum Cultivated

 Soils

 Table B.3: Some physicochemical properties of soil samples from Huhunya Virgin

 Soils

Soil	Denth(cm)	Sampled areas per site						
parameters	Depth(chi)							
P		1	2	3	4			
pН	HV1(0-10)	7.72	7.44	7.46	7.44			
	HV2(10-20)	7.64	7.49	7.47	7.37			
	HV3(20-30)	7.63	7.53	7.49	7.37			
ELECTRICAL CONDUCTIVITY	HV1 (0-10)	75	72	82	60			
	HV2(10-20)	49	48	46	32			
	HV3(20-30)	46	48	44	30			
PERCENTAGE ORGANIC	HV1(0-10)	1.16	1.96	1.89	0.86			
CARBON	HV2(10-20)	1.48	1.69	1.75	1.73			
	HV3(20-30)	1.07	1.70	1.63	1.51			
% SAND	HV1(0-10)	88.20	90.20	74.80	84.30			
	HV2(10-20)	90.00	84.30	72.50	82.40			
	HV3(20-30)	84.30	86.30	78.50	84.30			
% SILT	HV1(0-10)	7.90	2.00	9.80	9.80			
	HV2(10-20)	3.90	7.90	13.80	9.80			
	HV3(20-30)	7.90	7.80	5.90	5.90			
% CLAY	HV1(0-10)	3.90	7.80	11.80	5.90			
	HV2(10-20)	5.90	7.80	13.70	7.80			
	HV3(20-30)	7.80	5.90	15.70	9.80			
SOIL TYPE	HV1(0-10)	LOAMY SAND	LOAMY SAND	LOAMY SAND	LOAMY SAND			
	HV2(10-20)	LOAMY	LOAMY	LOAMY	LOAMY			
	HV3(20-30)	LOAMY SAND	LOAMY SAND	LOAMY SAND	LOAMY SAND			

Sample(depth/cm)	tot-P µg/g	Al-P μg/g	Fe-P μg/g	Ca-P µg/g
<b>HC1</b> (0-10)	11.981	1.842	3.158	6.094
HC2(10-20)	11.011	2.715	1.939	5.526
HC3(20-30)	10.416	2.576	2.950	3.587
<b>HC1</b> (0-10)	11.565	4.044	3.296	4.197
HC2(10-20)	8.601	1.537	1.454	5.277
HC3(20-30)	9.086	1.870	1.690	5.443
<b>HC1</b> (0-10)	13.920	1.898	1.884	7.521
HC2(10-20)	11.787	2.424	3.366	4.224
HC3(20-30)	19.044	1.870	1.620	6.565
<b>HC1</b> (0-10)	14.861	3.809	3.837	6.939
HC2(10-20)	14.986	2.576	2.410	12.465
HC3(20-30)	11.579	2.327	1.330	6.482
	Sample(depth/cm)         HC1(0-10)         HC2(10-20)         HC3(20-30)         HC1(0-10)         HC3(20-30)         HC1(0-10)         HC2(10-20)         HC2(10-20)         HC2(10-20)         HC2(10-20)         HC3(20-30)         HC3(20-30)         HC3(20-30)         HC1(0-10)         HC2(10-20)         HC3(20-30)	Sample(depth/cm)tot-P μg/gHC1(0-10)11.981HC2(10-20)11.011HC3(20-30)10.416HC1(0-10)11.565HC2(10-20)8.601HC3(20-30)9.086HC1(0-10)13.920HC2(10-20)11.787HC3(20-30)19.044HC1(0-10)14.861HC2(10-20)14.986HC3(20-30)11.579	Sample(depth/cm)tot-P μg/gAl-P μg/gHC1(0-10)11.9811.842HC2(10-20)11.0112.715HC3(20-30)10.4162.576HC1(0-10)11.5654.044HC2(10-20)8.6011.537HC3(20-30)9.0861.870HC1(0-10)13.9201.898HC2(10-20)11.7872.424HC3(20-30)19.0441.870HC1(0-10)14.8613.809HC2(10-20)14.9862.576HC3(20-30)11.5792.327	Sample(depth/cm)tot-P μg/gAI-P μg/gFe-P μg/gHC1(0-10)11.9811.8423.158HC2(10-20)11.0112.7151.939HC3(20-30)10.4162.5762.950HC1(0-10)11.5654.0443.296HC2(10-20)8.6011.5371.454HC3(20-30)9.0861.8701.690HC1(0-10)13.9201.8981.884HC2(10-20)11.7872.4243.366HC3(20-30)19.0441.8701.620HC1(0-10)14.8613.8093.837HC2(10-20)14.9862.5762.410HC3(20-30)11.5792.3271.330

Table B.4: Phosphorus fractionation of cultivated soil samples from Huhunya,Eastern Region
Site	Sample(depth/cm)	%Al-P	%Fe-P	%Ca-P
1	HC1(0-10)	16.60	28.47	54.93
1	HC2(10-20)	26.67	19.05	54.28
1	HC3(20-30)	28.27	32.37	39.36
2	HC1(0-10)	35.05	28.57	36.28
2	HC2(10-20)	18.59	17.59	63.82
2	HC3(20-30)	20.77	18.77	60.46
3	HC1(0-10)	16.79	16.67	66.54
3	HC2(10-20)	24.21	33.61	42.18
3	HC3(20-30)	18.60	16.11	65.29
4	HC1(0-10)	26.12	26.31	47.18
4	HC2(10-20)	14.76	13.81	71.43
4	HC3(20-30)	22.95	13.12	63.93

 Table B.5: Percentage Phosphorus fractions of Huhunya cultivated soils

Site	Sample	tot-P µg/g	Al-P µg/g	Fe-P µg/g	Ca-P µg/g
1	AC1(0-10)	20.097	2.562	4.765	9.903
1	AC2(10-20)	17.341	3.560	2.202	10.125
1	AC3(20-30)	19.488	3.366	2.936	8.740
2	AC1(0-10)	44.252	6.454	2.964	22.978
2	AC2(10-20)	39.058	6.496	2.493	30.000
2	AC3(20-30)	42.050	6.704	3.643	30.512
3	AC1(0-10)	32.853	6.191	6.343	13.269
3	AC2(10-20)	30.083	3.158	2.867	23.435
3	AC3(20-30)	22.479	2.313	4.792	14.654
4	AC1(0-10)	30.069	4.695	6.247	16.856
4	AC2(10-20)	27.853	2.230	2.133	21.440
4	AC3(20-30)	22.770	1.787	3.310	17.562

Table B.6: Phosphorus fractionation of cultivated soil samples from Akwadum,Eastern Region

Site	Sample	%Al-P	%Fe-P	%Ca-P
1	AC1(0-10)	12.75	23.71	49.28
1	AC2(10-20)	20.53	12.7	58.39
1	AC3(20-30)	17.27	15.07	44.85
2	AC1(0-10)	14.58	6.7	51.93
2	AC2(10-20)	16.63	6.38	76.81
2	AC3(20-30)	15.94	8.66	72.56
3	AC1(0-10)	18.84	19.31	40.39
3	AC2(10-20)	10.5	9.53	77.9
3	AC3(20-30)	10.29	21.32	65.19
4	AC1(0-10)	15.61	20.78	56.06
4	AC2(10-20)	8.01	7.66	76.98
4	AC3(20-30)	7.85	14.54	77.13

 Table B.7: Percentage Phosphorus fractions of Akwadum cultivated soils

Site	Sample	tot-P µg/g	Al-P μg/g	Fe-P µg/g	Ca-P µg/g
1	HV1(0-10)	11.884	1.122	2.133	7.964
1	HV2(10-20)	9.668	1.094	1.787	5.831
1	HV3(20-30)	9.321	1.177	1.371	7.936
2	HV1(0-10)	14.972	2.562	0.845	11.233
2	HV2(10-20)	17.770	8.809	1.330	7.008
2	HV3(20-30)	15.014	5.803	3.435	3.186
3	HV1(0-10)	22.271	1.496	2.936	16.620
3	HV2(10-20)	18.975	1.150	3.338	13.172
3	HV3(20-30)	18.116	2.133	5.042	8.006
4	HV1(0-10)	14.834	2.341	2.895	8.864
4	HV2(10-20)	10.720	2.590	2.479	4.834
4	HV3(20-30)	12.618	2.645	3.712	6.191

Table B.8: Phosphorus fractionation of virgin soil samples from Huhunya, EasternRegion

Site	Sample	%Al-P	%Fe-P	%Ca-P
1	HV1(0-10)	9.44	17.95	67.01
1	HV2(10-20)	11.32	18.48	60.31
1	HV3(20-30)	12.63	14.71	85.14
2	HV1(0-10)	17.11	5.64	75.03
2	HV2(10-20)	49.57	7.48	39.44
2	HV3(20-30)	38.65	22.88	21.22
3	HV1(0-10)	6.72	13.18	74.63
3	HV2(10-20)	6.06	17.59	69.42
3	HV3(20-30)	11.77	27.83	44.19
4	HV1(0-10)	15.78	19.52	59.75
4	HV2(10-20)	24.16	23.13	45.09
4	HV3(20-30)	20.96	29.42	49.06

 Table B.9: Percentage Phosphorus fractions of Huhunya virgin soils

## Table B.10: RANGE AND MEAN VALUES OF SOIL PROPERTIES

SAMPLE	PHYSICO- CHEMICAL PROPERTIES	RANGE	MEAN
	p H	6.70 - 7.05	$6.82 \pm 0.10$
	EC	24 - 135	$60.83 \pm 29.58$
	OC(%)	0.50 - 1.19	$0.83 \pm 0.24$
НС	SAND(%)	80.40 - 86.30	83.68 ± 2.10
	SILT(%)	9.80 – 15.70	$11.58 \pm 2.42$
	CLAY(%)	2.00 - 5.90	4.74 ± 1.32
	рH	7.33 - 7.90	$7.56 \pm 0.19$
	EC	50 - 143	92.50 ± 36.16
AC	OC(%)	0.82 - 2.15	$1.36 \pm 0.46$
AC	SAND(%)	62.70 - 86.30	72.21 ± 6.64
	SILT(%)	2.00 - 11.70	5.90 ± 2.63
	CLAY(%)	9.80 - 29.40	$21.89 \pm 5.08$
	p H	7.37 – 7.72	$7.50 \pm 0.11$
	EC	30 - 82	52.67 ± 16.37
HV	OC(%)	0.86 - 1.96	$1.53 \pm 0.34$
11 V	SAND(%)	72.50 - 90.20	83.36 ± 5.60
	SILT(%)	2.00 - 13.80	$7.70 \pm 3.08$
	CLAY(%)	3.90 - 15.70	8.65 ± 3.49

## Table B.11: RANGE AND MEAN VALUES OF TOTAL P AND P FRACTIONS

SAMPLE	P TOTAL AND FRACTIONS	RANGE	MEAN
	tot P	8 601 10 044	12 403 + 2 808
	101-1	8.001-19.044	12.403 ± 2.898
	Al-P	1.537 - 4.044	$2.457 \pm 0.780$
	Fe-P	1.330 - 3.837	$2.411 \pm 0.869$
НС	Ca-P	3.587 - 12.465	$6.193 \pm 2.304$
	tot-P	17.341 - 44.252	$29.033 \pm 9.093$
	Al-P	1.787 - 6.704	$4.126 \pm 1.881$
	Fe-P	2.133 - 6.343	$3.724 \pm 1.475$
AC	Ca-P	8.740 - 30.512	$18.289 \pm 7.472$
	tot-P	9.321 - 22.271	$14.680 \pm 4.037$
	Al-P	1.094 - 8.809	$2.743 \pm 2.309$
	Fe-P	0.845 - 5.042	$2.608 \pm 1.196$
HV	Ca-P	3.186 - 16.620	$8.404 \pm 3.723$