The Great Socialist People's Libyan Arab
Jamahiriya

Al-Tahaddy University
Faculty Of Agriculture
Soil and Water Department

Attachment and Release Potential of Phosphorus and Heavy Metals in Relation to Sand Size Fractions of Sandy Soil

A Thesis
Submitted to the Postgraduate Department in
partial Fulfillment of the Requirements for
Master Degree in Soil science

Presented by

Khalifa Sadeag Al-Atrish

Supervised by

ahjoub O.El-Gubbi **Dr.Mohamed A. Alaib**

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كلية الزراعة
قسم التربة والمياه

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بسم الله الرحمن الرحيم

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Dedicated
To
The Everlasting Memory of My Dear Parents
And, To
My brothers, sisters, wife, and, sons who have supported me along the way.

ABSTRACT

As plant absorption of nutrients depends on release of these nutrients from soils, therefore understanding this relationship may improve the precision of these elements diagnosis, fertilization recommendations and evaluation of leaching potential from soils. Association of P and heavy metals with different aggregate-sizes of sandy soils influences availability of these elements. The effects of aggregate-size on attachment and release potential of phosphorus and heavy metal, quantified by dry separating of five fractions (1.00-to 0.50, 0.50- to 0.25, 0.25- to 0.10, 0.10- to 0.05 and, <0.05mm) from fifteen sandy soil samples. Each aggregate-size characterized by phosphate sorption, sequential fractionation of P, total P and heavy metals, water- and Mehlich III-extractable concentrations of P and heavy metals. Variations in aggregate-sizes influence the amount and strength of element binding.

Attachment factor of P and heavy metals increased with decreasing aggregate-sizes, suggesting that P, and heavy metals are readily transported to surface waters through suspended fine particles. Water and Mehlich-III extractability of P and heavy metals from the aggregate-sizes of sandy soils, followed approximately the same manner. The highest extractability was in the 0.50-to 0.25mm size, and the lowest extractability was in the < 0.05mm size, suggesting that the extractability and the release potential of P and heavy metals is increasing as the aggregate-size increased in sandy soils.

P sorption capacity (S_{max}) and binding strength constant (K) of the aggregate sizes of sandy soils (determined by the Langmuir equation) varied greatly and appeared to be related to the aggregate-size and tended to decrease with decreasing surface area of particles. In general, the trend in S_{max} values was (< 0.05mm) > 0.050-to 0.10mm > 0.10-to 0.25mm > 0.25-to0.50mm or 0.5-to 1.00mm. Sorption capacity (S_{max}) of the aggregate-sizes of sandy soils was mainly depends on their contents of clay, Fe, Al and, Ca. These contents were in turn dependent on the surface area of the aggregate-sizes.

Results of P sequential fractionation suggested that the concentrations of all P fractions, influenced significantly with the aggregate-size in the sandy soil samples. Available P associated with sandy soil separates is relatively low and increased with increasing separates-size, and a high proportion of the total P was inorganic, mainly Ca- P of primary origin. The available P fraction extracted by water and $NaHCO_3$ were higher in the 1.00-to 0.50 and, 0.50-to 0.25 mm sizes than that in 0.25-to 0.10, 0.10-to 0.05 and, <0.05 mm. Ca- associated inorganic P extracted by HCl was higher in the 1.00-to 0.50mm and, 0.50-to 0.25 mm than the other sizes. Fe and Al- associated inorganic P fraction extracted by NaOH had the opposite order direction in which increased as particle size decreased.

TABLE OF CONTENTS

LIST OF TABLES

Table *Page*

LIST OF FIGURES

CHAPTER
1
INTRODUCTION

Understanding transport and fate of phosphorus and heavy metals, which arise from a number of industrial, mining and agricultural activities, provide a basis for explaining their capacity to accumulate in agricultural soils and plants that grow on these soils. It is also useful for assessing the potential for these metals to move into groundwater and surface water that can produce adverse effects on human or ecological health. The extent of movement of a metal in the soil system is, intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix.

The retention mechanisms of metals added to soils include sorption\desorption by the solid phase and precipitation in soil solution, these mechanisms correlated with some soil properties as pH, redox potential, surface area, cation exchange capacity, organic mater content, clay content, iron and manganese oxide content, and carbonate content (McLean and Bledsoe., 1992). In addition to soil properties, consideration must be given to the type of metal, its concentration, the presence of competing ions, complexing ligands, the pH and redox potential of the soil-waste matrix.

Puls *et al.*, (1991) reported that, transport of metals might be enhancing by:

1. facilitated transport caused by metal association with mobile colloidal size particles,

2. Formation of metal organic and inorganic complexes that not sorbed to soil solid surfaces,

3. Competition with other constituents of waste, both organic and inorganic, for sorption sites,

4. Availability Decease of surface sites, caused by the presence of a complex waste matrix.

More recently, Zhang *et al.*, (2003) reported that Size differences in sand, silt, and clay aggregates influence the amount and strength of element binding. Attachment of P and heavy metals in various fractions of sandy soils tended to increase with decreasing aggregate-size, suggesting that surface attachment mechanisms control the distribution of these elements among the different aggregate-sizes.

Fine soil fractions are often transport to surface water through runoff, and nutrients and toxic heavy metals or pesticide attached in the fine fractions discharged along with the runoff. This reflects the importantance of the assessment of metal concentration in soil particle–sizes to evaluate the pools of phosphorus and heavy metal in a particular aggregate-size of soil.

Studies have been conducted to the role of this pools in the relation of phosphorus by (He *et al.*, 1995, Wang *et al.*, 2001, Uusitalo *et al.*, 2001) and (Zhang *et al.*, 2003) regarding of both phosphorus and heavy metal in sandy soil aggregate-size fractions.

Particle-size separation, and metal concentrations in different sizes of the soil has been widely used to distinguish pools of different soil organic matter and nutrient quality with several experimental techniques included wet sieving, dry sieving, and physical dispersion (Agbenin and Tiessen., 1995, Wang *et al.*, 2001, Zhang *et al.*, 2003 and Mikha and Rice., 2004).

The chemical composition and behavior of plant nutrients and heavy metals in soil are dependent on chemical properties and composition of the soil matrix. Therefore, the variation of composition in the soil matrix may lead to significant variation of composition and behavior of soil nutrients and heavy metals. The distribution of a specific element in the solid phase can be important for controlling its initial rate of leaching. Elements that attached on particle surfaces will be more readily accessible to the soil solution. Consequently, the elements may leach more rapidly, especially if they are present in water-soluble forms, than elements that, uniformly distributed throughout the whole matrix.

Several microelements not uniformly distributed throughout fossil fuel wastes but attached in the smaller particle-sizes and on the particle surfaces (Eary *et al.*, 1990).

Some others (Anderson *et al.*, 1981, Tiessen and Stewart., 1983, Catroux and Schnitzer., 1987) have reported that a major part of the organic matter in predominantly inorganic soils usually found in the silt- and clay-size fractions. Nitrogen release (mineralization) increases with decreasing particle size (Cameron and Posner., 1979, Catroux and Schnitzer., 1987).

Linquist *et al.*, (1997) studied the role of aggregate-size on the sorption and release of P and they found that P sorption increased as mean aggregate diameter decreased, and P released from the aggregates correlated well with the reactive mass of the aggregates. They concluded that aggregation affects short- and long-term plant P availability. Distributions of P in different forms or in association with different particle-size fractions were, affected by the pedogenic processes, which in turn affect P availability. The association of P with different particle-sizes extensively investigated, but the relationships were far from clear (Agbenin and Tiessen., 1995).

Juo and Ellis (1968) measured Ca-P in clays of Michigan soils and concluded that physical breakdown of particles had probably been more rapid than chemical weathering.

Agbenin and Tiessen (1995) reported the distribution of P forms in different particles size changed with soil types and soil development, in contrast Syers et al., (1969) suggested that Ca-P was the dominant P form in sand and silt fractions.

Zhang *et al.,* (2003) concluded that the size differences in sand, silt, and clay aggregates influence the amount and strength of element binding, where attachment of P and heavy metals in various aggregate-sizes for the sandy soils tended to increase with decreasing aggregate-size. That suggesting, surface attachment mechanisms control the distribution of these elements among the different aggregate-sizes. The percentages of water-extractable and Mehlich-III extractable-P and heavy metals were higher in both the 0.50-to 0.25 and 0.25-to 0.10-mm aggregate-sizes, suggesting that P and heavy metals in these two sizes would be more readily released to surface runoff or leached to ground water. Phosphorus sorption capacity in various aggregate-sizes mainly determined by Al, Fe, and Ca contents. Phosphorus sorption maximum values of the < 0.05-mm size in all the sandy soils were much higher than the other aggregate-sizes. The results from sequential fractionation of P indicate that the 1.00-to 0.50-mm aggregate-size contained a larger percentage of the Ca-bound P, whereas the 0.50-to 0.25, 0.25-to 0.10, and 0.10-to 0.050-mm fractions had higher ratios of available-P forms (H_2O-P and $NaHCO_3$-P) and thus had greater P release potential. In addition, the available-P in the smaller aggregate appears to be more readily to release than in the larger aggregate-size.

Zhang et al., (2003), the wet sieving and dispersion methods may not be suitable for size fractionation to determine labile forms of elements. This is particularly evident for sandy soils, since sandy soils have low retention capacity for nutrients.

The objectives of this study were:

(i) Comparison of the aggregate-size distribution in two different soils (sandy and clay loam soils)

(ii) Evaluation of P and heavy metals status and distribution in various aggregate-sizes

(iii) Evaluation of the adsorption capacity of P in soil samples and in different aggregate-sizes; and

(iv) Fractionation of phosphorus associated with aggregate-sizes of sandy soil.

CHAPTER

2

LITREATURE REVIEW

2.1 Classifying and naming of soil fractions

Soil particles are the discrete units comprise the solid phase of the soil. They generally cluster together as aggregates but can be separated from one another by chemical and mechanical means. The particles have diverse composition and structure, and generally differ from one another in both size and shape. They may be organic or inorganic, crystalline or amorphous.

Table 2.1 presenting the scheme used by the U.S. Department of Agriculture for classifying and naming of different Size limits of soil separates (Day, 1965).

Since various sizes of particles have quite different characteristics, the nature of mineral soils is determined to a remarkable degree by the particular separate that is present in larger amounts. Thus, a soil possessing a large amount of clay has quite different properties from one made up mostly of sand and/or silt.

Mineral soils (that is, those soils consisting mainly of rock and mineral fragments, rather than plant remains and other accumulated organic materials) are a mixture of soil separates, and it is on the basis of the proportion of these various separates that the textural class names of soils are determined (Day, 1965).

(Table 2.1) **Size limits (diameter in millimeters) of soil separates in the USDA soil textural classification system.**

Name of soil separate	Diameter limits (mm)
Very coarse sand *	2.00 - 1.00
Coarse sand	1.00 - 0.50
Medium sand	0.5 - 0.25
Fine sand	0.25 - 0.10
Very fine sand	0.10 - 0.05
Silt	0.05 - 0.002
Clay	Less than 0.002

* The sand separate is split into five sizes (Very coarse sand, Coarse sand, Medium sand, Fine sand, Very fine sand).the size range for sands ,considered broadly, comprises the entire range from very coarse sand to very fine sand, i.e.,2.00-0.05mm (Day, 1965).

Soil materials classified as sands must contain 85-to 100% sand-sized particles, 0-to 15% silt-sized particles, and 0-to 10% clay-sized particles. These percentages specified by the boundaries of the sand portion of the USDA textural triangle (Day, 1965).

The solid phase of soils consists of both inorganic and organic components. Inorganic components range in size from tiny colloids (< 2μm) to large gravel (> 2mm) and rocks, and include many soil minerals, both primary and secondary (Bohn *et al.*, 1979).

2.2 Characteristics of soil aggregate fractions

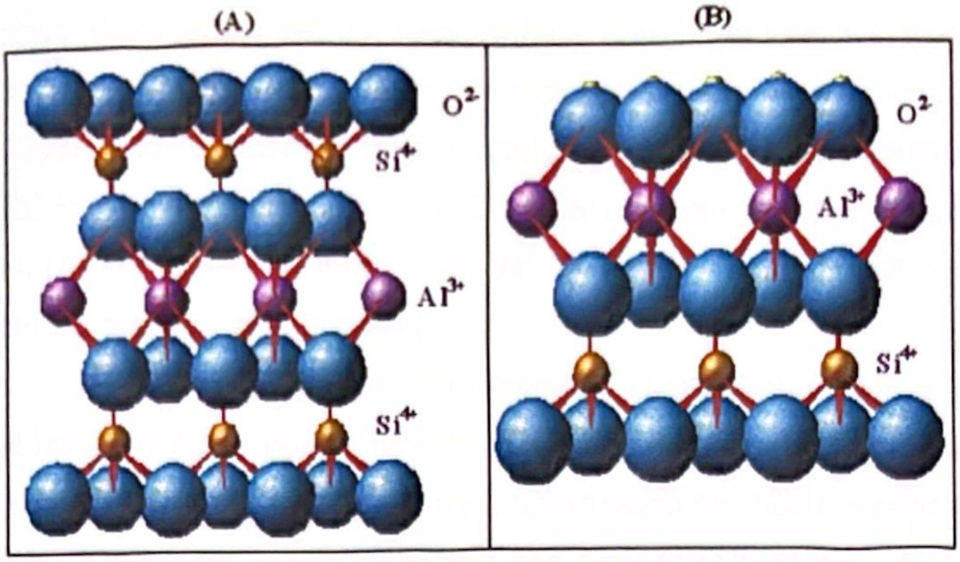
Soil has the ability to immobilize introduced chemicals like heavy metal ions, due to sorption properties which are determined by physicochemical properties of the soil such as: amount of clay, organic fraction, pH, water content, temperature and properties of the particular metal ion (Dube *et al.*, 2001).

The solid state of soils composes an average of 45% of soil bulk. It consists of mineral particles, organic matter and organic-mineral particles. They all play a very important role in giving the soil the ability to adsorb, exchange, oxidise, reduce, catalyse, and precipitate chemicals and metal ions in particular. Particles of Silt, sand and gravel tend to consist of relatively unweathered 'primary' minerals such as quartz, feldspar, iron oxide etc. Clay particles may also consist of primary minerals, but tend to be mostly secondary minerals or clay minerals made of aluminosilicate sheets. Different types of clay minerals have different amounts of surface area (the smaller the particle size, the larger the specific surface area (Dube *et al.*, 2001).

2.2.1 Inorganic soil fraction

Bohn *et al.*, (1979) the inorganic colloidal fraction of soil is the most responsible for sorption by its mineral particles. It is comprised of clay minerals, oxides, sesquioxides and hydrous oxides of minerals. The clay minerals are hydrous aluminum, magnesium or iron silicates; they originated from other forms of silicates.

There are two major types of clay minerals found in soils: 1:1 and 2:1 (*Figure 2.1*). The 2:1 type is typical for clays montmorillonite and illite. The unit cell here is built from two silica tetrahedral layers, (Si_2O_5), surrounding an aluminum octahedral layer, $Al_2O_4(OH)_2$. Only weak Van Der Waals forces exist between two units so that water, nutrients, chemicals can readily enter the



(*Fig. 2.1*) **Arrangement of silica tetrahedral layers and aluminum octahedral layers in montmorillonite (A) and kaolinite (B).**

interlayer regions and, react with the inner surface, often being immobilized.

This also causes the ability to expand montmorillonite or illite when in contact with water. The water content in montmorillonite can vary so that its chemical formula can be written $Al_2(OH)_2(Si_2O_5)_2 \cdot nH_2O$. The 1:1 type is typical for clay kaolinite (Dube *et al.*, 2001).

A unit cell of kaolinite is composed of one silica tetrahedral layer bonded to an aluminum octahedral sheet. The unit cells in 1:1 type are hydrogen bonded together providing no interlayer regions. Thus water and chemicals cannot enter between cells so the distance between them remains constant opposite to montmorillonite. The chemical formula of kaolinite is $Al_2(OH)_4(Si_2O_5)$ (Bohn *et al.*, 1979).

The major difference between expandable, type 2:1, and nonexpanding clays 1: 1 is in the surface area. The 2:1 type of clays have much higher total surface area than the 1:1 type because of the existence of the internal surface area (Brown, 1998). The expandable clay minerals have also a much greater cation exchange capacity (C.E.C.) than the nonexpanding types and thus have a much greater tendency for immobilizing chemicals such as metal ions.

Clay particles are usually negatively charged and there are at least two major possibilities as to how these charges are formed (Brown, 1998), firstly the hydroxyl groups which exist on the edges and on the outer layers of minerals can dispose of hydrogen which is bonded with oxygen probably covalently, not very tight. This is a pH-dependent process and the ability to split the hydrogen atom decreases when pH decreases. When pH is above 6 hydrogen may easily by replaced by other ions like Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}.

Secondly, the creating negative charge process which related to the isomorphous ion replacement in the minerals. In the silica tetrahedral Al^{3+} ion can replace the silicon ion Si^{4+} because these two have a similar ionic radius, whereas Mg^{2+} and Fe^{2+} can exist in the octahedral layers instead of Al^{3+}. The negative charge, which appears as a result of isomorphous ion replacement, is pH-independent and therefore quite persistent. The ability to create negative charges is the highest for 2:1 type of clays (Brown, 1998).

The total amount of clay minerals in soil bulk is very important, as they are the major inorganic component of soil sorption complex. The oxides and hydrous oxides of iron and aluminum are commonly found in soils in several mineralogical forms including hematite, goethite and gibbsite, and bohemite. Manganese oxides are also found in moderately high amounts in some soils. These minerals have a pH-dependent charge and thus may exist as positively, neutral or negatively charged particles (Brown, 1998).

2.2.2 Organic soil fraction

Soil organic matter may range in soils from 0.1% in desert soils to 90% in organic soils. Humic substances make up approximately 85-to 90% of the total organic carbon in soils (Stevenson, 1992).

Soil organic matter is the second main component of the soil solid fraction. The term soil organic matter is generally used to represent the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition products, and soil biomass. Thus, this term includes: identifiable, high-molecular--weight organic materials such as polysaccharides and proteins, simpler substances such as sugars, amino acids, and other small molecules and humic substances (Stevenson, 1992).

On the other hand soil organic matter is frequently said to consist of humic substances and nonhumic substances. Nonhumic substances are all those materials that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fats and so on. Humic substances are the other, unidentifiable components. This apparently simple distinction, however, is not as clear-cut as it might appear. From the point of view of sorption properties of soils humic substances have a major importance (Stevenson, 1992).

Humic substances traditionally defined according to their solubility:

Fulvic acids are those organic materials that are soluble in water at all pH values. Humic acids are those materials that are insoluble at acidic pH values < 2. Humic is the fraction of natural organic material that is insoluble in water at all pH values (Stevenson, 1992). Humic acids have larger average molecular masses than fulvic acids and are not so movable in soils as fulvic ones. They are strongly sorbed by clay minerals. The percentage of carbon and oxygen is also higher in humic acids and hydrogen and nitrogen are in comparable amounts when compared to fulvic acids. Fulvic acids have more alkyl groups than humic ones.

Stevenson, (1992), the existence of humic material in soils strongly influences sorption of chemicals. Humic and fulvic acids can exist in a dissociated form and thus are negatively charged. The main sources of these charges are carboxylic and phenolic groups in which hydrogen can be replaced by metal ions. This source of negative charges in soil colloids is strongly pH-dependent so the sorption of heavy metals in organic soils or in soils with relatively high organic content is mostly pH dependent.

Dube *et al.*, (2001), the inorganic part of soil and soil organic matter do not exist separately in soil; both nonhumic and humic organic substances can bind to inorganic particles of soils like aluminum and iron oxides and clay minerals. The ways in which organic material is combining with mineral portions of soil are as:

(i) Salts of low-molecular, organic acids (acetate, oxalate, lactate),
(ii) Salts of humic substances with alkaline cations – humate and fulvate,

(iii) Chelate with metal ions,

(iv) Substances held on clay mineral surfaces.

The complexing ability of humic and fulvic acids results largely from their content of oxygen-containing functional groups, such as carboxylic-COOH, phenolic-OH and carbonylic-C=O group. Chelate complexes are of especially major importance. The humic and fulvic functional groups play a role as ligands. Each group may occupy two or more coordinating positions about metal ions and form closed rings.

Organic substances can bind to silicate surface in clay minerals via several mechanisms:

(i) Al^{3+}, Fe^{2+}, Ca^{2+} and Mg^{2+} bridges,

(ii) Van der Waals forces,

(iii) Hydrogen bonding,

(iv) Sorption by association with hydrous oxides.

The organic-mineral particles have great influence on the physicochemical soil properties. They mostly determine the texture of soil. The contribution of soil organic matter to cation exchange capacity is larger in sand and silt than in clay fraction (it is worth remembering that the negative charge of soil organic matter is strongly pH-dependent). Hence in typical sandy soil C.E.C. is pH-dependent for the most part (Dube *et al.*, 2001).

Organic-mineral particles can vary widely in their adsorption properties because of diverse specific surfaces, charge densities and widely different soil organic matter content. The C.E.C. decreases with increasing particle size. The distribution of xenobiotics like, for instance, heavy metals between different size classes of organic-mineral particles is important because the physical movement of these particles leads to their re-distribution in the landscape. The content of heavy metals usually decreases from clay to coarse silt Dube *et al.*, 2001; the high surface area of clay minerals and weak pH dependence of C.E.C. cause it. Hence, soils with high amounts of clay and organic matter may contribute with heavy metals than others.

Dube et al., (2001) the binding forces between heavy metals and soil fractions are dependent on pH and ion properties like charge, ionic radius. The binding forces of metal ions to soils decrease with increasing pH of the environment. The ions with higher charge like Al^{3+} are stronger bound to soil particles than smaller charges such as Ca^{2+}. When considering metal ions with the same charges the most important factors are ionic radius and rank of hydration. The bigger ionic radius the smaller electric field the ion emits; consequently it is less hydrated than ions with smaller radius which emit stronger electrical fields (Dube *et al.*, 2001).

2.3. Heavy metals in soil environment

Shuman, (1991) reported (*cited after* McLean and Bledsoe, 1992), that metals found in one or more of several "pools" of the soil, as described by:

1) Dissolved in the soil solution;
2) Occupying exchange sites on inorganic soil constituents;
3) Specifically adsorbed on inorganic soil constituents;
4) associated with insoluble soil organic matter;
5) Precipitated as pure or mixed solids;
6) Present in the structure of secondary minerals; and/or
7) Present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fractions, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary importance when considering the migration potential of metals associated with soils.

Multiphase equilibria must be considered when defining metal behavior in soils (McLean and Bledsoe, 1992), *(Figure 2.2)*. Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for (Hg), (Se), and (As). At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation, reduction reactions, precipitation/dissolution reactions, and sorption/ desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated.

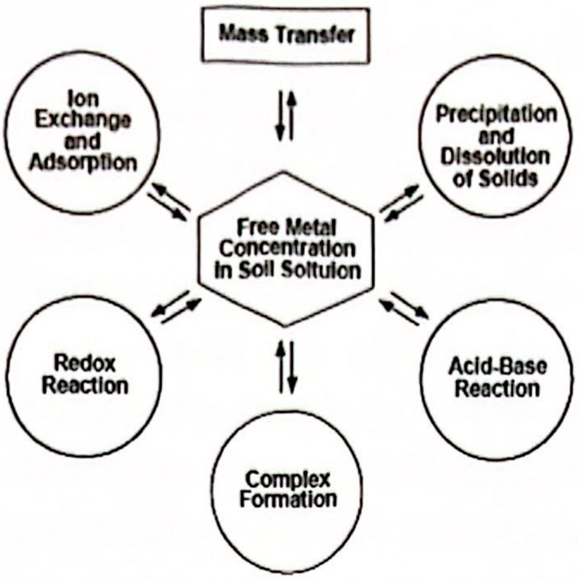


Figure 2.2 **Controls of free trace metal concentrations in soil solution.**

2.4. Soil Solution Chemistry

Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., $CdSO_4^0$,$ZnCl^+$, $CdCl_3^-$), or associated with mobile inorganic and organic colloidal material. A complex is defined as a unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g. $ZnSO_4^o$, $CdHCO_3^+$, $Cr(OH)_4^-$. The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-}, HCO_3^-, and OH^- are ligands. The total concentration of a metal, in the soil solution is the sum of the free ion concentration $[Me^{z+}]$, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material (Mclean and Bledsoe, 1992).

2.5. Surface Reactions

Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption differs from precipitation in that the metal does not form a new three dimensional solid phase but is instead associated with the surfaces of existing soil particles. The soil matrix often includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates, Fe, and Mn oxides are the principal soil surfaces that control the mobility of metals in soils and natural water (Mclean and Bledsoe, 1992).

In arid soils, carbonate minerals may immobilize metals by providing an adsorbing and nucleating surface (Dudley *et al.*, 1991).

A surface complexation model is often used to describe adsorption behavior (Mclean and Bledsoe,1992), several types of surface complexes can form between a metal and soil surface functional groups and are defined by the extent of bonding between the metal ion and the surface (*Figure 2.3*).

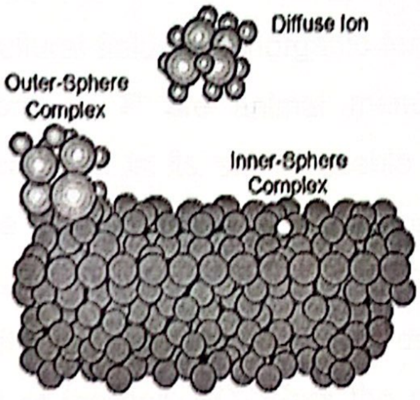


Figure 2.3 **The three mechanisms of cation adsorption on a siloxane surface (e.g., montmorillonite).**

Metals in a diffuse ion association or in an outer sphere complex are, surrounded by water of hydration and, not directly bonded to the soil surface. These ions accumulate at the interface of the charged surfaces in response to electrostatic forces. These reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. These two metal-surface interactions have also been termed exchange reactions because the introduction of other cations into the system, in sufficient concentration, causes the replacement or exchange of the original cations. Metals associated with exchange sites may, depending on the environment, be relatively mobile (Mclean and Bledsoe, 1992).

Exchangeable metals may be the most significant reserve of potentially mobile metals in soil.

2.6. Chemistry of Phosphorus

Phosphorus is one of the essential nutrients needed for crop growth; it is the second key plant nutrient. Phosphorus exists in organic and inorganic forms within the soil. Major sources of inorganic P in agricultural fields are inorganic fertilizers, while the main sources of organic P are animal manure. Phosphorus interacts with soil particles in its exchangeable form, known as orthophosphate. The different forms of orthophosphoric acid that can exist in the soil solution are H_3PO_4, $H_2PO_4^{-1}$, HPO_4^{-2}, and PO_4^{-3}. The availability of the different forms is dependent on pH; however, at the pH of the soil, PO_4^{-3} has the strongest binding affinity to the soil. Organic P forms include relatively labile phospholipids, inositols and fulvic acids, and the more resilient forms are humic acids (Tisdale and Nelson, 1975).

The different phosphate (PO_4^{-3}) anions in solution are attracted to positively charged sites, on the surface of soil particles, according to the soil anion exchange capacity (AEC). Soils that develop positive charges are soils rich in Fe, Al, Ca oxide minerals, and layers of silicates; these positive charges can occur as well on the edges of broken octahedral sheets. The anion exchange capacity of various hydroxide minerals is dependent on the pH and electrolyte concentrations of the surrounding medium, which might lead to competition among different anions in the soil solution (Goldberg and Sposito, 1985). The pH dependent charges arise from associations and disassociations of potential determining ions OH^- / H^+. It all depends on the zero point charge (ZPC) of the soil. The ZPC is the pH at which the soil has no charge. For example if the pH is less than the ZPC then soil particles will develop positive charges on their surface and vice versa, phosphate (PO_4) anions can also adsorb to the surface of the soil particle through specific adsorption reactions (non-electrostatic forces) and/or precipitate in the soil aggregates. The specific adsorption reaction is the formation of covalent bonds in mono-dentate complexes, between the PO_4 anions in solution and the soil metal complexes, while displacing OH- groups on the surface of the soil particle (Goldberg and Sposito, 1985). In acidic conditions, PO_4 anions form covalent bonds with Fe^{+3}, Al^{+3}, and Mn^{+2} complexes, and while in basic soils they form bonds with Ca^{+2} complexes. In addition, PO_4 adsorption (retention) can occur in clay minerals that have hydroxyl surfaces.

Goldberg and Sposito, (1985) defined the PO_4 precipitation process as more-physically adsorbed P, where the PO_4 anions diffuse further into the soil structure forming bi-dentate and binuclear complexes, rendering them more insoluble and the reaction tends to be irreversible. These anions are referred to as the PO_4 anions that cannot be extracted by dilute acid. The process of PO_4 precipitation is considered to be slow.

2.7. The Phosphorus Cycle

The P cycle, as indicated by (*Figure 2.4*), describes the interactions and transformations of P taking place in an array of physical, chemical, and biological processes to determine the different forms of P, their availability for the plant uptake, and their transport in surface and runoff and/or leaching (Ritter and Shirmohammadi, 2001).

According to (*Figure 2.4*), the major sources of P in the soil are inorganic fertilizers directly applied to the field, and organic fertilizers introduced as plant residues, animal manure, municipal and industrial waste, and rock weathering.

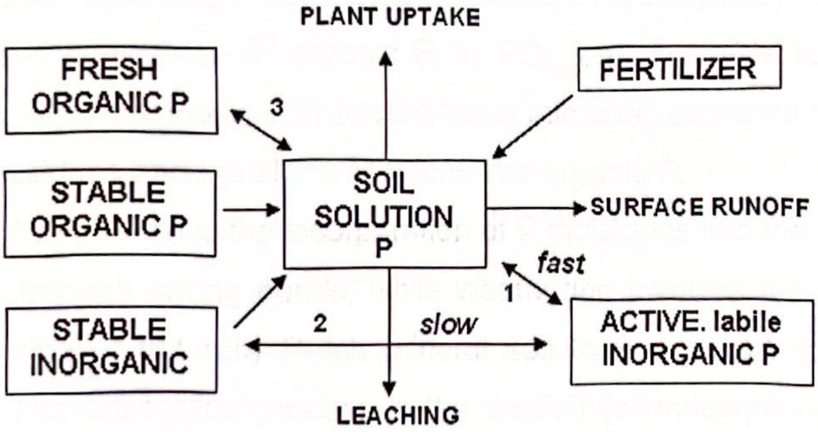


Figure 2.4: Phosphorus Cycle

1: Adsorption / Desorption; 2: Precipitation / Dissolution;
3: Immobilization

Phosphorus is lost from the soil through plant uptake, leaching into the groundwater, and/or surface run-off and soil erosion.

However, P, in the soil-water solution, can exist in several forms: dissolved in solution (labile), adsorbed to the soil functional groups (active inorganic P), precipitated (stable inorganic P), fresh organic P (freshly added), and stable organic P (Matthews, 1998).

The concentration and the rate at which P is transformed from one form to another are highly complex, and are mainly a function of the soil properties, climate conditions, and land use and its management. Yet, the different forms of P in the soil are not in discrete entities, as intergrades and dynamic transformations occur continuously between the different available forms to maintain equilibrium conditions (Sharpley, 1995a), the major transformation processes of P in the soil are: mineralization and immobilization, precipitation and dissolution, and adsorption and desorption. Weathering, mineralization, and desorption increase P availability in solution, while immobilization, precipitation, and adsorption decrease P availability in solution. Mineralization is the microbial conversion of organic P to PO_4 ions available to the plants, while immobilization occurs when microbes consume fresh plant residues and transform PO_4 ions into organic P.

Precipitation is the incorporation of P molecules into the solid phase through strong bonds, while weathering involves the slow conversion of naturally P-rich mineral soil to P available to the plant. The adsorption process is the fixation (chemisorptions) of the PO_4 ions onto the soil surface and is characterized as a fast process, while the desorption process is the release of these adsorbed PO_4 ions back in solution and is usually a much slower process (Matthews, 1998).

The relation between the adsorption and desorption process is controlled by an equilibrium constant. As the concentration of PO_4 increases in the soil solution, the PO_4 ions spontaneously adsorb to soil charged surfaces to restore the equilibrium. In the same way, if the concentration of PO_4 in solution depleted, the adsorbed PO_4 ions to the soil surface dissolve back into solution according to the equilibrium constant (Lindsay, 1979).

However, under a continuous increase of PO_4 ions in solution, the additional PO_4 ions are less strongly bound to the soil resulting in a higher equilibrium of PO_4 concentration in solution. Consequently, these elevated PO_4 concentrations become more prone to be leached down into the soil profile through infiltrating water (Sharpley, 1995b). Therefore, it is vital to understand the dynamics between the source and the sink passing through an equilibrium state, so as to limit and control P impacts on the environment.

2.8. Chemical conditions influencing phosphorus behaviors in soils

The processes that cause retention or release of P are summarized in (*Table 2.2*), including the main soil types for which the processes are relevant.

The left column shows processes leading to the retention of P by the solid phase; the middle shows corresponding processes that release P, and the right column shows the soil types where these processes are important (Chardon and Schoumans, 2002).

(*Table 2.2*) **Retention and release of phosphorus, according to the soil type.**

retention	release	soil types
fast adsorption	fast desorption	all soils
slow 'absorption' on amorphous Fe/Al-oxides	slow desorption	non-arid soils
precipitation (mainly Ca-P and NH_4-P)	dissolution	calcareous soils over-fertilized soils
particle settling	sedimentation detachment	all soils

2.9.1 Phosphorus in soils

In non-calcareous sandy soils, amorphous Al- and Fe-(hydr) oxides and complexes of Al- and Fe-(hydr) oxides with organic matter are the main reactive constituents. The overall reaction of inorganic P with Al- and Fe- (hydr)oxides is the result of a fast adsorption reaction at surface sites (<1 day) and a slow one: diffusion through the solid phase or micropores of Al- and Fe-(hydr)oxides followed by precipitation or adsorption inside the aggregates. The fast reaction described as a ligand exchange reaction between phosphate anions and OH^- or H_2O groups at the surfaces of Al- and Fe- (hydr) oxides (Koopmans *et al.*, 2003).

Phosphorus can be released by desorption of adsorbed P, or dissolution of precipitated P inside the aggregate, followed by diffusion to the soil solution. Since diffusion is slow, adsorbed P becomes available again only on the long-term. Therefore, the reaction is considered to be 'irreversible' under common agricultural conditions (Koopmans *et al.*, 2003). The term P fixation has often been used to indicate P absorption, which is then treated as an irreversible reaction. Besides adsorption and desorption, precipitation of P can occur in non calcareous sandy soils. At a low pH (< 4), Al-and Fe (hydr) oxides may dissolve, resulting in high Al and Fe concentrations. In combination with a high P concentration, Al and Fe may precipitate with P (e.g., strengite and variscite). Furthermore, in soils saturated with P, that are unable to retain additional P by sorption, precipitation of Ca-P minerals may occur after application of animal manure (pH >5.5).

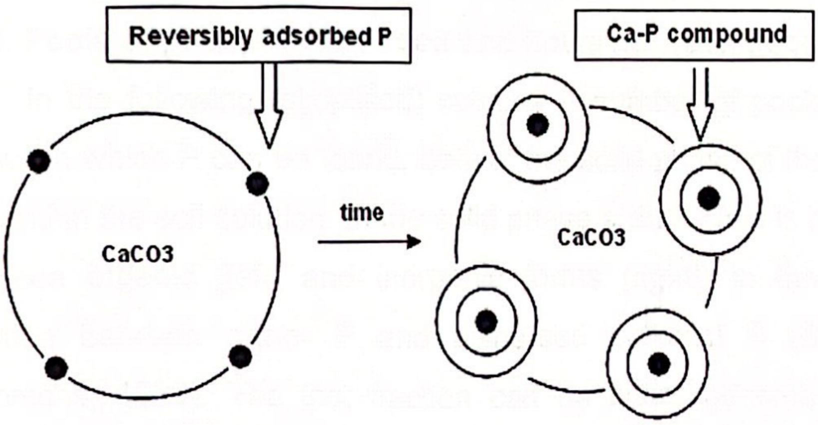
De Haan and Van Riemsdijk, (1986) *cited after* Koopmans *et al.*, (2003) found indications for the existence of dicalcium phosphate (i.e., brushite, DCP) in non-calcareous sandy soils receiving large applications of pig slurry. Depending on the solubility of the P mineral, P can become available in soil due to dissolution. In non calcareous peaty soils, P adsorption was highly positively correlated with Al and Fe content, whereas correlation with organic matter was poor or negative, Cuttle, (1983).

In soils with a high clay content, Al- and Fe-(hydr)oxides may be associated with the negatively charged surface of clay minerals, and P may adsorb at surface sites of these Al- and Fe-(hydr)oxides (Koopmans *et al.*, 2003).

2.9.2. Phosphorus in Calcareous soils

Matar et al., (1992) the availability of added P to crops, among other factors, depend on the rate at which converted to less soluble forms in soils. The addition of P fertilizer to a calcareous soil resulted in a series of chemical reactions with soil compounds that decrease its solubility, a process named as P retention. The mechanisms of retention are characterized as P adsorption on clay minerals and $CaCO_3$ surfaces and precipitation of Ca-phosphates. An understanding of the mechanism of sorption reactions and their rates is a prerequisite to predict the amount of P fertilizer that can be applied to the soil.

In calcareous soils, calcium carbonate is the main reactive constituent. At a low P concentration in soil solution (up to 10 mg P L^{-1}), the reaction of P with calcite ($CaCO_3$) can be considered as a fast adsorption reaction (Koopmans *et al.*, 2003), Hence, the adsorption reaction to be completely reversible. In contrast, precipitation of P is the main process at a higher P concentration (up to 100 mg P L^{-1}). The reaction was described as a slow nucleation process, where precipitation of P with Ca on nuclei of adsorbed P at the $CaCO_3$ surface results in the 'three dimensional growth' of a Ca-P mineral (5-to 8 μm). As the Ca-P precipitate covers the calcite surface, the Ca-P precipitate is referred to as a 'surface precipitate' (*Fig. 2.5*).



(*Figure 2.5*) Concept of P retention by $CaCO_3$.

In the beginning, DCP may form, but within three months, DCP may slowly transform into octacalcium phosphate. If the P concentration is > 100 mg P L^{-1}, a fast process may occur: nuclei can cluster into large Ca-P minerals (about 500µm).

The pH and Ca concentration in the solution considerably affect the precipitation reaction, Depending on the solubility of the Ca-P mineral, P can dissolve in the soil solution (Lindsay, 1979).

Solis and Torrent, (1989) understanding the main governing factors in the recovery of applied P require a knowledge of the P reactive compounds in the soils. These compounds clay minerals, Fe and Al oxides, and calcite, the first two types of minerals provide most of the active P- adsorbing surfaces, as shown by the positive relationships between P-adsorption capacity at a low equilibrium concentration and clay or Fe content.

In contrast, calcite surfaces have a relatively low P-adsorption capacity, but induce slow precipitation of Ca phosphates (Freeman and Rowell, 1981).

2.10. Pools of phosphorus in soil and flows between pools

In the following (simplified) scheme a number of pools are shown in which P can be found, both in the solid phase of the soil and within the soil solution. In the solid phase a distinction is made between organic (left) and inorganic forms (right), in the soil solution between ortho- P and dispersed colloidal P (Bril & Salomons, 1990). The last fraction can be either adsorbed on inorganic colloids (clay particles, Fe / Al- hydroxides), or is bound to dissolved organic matter (DOC).

In the solid phase the precipitated pool mainly consists of Ca- P in calcareous soils, and in heavily manured neutral soils besides Ca-P also struvite can be expected when the sorption capacity of the soil is exceeded. Sorbed P distinguished into adsorbed P, on the surface of aggregates, and P sorbed inside aggregates (fixed, 'absorbed'). Also, P can be associated with colloids which are part of the soil matrix (Bril & Salomons, 1990).

Solid phase	Solution	Solid phase
Organic forms		Inorganic forms
Living biota		Precipitated
Fresh organic material Stable organic matter ('Humus')	Ortho-P	Adsorbed Absorbed (In aggregates
	Dispersed Colloidal/Organic P	Attached Colloids

The flows of P between the pools can be summarized as follows. Living biota can die, and P becomes part of fresh organic material. From this pool, P can be released by biological breakdown (mineralization), forming more stable organic matter and/or inorganic P in solution. Especially on calcareous soils, soluble ortho- P can precipitate (as a separate phase or on the surface of e.g. carbonates) or adsorb on the surface of Fe / Al-hydroxides (Hens and Merckx, 2001).

Adsorption is a fast process, which can be followed by diffusion into aggregates and sorption on internal surfaces; this process is mainly important with amorphous hydroxides. Also, P can be associated with colloidal material; depending on soil conditions, this material can be attached to the soil matrix or be dispersed in the soil liquid (Hens and Merckx, 2001).

Particle bound P soil solution can represent the majority of total P. It was shown that the particle size forms a continuum, which makes the distinction between soluble P and particle bound P questionable. Flows that can bring P in solution (solubilize) are: mineralization of organic material, dissolution of precipitated P; desorption of adsorbed P; diffusion of P from the interior of aggregates, followed by desorption; breaking of the association between P and dispersed colloids, and detachment of P containing colloids from the soil matrix (Hens and Merckx, 2001).

2.11. Adsorption and Desorption Reactions

The soil as a whole is made up of particles that generally have a net negative charge on their surfaces. Nevertheless, soil particles are still capable of strongly retaining anions such as P. This process of retention by the soil is referred to as adsorption. The adsorption process involves two interacting elements, the adsorbate (e.g. P) and the adsorbent (e.g. the soil) and thus, the properties of these two components govern the adsorption process (Bohn *et al.*, 1979).

Tisdale and Nelson,(1975) and Bohn *et al.*, (1979), anions can be classified into two groups: (1) non-specifically adsorbed ions; and (2) specifically adsorbed ions. The non-specifically adsorbed ions (e.g. Cl- and NO_3^-) are those that are retained on positive sites by simple electrostatic attraction following anion exchange. These groups of ions are assumed to obey the diffuse layer equilibrium and are easily displaced or exchanged. The second group consists of anions that have a far greater affinity for soil surfaces than their concentration in solution would suggest. In the adsorption of these ions, simple electrostatic attraction gives way to the formation of chemical ionic and/or covalent bonds with the surface groups. The phosphate ion belongs to this group, the specifically adsorbed ions. In soils, the main adsorbents of phosphates are iron (Fe) and aluminum (Al) oxides and hydrous oxides, aluminum-silicate clay minerals, carbonates, and soil organic matter.

In the soil solution, $H2PO_4^-$ and HPO_4^{-2} are the most common forms of phosphorus that sorb to soil adsorbents with $H2PO_4^-$ dominating at low pH. Fe and Al oxides exist in soil as discrete particles, surface layers/coatings on soil particles, and in clay minerals as gibbsite (Al oxide layer in silicate clay). Fe oxide surfaces are hydroxylated in the presence of water, either single hydroxyls (Fe-OH) or double hydroxyls (OH- Fe -OH). This chemisorbed water controls the reactivity of the Fe and Al oxides (Tisdale and Nelson, 1975 and Bohn *et al.*, 1979).

The surface charge is determined by the solution pH that controls the adsorption and desorption of H^+ ions in the chemisorbed layer. At low pH, $Fe\text{-}OH^{2+}$ dominates (positive surface charge). As pH rises, H^+ is lost from -OH groups and eventually the net surface charge is zero (point of zero charge, PZC). For various Fe-oxides the PZC varies from pH 7.5 to 9.3 therefore Fe oxides will have a net positive surface charge in most soils but some of them will have a net negative charge in alkaline soils. Al-oxides show a similar change in surface charge with pH. The charged oxide surface can hold HPO_4^{-2} via “non-specific adsorption” (outer sphere complexes) which is easily reversible as the ions are held electrostatically by the charged $\text{-}OH^{2+}$ surface groups. Specific adsorption or inner sphere complexes are much stronger and form when ions penetrate the coordination shell of the Fe (or Al) atom and exchange (or displace) $-OH$, $-OH^2$, or H^+ and are bound by covalent bonds. In mono dentate bonding, the anion (e.g. HPO_4^{-2}) replaces an aquo group ($-OH^2$) and bonds directly to the Al or Fe atom (aquo groups will be replaced preferentially to hydroxyls). In bi dentate bonding, the HPO_4^{-2} replaces two hydroxyls resulting in two bonds to a Fe or Al atom or a bond to two adjacent atoms. In bi dentate bonding $H2PO_4^-$ will lose a proton during bonding to allow for the formation of two bonds. Soil pH affects specific adsorption by controlling the ionic species of the adsorbate (P) and by affecting the surface charge of the adsorbent. Phosphate will adsorb in the entire pH range of soils (more below pH 5 than above 7 i.e. more as $H_2PO_4^-$ than as $HPO4^{-2}$, more below PZC than above). In comparison sulphate will not adsorb above pH 6 (only on the acid side of the PZC of the oxide, only replaces aquo groups), while silicate adsorption increases as pH increases and in alkaline soils can decrease phosphate retention due to competition for binding sites (Tisdale and Nelson, 1975 and Bohn *et al.*, 1979).

Using anion exchange resin, Taylor and Ellis, (1978) concluded that at low concentration, P was bonded by two points of attachment (bi dentate bonding). This was followed by one point attachment (monodentate bonding) at high P concentrations during adsorption on resin surface. This resulted in a deviation of the adsorption plot from that predicted by the Langmuir equation due to the increase in potential adsorption sites as P concentration increases. Electrostatic binding results in anions that are easily exchange and release if soil solution composition changed, therefore anions held by electrostatic binding are highly bioavailable. Monodentate binding is stronger than electrostatic binding but anions held by monodentate binding are still exchangeable and therefore also bioavailable. Bidentate bonding is the strongest and is largely irreversible under normal soil conditions (Taylor and Ellis, 1978).

Phosphorus (P) retention by soils is an important parameter for understanding soil fertility problems, as well as for determining the environmental fate of P. The P adsorption capacity of a soil or sediment is generally determined by batch-type experiments in which soils or sediments are equilibrated with solutions varying in initial concentrations of P. Equations such as the Langmuir, Freundlich and Tempkin models have been used to describe the relationship between the amount of P adsorbed to the P in solution at equilibrium (Graetz and Nair, 2000).

Advantages of the batch technique include:

Soil and solution are easy to separated, a large volume of solution is available for analysis, and the methodology can be easily adapted as a routine laboratory procedure. Disadvantages include difficulties in measuring the kinetics of the sorption reaction and optimizing the mixing of solution and soil without particle breakdown. Despite the disadvantages, the batch technique has been, and still is, widely used to describe P sorption in soils and sediments (Graetz and Nair, 2000).

Adsorption isotherms are used to summarize or characterize P sorption in soils. As such, adsorption isotherms are the basic tool for comparing the effects of various amendments, conditions, and treatments on the retention of P by soils. The usefulness of adsorption isotherms in describing phosphorus adsorption is indicated by its utilization in one form or another by many researchers dealing with P adsorption (Taylor and Ellis, 1978).

The most widely used equations to describe adsorption isotherms are the Freundlich, Langmuir, Gunary, Temkin, BET and the polynomial equations. Although adsorption isotherm equations are useful in characterizing P retention by soils, they cannot be interpreted to indicate a particular adsorption mechanism or even if adsorption rather than precipitation has occurred (Graetz and Nair, 2000).

2.12. The Langmuir isotherm

In contrast to the Freundlich isotherm, the Langmuir adsorption isotherm was formulated from the kinetic theory of gases and was used extensively to describe gas adsorption on solids. The isotherm has been found to be applicable to phosphorus adsorption under more dilute equilibrium phosphorus concentration. (Olsen and Watanabe, 1957) reported that the adsorption of phosphorus by soils from dilute solutions showed a closer agreement with the Langmuir isotherm than the Freundlich isotherm. Apart from the mode of derivation, the popularity of the Langmuir isotherm stems from the ability to generate adsorption parameters which can be of practical significance. According to these earlier workers, the major advantage of the Langmuir equation over the Freundlich is that an adsorption maximum can be calculated. This parameter can be related to various soil properties and supply information about the nature of the reaction between the soil and fertilizer phosphorus.

The Langmuir equation is written as:

$$S = k\, C_e\, S_{max} / 1 + kC_e \qquad [1]$$

Where

S = amount adsorbed per unit mass of adsorbent ($mgKg^{-1}$)

C_e = equilibrium concentration of the adsorbate (mgL^{-1})

S_{max} is the capacity factor referred to as the "adsorption maximum" and k is the "affinity" factor, which reflects the relative rates of adsorption and desorption at equilibrium (Graetz and Nair, 1995).

Conformity with the Langmuir isotherm is verified by a plot of the experimental data to the linearized form of equation [1]. It is worth noting that equation [1] can be linearized in several ways each giving slightly different parameters when applied to the same adsorption data. The most common or universal form is given by

$$C_e / S = 1 / (K S_{max}) + C_e / S_{max} \qquad [2]$$

If the data conforms to the Langmuir isotherm, a plot of C_e / S against C_e will yield a straight line whose slope is $1/S_{max}$ and intercept is $1 / k S_{max}$, A combination of these regression coefficients allows the calculation of S_{max} and K (Graetz and Nair, 1995).

2.13. Effect of Soil Texture on Phosphorus Retention and Release

The texture of a soil refers to the relative proportions of sand, silt and clay in the mineral fraction of a soil. As the proportions of silt and especially clay increase relative to sand, the surface area of the mineral particles expressed per unit mass (or volume) will increase. Fine colloidal clay has about 10000 times greater surface area than the same mass of medium-sized sand (Buol et al., 1980). The colloidal clay surface area ranges from about 10 to 1000 $m^2 g^{-1}$.

P adsorption and precipitation are processes that occur on surfaces therefore it is not surprising that texture has a large effect on P retention characteristics of a soil.

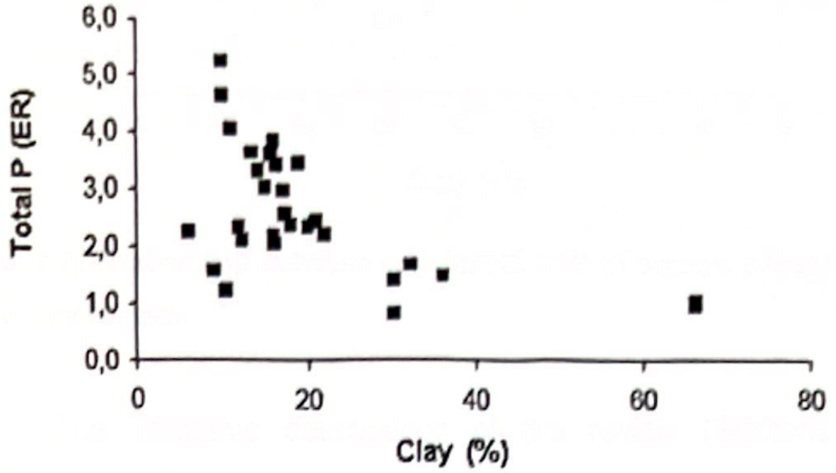
In early P sorption study, Olsen and Watanabe, (1957) showed that the Langmuir sorption maximum for P correlated closely with surface area (their study soils had clay contents ranging from 3.5 to 37%), Amer *et al.,* (1985) Nine calcareous samples with surface areas ranging from 250 to 12 780 m^2 kg^{-1} were studied for their ability to sorb P and it was found that 92.8% of the variation in P sorption could be explained on the basis of differences in surface area, Ryan *et al.,* (1984) multiple regression analysis of P sorption and several soil characteristics of 20 calcareous soils with a wide range in clay, $CaCO_3$, Fe-oxide, and organic carbon contents showed that P sorption increased as clay content and oxalate iron content increased and decreased as CEC increased. They concluded that when present, Fe oxide effects on P sorption and desorption are dominant and mask the effects of $CaCO_3$ due to their greater affinity for P. This clearly shows that not only is the amount of surface area important for the retention of P but the kind of surface as well, (Mozaffari and Sims; 1994) Clay content and soil P sorption maxima were highly correlated (R^2 = 0.94) in several Delaware soils and, (Leclerc *et al*., 2001) evaluated soil survey data and found that soil texture was the main factor affecting soil P sorption capacity (PSC) followed by the dominant soil forming process. The PSC increased with increasing clay content (soil surface area) within Gleysolic soils and within Podzolic soils but the relationship was less clear when the two soil orders were grouped together.

Samadi and Gilkes, (1999) reported that Phosphorus retention increases with the ratio of clay (or Fe oxides) to total (or active) $CaCO_3$ equivalent and, Al and Si were the dominant elements associated with P, while Ca, Fe, and Mn generally were present at low concentration in such associations.

2.14. P concentration in soil particles

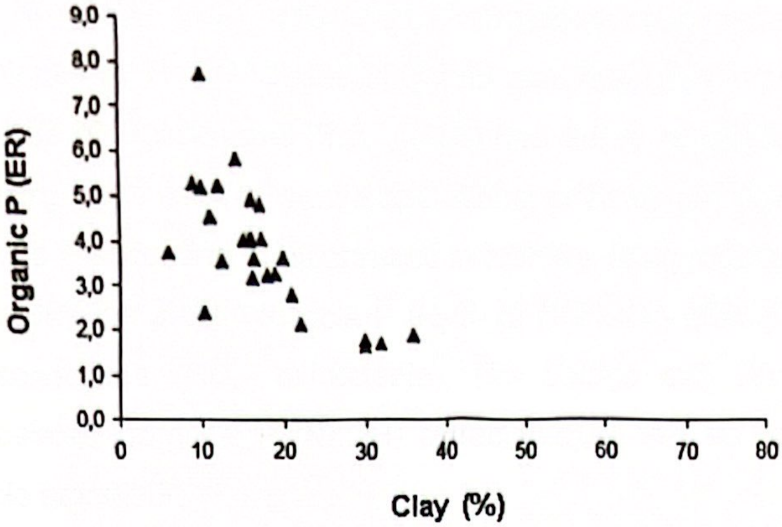
Barberis & Withers, (2002) In an review of an experimental data, according to the following classification that clay (< 2μ) silt (2 - 20 or 50μ) sand (20 or 50 -2000 μ), reported The following results: Total P increases with a decrease of particle size [Williams and Saunders 1956a; Bates and Baker, 1960; Syers *et al.*, 1969; Hanley and Murphy, 1970; Tiessen *et al.*, 1983; Zhu *et al.*, 1983; Day *et al.*, 1987; Choudhry, 1988; Guzel and Ibrikci1994; Agbenin and Tiessen, 1995; Oggard, 1996 ; Sinaj *et al.*, 1997 *cited after* Barberis & Withers (2002)]. The concentration of total P in the sand is relatively low, and a fairly high proportion is inorganic, mainly Ca- P, and of primary origin. The P in the clay fractions is largely of secondary origin, mainly Fe- bound, and is the result of accumulation of both organic and inorganic P, that can be ascribed to the greater surface area and retention capacity of the clay [Williams and Saunders, 1956a; Bates and Baker, 1960; Bates and Baker, 1960; Juo and Ellis, 1968; Syers *et al.*, 1969; Tiessen *et al.*, 1983; Choudhry, 1988; Sinaj *et al.*, 1997 *cited after* Barberis & Withers (2002)]. Data of enrichment ratios (ER), calculated as the ratio of the total P content of separates to that of soil (Sharpley, 1985) show an inverse trend with clay content (*Figure 2.6*). Organic P is also concentrated in the finest separates (clay>silt) [Williams and Saunders,1956a; Bates and Baker, 1960;

Syers *et al.*, 1969; Hanley and Murphy, 1970; Tiessen *et al.*, 1983; Zhu *et al.*, 1983; Choudhry, 1988; Guzel and Ibrikci 1994 *cited after* Barberis & Withers (2002)] and represent from 6 to 83 % of total P in the clay, while in the soil it represented from 2 to 73% of total P in the soil.



(*Fig. 2.6*) **Relationship between enrichment ratio (ER) of total phosphorus and clay content**

Agbenin and Tiessen, (1995), studying soils from a top sequence in Northeast Brazil, demonstrated that even when organic P constitutes an insignificant portion of total P the lowest amounts are associated with the sand and the highest with the clay showing the role of surface stabilization. Also for organic P the inverse trend versus clay content exist (*Figure 2.7*).



(*Fig. 2.7*) Relationship between enrichment ratio of organic phosphorus, and clay content.

The Tentative conclusions of the review (Barberis and Withers, 2002) are Clays particularly enriched in total P in soils poor in clay content. P on clays is organic or bound to iron and aluminum oxides. Consequently, an enrichment ratio (ER) is higher than one for total P, organic P, and resin P. Nevertheless, clays are rich in available sorption sites so often these particles can act either as a sink or as source of P.

2.15. Fractionation of soil phosphorus

The sequential fractionation procedures are based on the assumption that chemical extractants selectively dissolve discrete groups of phosphorus compounds and such operationally defined soil P fractions are subject to broad interpretations. Nevertheless, the information obtained from P fractionation schemes has been useful for interpretations of soil development as will as plant availability of P (Tiessen and Moir, 1993).

A widely used sequential P fractionation approach was developed by Hedley et al.(1982) and modifications thereof [such as those of Tiessen and Moir, (1993) and Sui *et al.*, (1999)] have regularly been used to isolate operational pools of inorganic P and organic P according to differences in labiality, this procedure aims to quantifying plant available P (H_2O- or $NaHCO_3$- extractable P), Ca-associated (HCl- extractable), Fe- oxides and Al- oxides associated inorganic P (NaOH- extractable),as well as labile and stable organic P.

Sui *et al.*, (1999) procedure differed from the standard Hedley fractionation procedure in that they used H_2O as the first extracting instead of equilibrating the soil sample with an anion-exchange resin. They also found in a preliminary study that an anion– exchange resin was not required to extract detectable levels of labile P from the soil samples. This fraction is intended to represent the most labile P in the soil, and would be more closely related to P bioavailability than would reisn exchanged P. In this study, we pursue this line of research combining with physical fractionation of soil according to particle size. Aggregate (or particle)-size separation has been widely used to distinguish pools of different soil organic matter and nutrient quality (Christensen, 1992; Agbenin and Tiessen, 1995; Zhang *et al.*, 2003).

CHAPTER

3

MATERIAL AND METHODS

3.1 soil sampling

The sites selected were a cultivated sandy soil used for forage crop production located in misurata counties, and fifteen composite samples (S1, S2, S3..., and S15) collected from the layers of 0-to 20-cm in autumn 2004. For comparison, a composite clay loamy soil sample (CL1) also taken from the 0-to 20-cm layer in a vegetable crops field in Albeda County. These soils had a long history of crop production ranging from 20-to 40 years, where about 60 kg P ha^{-1} annually applied as basal fertilizer. Each soil sample composted from five samples taken from five locations across the same field. Soil samples were air-dried and subsamples of the air-dried bulk soil samples were dry screened and fractionated into five (or six) different aggregate-sizes. The remaining soil samples were ground, and passed through a 2-mm sieve before physical and chemical analyses.

3.2 Characterization of soil samples and aggregate-sizes

Characterization data included:

- Soil reaction (pH) measured in water and 1 *M KCl* at a 1:1 soil/solution ratio using a pH-meter (Oacton EW-3519-30 pH meter); the pH meter standardized according to the manufacturer's instructions. Before measuring the pH of the test samples, the electrode was washed thoroughly first with distilled water and then with the sample extracts, the electrode was dipped into the sample solution and system was allowed to stabilize before making the final reading.

The main advantage of measuring soil pH in salt solution is the tendency to eliminate interference from suspension effects and from variable salt contents, such as fertilizer residues, Ryan *et al.*, (2001) mentioned that this is hardly needed in alkaline calcareous soils of Central and West Asia and North Africa region .

- Electrical conductivity (EC) was measured in water at a 1:2 soil/water ratio, the apparatus used for this analysis was (Oacton EW-3519-51 EC-meter), and the samples were shaken thoroughly, allowed to stabilize, filtered before starting measurements. EC-meter standardized with the help of standard solution of potassium chloride. Then conductivity cell thoroughly rinsed with distilled water as well as a small amount of sample solution.
- The textural analysis performed using the hydrometer method as described by Ryan *et al.*, (2001). 40-g of air dried samples or aggregate-sizes; dispersed with 60-mL solution of (40-g Na_3PO_3)$_{13}$ + 10-g (Na_2CO_3) + 1-L H_2O, suspension leaved overnight, transferred to a stirring cup, then to a 1-L calibrated cylinder (hydrometer jar), bring to volume with water, a blank included as well, amyl alcohol used to disperse any froth. Soil textural class name was determined using textural triangle.

- The organic matter determined by walkley and black method as described by Ryan *et al.*, (2001). 1-g air-dry soil mixed with 10-mL 1*N* ($K_2Cr_2O_7$) potassium dichromate solution + 20-mL concentrated sulfuric acid (H_2SO_4), allowed to stand for 30-min, 200-mL of distilled water added + 10-mL H_3PO_4. After cooling 10-drops of diphenylamine used as indicator before titrating with 0.5*M* [$(NH_4)_2SO_4.FeSO_4.6H_2O$] ferrous ammonium sulfate on a magnetic stirrer, until color changes from violet-blue to green, two blanks prepared and treated the similarly as the soil suspensions. Results were as the percentage of oxidizable organic carbon converted to percentage total organic carbon (TOC) and organic matter (OM) using a constant conversion factors.

- Calcium carbonate (%$CaCO_3$), determined by the method presented in by Ryan *et al.*, (2001). 1-g air-dry soil reacted with 20-mL (1*N* HCl) hydrochloric acid, heated to 50-60^{0}C. After cooling 50-mL H_2O added + two-drops of phenolphthalein as indicator and titrated with (1*N* NaOH) sodium hydroxide until a faint pink color developed, blanks prepared and treated in the same way. The above-mentioned analysis results performed at the Soil Laboratory of Misurata Agricultural Research Station (ARS).

- Available P in soil samples extracted by 0.5 *M* $NaHCO_3$ (Olsen-P, 1:20 soil/solution ratio) according to (Sims, 2000). A 1.0-g of sieved (< 2-mm), air-dried soil was weighed out into 50-mL polystyrene centrifuge tubes and 20-mL of Olsen extracting solution [pH adjusted to 8.5

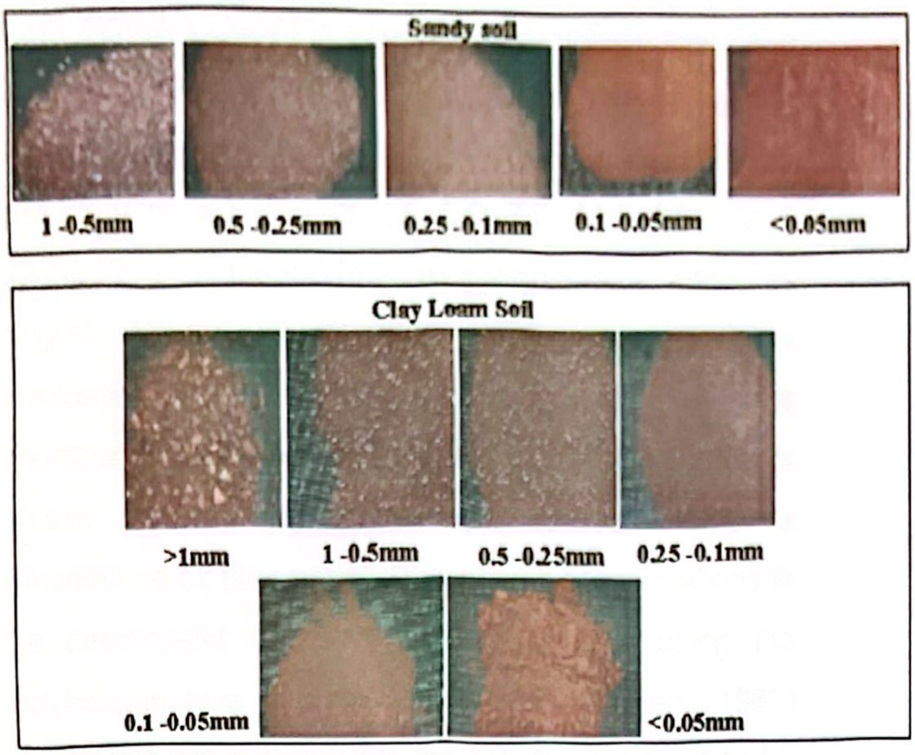
with (50% NaOH) sodium hydroxide] was added, the suspension was shaken for 30-minutes at room temperature, and filtered through whatman no. 42 filter paper. Concentration of phosphorus in the extract was determined by the molybdenum-blue method (Olsen and Sommers, 1982) using a blank and standards prepared in the Olsen-P extracting solution, (UV-120-01 spectrophotometer) used after allowing 30-minutes for color development.

- Total phosphorus and heavy metals determined in soil samples and all the aggregate-sizes. A 1-g of air-dried soil or aggregate-size digested with aqua regia (3:1 hydrochloric / nitric acid), 18-mL of HCl and 6-mL of HNO_3 in a 40-ml beaker, on a hot plate until about 5-to10-mL of extract remains in the flask, ensuring that the sample covered with solution. After cooling boiling repeated in the same manner, after cooling 20-mL of distilled water added and the extract filtered through an acid washed (1%HNO_3) Whatman no.42 filter paper into 50-ml volumetric flask and make up to the mark by distilled water. A reagent blank with no soil included with each process batch of samples. Concentrations of total P and heavy metals in the extract analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, HITACHI) at (LISC).

- Available-P and heavy metals in different aggregate fractions were determined using the Mehlich-III method (Sims, 2000). A 2.5-g air-dried fraction sample was weighed out into 50-ml polystyrene centrifuge tubes and 25-mL Mehlich-III extracting solution (0.2*M* CH_3COOH, 0.25*M* NH_4NO_3, 0.015*M* NH_4F, 0.013*M* HNO_3, 0.001*M* EDTA [$(HOOCCH_2)2NCH_2CH_2N$ $(CH_2COOH)_2$] was added, the suspension was shaken for 5-min, and filtered through whatman no.42 filter paper. Concentrations of metals in the extract analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, HITACHI) at (LISC).

- Water-soluble P and heavy metals determined by, shaking 4-g of the aggregate sample in 40-mL of distilled water for 8-d (Zhang *et al.*, 2003). The suspension centrifuged at 7500-rpm for 30-min, filtering the supernatant solution through a whatman no.42 filter paper, and then measuring the concentrations of P and heavy metals in the filtrate using the ICP-AES at (LISC).

- Sand aggregate-sizes separated by manually moving the sieve in an up and down motion about 50-times (Zhang *et al.*, 2003). Approximately 1.5-to 2kg of each soil separated by dry sieving into different aggregate-sizes in similar way to sand-aggregate-sizes in USDA method (Day, 1965). The > 1.00-mm aggregates collected and sieving repeated with the < 1.00-mm fraction for next sample-sized sieve. This procedure repeated until all the aggregate-sizes (1.00-to 0.50, 0.50-to 0.25, 0.25-to 0.10, 0.10-to 0.05, and, < 0.05-mm) were obtained (Fig. 3.1).



(Fig. 3.1) **sand-aggregate-sizes separated by dry sieving from the soils sampled.**

All aggregate-sizes weighed and used for extractions of available elements, and studies of P adsorption. Subsamples of the aggregate-sizes ground to pass through a 0.10-mm sieve for determining total concentrations of P and elements.

- Phosphate sorption measured in bulk soils and all of the aggregate-sizes separated from the different soils. Soils, 1-g each placed in polystyrene centrifuge tubes and 30-mL of 0.02*M* KCl solution containing 0, 2.5, 5, 7.5, 10, 15, and, 20-mg p L^{-1} as KH_2PO_4. For different aggregate size samples, (1.00-g used for, the >0.05-mm aggregate-sizes and, 0.50-g for the < 0.05-mm aggregate-size). Samples placed in polystyrene centrifuge tubes and treated with 30-mL of 0.02*M* KCl solution containing: For the > 0.05-mm aggregate-sizes, (0, 1.5, 3.0, 4.5, 6.0, 7.5, and, 10.0-mg p L^{-1}) or (0, 2.5, 5.0, 7.5, 10.0, 15.0, and, 20-mg PL^{-1}), for the < 0.05-mm aggregate-size, added as KH_2PO_4 (Zhang *et al.*, 2003). Tubes placed on a mechanical shaker for 24-h equilibration. Following equilibration, samples were centrifuged at 10000-rpm for 10-min and the supernatant was filtered through a whatman no.42 filter paper. Phosphorus concentrations in the supernatant solutions were determined using the molybdenum-blue method (Olsen and Sommers, 1982) phosphorus not recovered in the solution assumed to be retained by the different soil particles and calculated as follows (Reddy *et al.*, 1998):

$$[(C_i * V) - (C_e * V)] / M = S' \qquad [1]$$

Where

C_i = initial concentration of P, (mg L^{-1})

V = volume of liquid, L

C_e = concentration of P in solution after 24-h equilibration, (mgL^{-1})

M = mass of soil fraction, (kg)

S' = P-sorbed by solid phase, (mg kg^{-1}).

Equation [1] used primarily to calculate the P adsorbed or released in relation to P added to the soil. These calculations do not account for the native-soil P in the adsorbed phase. The total amount of P (native + added) retained by soil calculated as follows:

$$S = S' + S_o \qquad [2]$$

Where

S = total amount of P-sorbed (mg kg^{-1}),

S' = p retained by the solid phase (mg kg^{-1}),

S_o = initial soil-P present in adsorbed phase (mg kg^{-1}).

The S_o can be estimated using a least squares fit of S' measured at low equilibrium concentrations C_e. At these concentrations the relationship between S' and C_e is typically Linear and described by the following equation:

$S' = k\, C_e - S_o$ [3]

Where

S_o = the y-axis intercept representing the initial soil P present in the adsorbed-phase, (mg kg^{-1}).

K = linear adsorptions coefficient (estimated without considering native adsorbed-P, S_o), (L kg^{-1}).

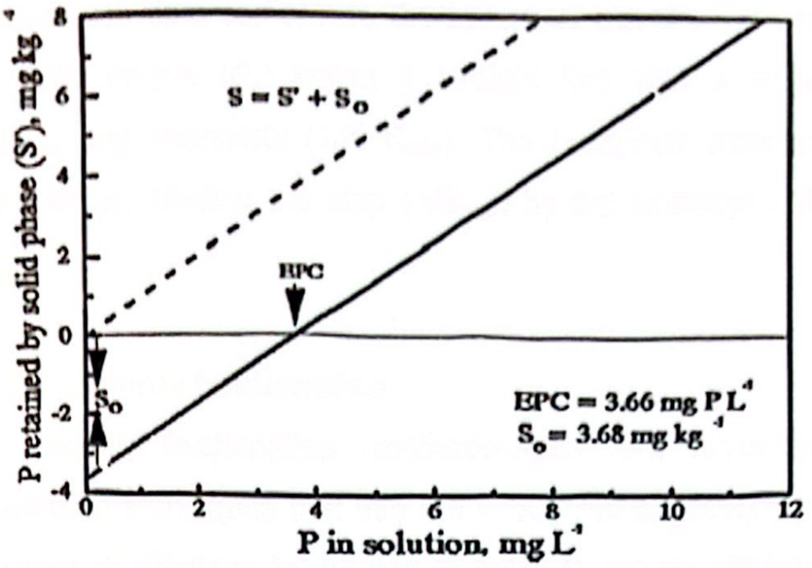
The EPC (equilibrium-P concentration) is defined as the concentration of P in solution where adsorption equals desorption ($S' = 0$). Thus,

$C_e = S_o / K$ [4]

Where

C_e = EPC, (mg L^{-1})

The method used to obtain EPC and S_o is shown in (Fig.3.2) using a data point as an example of the calculations (Graetz and Nair, 1995).



(*Fig.3.2*) Illustration of procedure used to adjust the total amount of P- adsorbed by the soil, taking into consideration s_o, the initial p present in the soil.

A common form of the Langmuir equation employed to describe the P sorption isotherms:

$S = k\,C\,S_{max} / 1 + kC$ *[5]*

Equation (5) rearranged to the linear form to permit easy verification of whether data conform to the Langmuir model

$C_e / S = 1 / (K\,S_{max}) + Ce / S_{max}$ *[6]*

Where

S = the total amount of P in adsorbed phase ($S' + S_o$), (mg kg^{-1})

S_{max} = P-sorption maximum, (mg kg^{-1})

K = a constant related to binding energy, (Lmg^{-1}p)

C_e = concentration of P measured after 24-h equilibration, (mg L^{-1}).

If adsorption data conform to the Langmuir equation, a plot of (C_e/S) versus (C_e) yields a straight line with a slope ($1/S_{max}$) and intercepts ($1/K\ S_{max}$). The Langmuir constant obtained by, dividing the slop ($1/S_{max}$) by the intercept ($1/K\ S_{max}$).

- **Phosphorus fractionation**

Soil-P fractionation methodologies are selective dissolution techniques that use the sequential application of a series of solutions to the soil in order to extract different soil P compounds. It is thought that these soil P compounds are related to different soil P forms and therefore could have variable availability to plants (labile-P, Fe and Al-phosphates, Ca-phosphates, Occluded-P, Organic-P, etc.).

The procedure used in this study suggested by Sui *et al.*, (1999) to extract empirically defined pools of P. Diagrammatic representation of this scheme in (Fig.3.3).

A 0.5-g aggregate sample placed into a 50-mL centrifuge tube and sequentially extracted with 30-mL each of the following extracts:

1. Distilled water,
2. 0.5 *M* $NaHCO_3$ (pH = 8.2),
3. *0.1M* NaOH, and
4. 1 *M* HCl.

Step 1: Shaking a 0.5-g of aggregate sample in 30-mL of distilled water for, 16-h. The suspension centrifuged at 6000-rpm for, 30-min, filtering the supernatant solution through a whatman no.42 filter paper. Then the conc. of P measured in the filtrate by the molybdenum-blue method

(Olsen and Sommers, 1982) using a blank and standard solutions prepared in the same extracting solution by using (UV-120-01 Spectrophotometer) after 30-minutes to allow the color to develop.

Step 2: Soil in the filter paper washed back into the tube with a few amount of 0.5*M* $NaHCO_3$ (pH-8.5) solution. More $NaHCO_3$ solution added to bring solution volume to 30-mL, shaking the suspension for, 16-h on the mechanical shaker, centrifuging soil suspension at 6000-rpm for 30-min, filtering the extract through a whatman no.42 filter paper, and then measuring the concentrations of inorganic and total P in the filtrate.

Step 3: Soil in the filter paper washed back into the tube with a few amount of 0.1*M* NaOH solution. More NaOH solution added to bring the solution volume to 30-mL, shaking the suspension for 16-h on the mechanical shaker, centrifuging soil suspension at 6000-rpm for 30-min, filtering the extract through a whatman no.42 filter paper, and then the concentrations of inorganic and total-P in NaOH extract were measured.

Step 4: Soil in the filter paper washed back into the tube with a few amount of 1*M* HCl solution. More HCl added to bring volume to 30-mL, shaking the suspension vigorously for, 16-h after making sure all soil is free from bottom of tube before putting on the shaker. Soil suspension centrifuged at 6000-rpm for 30-min, filtering the extract through a whatman no.42 filter paper, and then the concentrations of inorganic P in extract were measured.

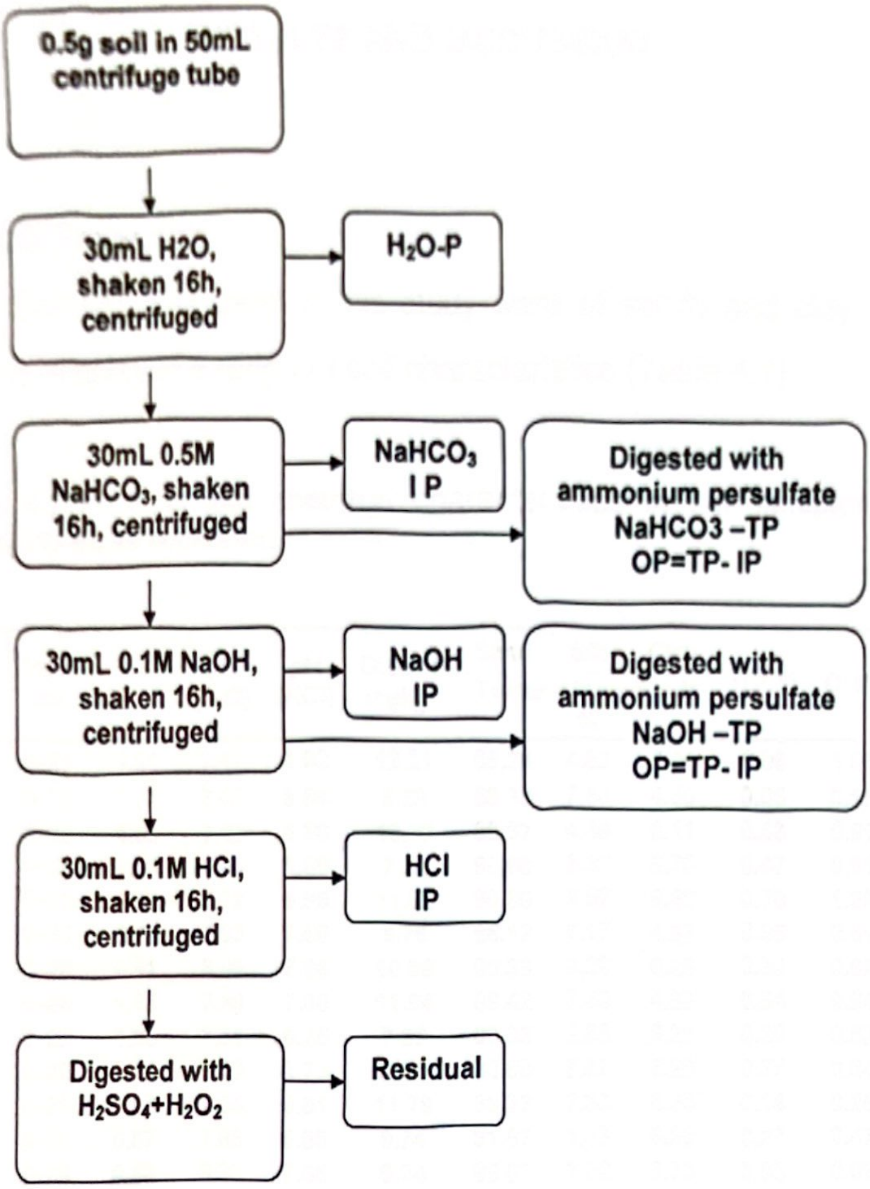
Step 5: residual P was determined in the soil residue left in the centrifuge tubes by digesting the soil sample with H_2SO_4-H_2O_2 (Tiessen and Moir, 1993). A minimum amount of distilled water used to transfer the entire soil residue into 75-mL digestion tubes + 5-mL conc.H_2SO_4. Put on a cold digestion block, temperature raised slowly up to 360^{0}C, cooling to hand warm, 0.5*ML* H_2O_2 added, reheating for 30-min, this step repeated until the liquid is clear, after cooling and making to volume the extract centrifuged and filtered to determine P concentration.

Determination of inorganic-P on 0.5*M* $NaHCO_3$ and 0.1*M* NaOH:

10-mL of solution acidified to pH-1.5 and set in the fridge for 30-min, where 6-mL of 0.9*M* H_2SO_4 used to acidify 0.5*M* $NaHCO_3$ and 1.6-mL to acidify 0.1*M* NaOH (for organic matter precipitation), centrifuged at 6000-rpm for 10-min.

Determination of total-P in 0.5*M* $NaHCO_3$ and 0.1*M* NaOH:

A 5-mL of, 0.5*M* $NaHCO_3$ extract + 10-mL of 0.9 *M* H_2SO_4 + 0.5-g of ammonium persulfate $(NH_4)_2S_2O_8$, (autoclave for 60-min). A 5-mL of 0.1M NaOH extract + 10-mL of 0.9*M* H_2SO_4 + 0.6-g of ammonium persulfate, (autoclave for 90-min) (Greenberge, 1992). Orthophosphate-P (iP) in the initial filtrates and, in the digests of each extract were determined calorimetrically by the molybdenum-blue method (Olsen and Sommers, 1982). Using a blank and standards solutions prepared in the same extracting solution by using (UV-120-01 Spectrophotometer) after allowing 30-minutes for color to develop, differences between the total and the inorganic-P represent organic P (oP) as show in (Fig.3.3).



(Fig. 3.3) **Sequential P Fractionation Scheme, according to Sui et al. (1999)**

CHAPTER
4

RESULTS AND DISCUSSION

4.1 Soil Properties

Soil samples used in this study were of sandy and clay loam texture, displayed a range of soil characteristics (*Table 4.1*).

Table 4.1 **Physical and chemical characteristics of soil samples and aggregate-sizes separated.**

Soils	Depth cm	EC dSm-1	pH (H_2O)	pH (KCl)	Olsen P mgkg^{-1}	Sand	Silt	Clay	TOC%	OM%	$CaCO_3$%
						Textural ingredients %					
S1	0–20	1.31	7.17	6.92	12.21	89.29	4.82	5.89	0.96	1.65	5.76
S2	0–20	0.94	7.42	6.84	8.69	88.38	7.54	4.50	0.06	0.10	6.00
S3	0–20	1.62	7.23	6.88	10.38	89.57	4.30	6.11	0.53	0.91	6.52
S4	0–20	1.39	7.68	6.89	7.36	90.60	3.37	5.70	0.47	0.81	5.12
S5	0–20	1.13	7.72	6.90	11.82	90.80	2.57	6.63	0.70	1.20	4.82
S6	0–20	2.01	7.93	7.50	9.76	88.17	7.17	4.67	0.35	0.61	8.14
S7	0–20	0.61	8.09	7.08	10.08	90.33	3.22	6.28	0.39	0.67	3.90
S8	0–20	1.18	7.86	7.06	11.04	88.42	7.50	4.50	0.54	0.94	3.12
S9	0–20	1.18	7.51	6.75	7.65	90.33	2.88	6.28	0.30	0.52	3.55
S10	0–20	1.76	7.19	6.73	9.56	88.80	5.67	6.20	0.37	0.64	6.88
S11	0–20	1.17	7.54	6.81	11.78	88.33	7.33	4.33	0.14	0.25	4.45
S12	0–20	0.87	7.86	6.88	9.74	91.67	1.43	6.90	0.27	0.47	4.13
S13	0–20	0.58	8.33	7.56	9.04	89.67	7.00	3.33	0.05	0.09	5.68
S14	0–20	0.76	7.88	7.31	5.16	90.27	2.33	7.40	0.08	0.14	3.32
S15	0–20	0.49	8.29	7.56	9.02	89.00	4.67	6.33	0.03	0.06	3.50
CL1	0–20	0.41	7.96	7.42	11.31	28.67	33.00	38.33	1.57	2.71	3.25

S = Sandy soils.
CL = clay loam soil (Average of triplicate sample).
TOC = %Total organic carbon = % Oxidizable organic carbon ×1.334
OM = %Organic mater = % TOC × 1.724
EC = Electrical conductivity.

Table 4.1 Continued

Soils	Total Concentration (g Kg^{-1})													
	Al	Fe	P	Ca	K	Mg	Na	Mn	Ba	Cd	Ni	Cr	Pb	Cu	Zn
S1	6.37	4.67	0.36	81.23	13.76	18.82	1.77	0.23	0.17	3.87	1.21	1.08	2.46	0.60	0.80
S2	11.12	4.99	0.24	157.33	20.88	19.54	7.78	0.16	0.10	3.17	1.09	0.60	1.18	0.59	0.88
S3	8.34	5.88	0.40	137.58	16.71	20.26	2.65	0.26	0.10	3.87	1.32	1.03	0.28	0.87	0.85
S4	11.85	5.25	0.15	119.89	16.33	16.24	5.77	0.20	0.10	2.27	0.87	0.60	0.32	0.53	0.72
S5	11.45	6.32	0.27	114.67	16.35	16.81	5.68	0.21	0.10	2.66	0.93	0.68	1.31	0.57	0.70
S6	7.00	5.55	0.31	116.58	13.41	16.25	5.56	0.11	0.11	2.80	0.97	0.58	2.63	0.39	0.66
S7	15.22	6.43	0.34	113.16	16.06	15.94	5.42	0.19	0.12	2.78	0.85	0.60	0.37	0.42	0.72
S8	5.18	4.86	0.38	100.65	9.54	12.73	2.54	0.11	0.11	2.86	0.92	0.52	6.04	0.34	0.46
S9	10.74	5.13	0.35	74.80	13.00	12.94	4.45	0.16	0.09	1.81	0.69	0.49	0.28	0.41	0.58
S10	5.17	3.27	0.45	87.58	9.12	11.61	3.74	0.10	0.08	1.26	0.65	0.41	0.22	0.31	0.54
S11	8.05	5.47	0.30	123.57	10.39	12.13	4.15	0.11	0.06	2.16	0.69	0.45	0.22	0.30	0.53
S12	10.18	6.36	0.25	132.23	11.49	10.96	3.87	0.14	0.10	2.51	0.59	0.41	0.28	0.19	0.49
S13	7.19	2.33	0.36	87.94	8.89	8.81	2.92	0.07	0.08	1.14	0.46	0.33	0.22	0.25	0.41
S14	7.51	5.51	0.31	104.00	9.95	13.02	3.85	0.13	0.09	1.23	0.46	0.33	0.21	0.39	0.45
S15	7.39	4.06	0.38	100.58	10.76	10.68	3.57	0.11	0.10	1.40	0.56	0.40	0.26	0.31	0.51
CL1	79.40	38.03	2.02	311.61	10.76	4.66	1.63	0.32	0.23	1.34	0.20	0.12	0.12	0.18	0.20

Table 4.2 Average total concentration of metals in the aggregate sizes of soils sampled.

aggregate sizes of the sandy soil (mm)	concentration (g Kg^{-1})													
	Al	Fe	P	Ca	K	Mg	Na	Mn	Ba	Cd	Ni	Cr	Pb	Cu	Zn
< 0.05	89.35	42.09	1.23	212.02	121.71	166.37	24.60	1.22	1.39	27.10	6.93	7.13	18.09	6.83	6.33
0.10 - 0.05	18.41	7.17	0.52	173.48	38.47	18.88	6.83	0.33	0.25	3.64	0.99	0.97	2.65	0.96	0.89
0.25 - 0.10	9.23	7.53	0.39	146.68	8.43	20.93	5.87	0.15	0.08	3.55	1.52	0.67	0.77	0.20	0.90
0.50 - 0.25	2.58	1.91	0.21	67.15	2.42	4.42	1.78	0.05	0.02	0.54	0.21	0.14	0.27	0.13	0.20
1.00 - 0.50	4.83	3.66	0.12	95.18	10.92	9.86	3.99	0.16	0.06	1.04	0.50	0.35	0.98	0.32	0.33

aggregate sizes of the clay loam soil (mm)	concentration (g Kg^{-1})													
	Al	Fe	P	Ca	K	Mg	Na	Mn	Ba	Cd	Ni	Cr	Pb	Cu	Zn
< 0.05	82.70	39.89	2.39	344.47	11.30	4.83	1.78	0.34	0.40	1.41	0.40	0.22	0.13	0.38	0.39
0.10 - 0.05	81.59	39.54	2.20	332.38	11.30	4.65	1.78	0.33	0.30	1.37	0.23	0.20	0.13	0.21	0.22
0.25 - 0.10	80.58	38.98	2.20	325.87	11.05	4.65	1.71	0.32	0.20	1.37	0.21	0.10	0.12	0.19	0.20
0.50 - 0.25	80.27	38.77	2.02	324.16	10.72	4.65	1.71	0.32	0.20	1.32	0.17	0.10	0.12	0.15	0.17
1.00 - 0.50	77.19	37.65	1.89	318.36	10.38	4.64	1.56	0.31	0.20	1.31	0.15	0.10	0.12	0.14	0.15
> 1.00	76.61	33.73	1.61	216.70	10.30	4.59	1.26	0.29	0.20	1.28	0.15	0.09	0.11	0.10	0.15

The analytical data revealed that both soils in the (0-to 20cm) layer were alkaline in reaction, calcareous in nature with an average of 7.71 (pH- H_2O), 7.04 (pH- KCl) and 4.99% ($CaCO_3$) for sandy soils and 7.96 (pH- H_2O), 7.42 (pH- KCl) and 3.25% ($CaCO_3$) for clay loam soil.

I found that the pH values of the soils measured in 1M KCl were almost not similar to those measured in water; they were 0.66 units lower on average.

Significance of pH lies in its influence on availability of soil nutrients, solubility of toxic nutrient elements in the soil, physical breakdown of root cells, cation exchange capacity in soils whose colloids (clay/humus) are pH dependent, and on biological activity. At high pH values availability of phosphorus (P) and most micronutrients, except boron (B) and molybdenum (Mo), tends to decrease. Soils of dray areas are generally alkaline, i.e., above pH 7.0 because of the presence of calcium carbonate ($CaCO_3$), (Ryan *et al.* 2001).

Electrical conductivity (EC) of sandy soils (1.13 dSm^{-1} on average) were higher than that of clay loam soil (0.14 dSm^{-1} on average), in contrast of organic matter which were (2.71 % on average in clay loam soil) higher than that of sandy soils (0.60% on average) almost certainly due to dissimilar of regions and clay content.

Available soil P values were (9.55 mg Kg^{-1} and 11.31 mg Kg^{-1} on average) respectively for sandy and clay loam soils.

Sims (2000) the Olsen P method is best suited for calcareous soils, particularly those with > 2% calcium carbonate. The method is based on the use of the HCO^{3-}, $CO3^{-3}$ and OH- in the pH 8.5, 0.5M $NaHCO_3$ solution to decrease the solution concentrations of soluble Ca^{2} by precipitation as $CaCO_3$ and soluble Al^{3+} and Fe^{+3} by formation of Al and Fe oxyhydroxides, thus increasing P solubility.

4.2 Distribution of Aggregate-Size Fractions in Different Soils

The relative distribution differences in aggregate-sizes separated from sandy soils were higher when compared with those from clay loam soil. Generally, results of separated aggregate-sizes from fifteen sandy soil samples showed that the 1.00-to 2.00mm size fraction was negligible and accounted for 0%, and < 0.05mm size fraction accounted for (1.49-to 2.29%) of the soil air dry weight. Sandy soils were dominated by the 0.50-to 0.25 and 0.25-to 0.10mm these two sizes, accounted on the average for 50.75% and 24.66% of the soil air dry weight respectively (*Table 4.3* and *Fig 4.1).*

The results reported are different from those of Linquist *et al.* (1997), who found that about 50% of soil aggregates exceeded 1.00mm in diameter, and more or less agree with those of Zhang *et al.* (2003), who reported that the aggregate-sizes from an sandy soil was dominated by the 0.50-to 0.25 and 0.25-to 0.10mm sizes. These two fractions, on the average, accounted for 80.6% of the dry soil weight, and the proportion of < 0.053mm aggregate was below 1.5% in all sandy soil samples.

The particle composition of different separates of sandy soils was mainly of the same size of individual particles, the aggregate-sizes 1.00-to 0.50, 0.50-to 0.25, 0.25-to 0.10 and 0.10-to 0.05mm contained 92.32% of the 1.00-to 0.50-mm, 93.8% of the 0.50-

(*Table 4.3*) **Soil composition of dry-separated aggregate-sizes in (0-to 20cm) layer.**

Soils	Aggregate fractions, mm (%)					
	>1.00	1.00–0.50	0.5–0.25	0.25–0.10	0.10–0.05	<0.05
S1	0.00	3.95	52.50	24.54	16.76	2.29
S2	0.00	4.14	41.45	30.37	22.08	1.95
S3	0.00	4.14	41.25	30.17	22.28	2.20
S4	0.00	6.26	52.43	20.17	19.47	1.67
S5	0.00	7.58	50.30	19.98	20.27	1.88
S6	0.00	7.48	46.67	31.65	12.71	1.49
S7	0.00	5.10	52.08	20.14	20.44	2.25
S8	0.00	2.07	56.71	30.33	9.16	1.74
S9	0.00	5.10	52.47	20.24	20.44	1.75
S10	0.00	2.38	52.32	31.89	11.69	1.72
S11	0.00	3.35	49.91	29.41	15.61	1.73
S12	0.00	9.10	48.07	19.79	21.07	1.99
S13	0.00	4.76	53.67	19.96	19.57	2.05
S14	0.00	5.12	54.66	20.98	17.77	1.49
S15	0.00	1.31	56.79	20.30	19.81	1.81
CL	13.40	27.60	19.48	16.54	12.39	10.59

***Table 4.3* continued**

Fraction Size (mm)	Soils	*Mean (%)	Std. Deviation	Std. Error	Minimum	Maximum
>1.00	Sandy Soil	0.00a	0.00	0.00	0.00	0.00
	**Clay loam	13.40b	0.52	0.30	13.10	14.00
1.00-0.50	Sandy Soil	4.79a	2.15	0.56	1.31	9.10
	Clay loam	27.60b	2.36	1.36	25.60	30.20
0.50-0.25	Sandy Soil	50.75b	4.71	1.22	41.25	56.79
	Clay loam	19.48a	0.42	0.24	19.00	19.72
0.25-0.10	Sandy Soil	24.66b	5.20	1.34	19.79	31.89
	Clay loam	16.54a	0.80	0.46	15.62	17.00
0.10-0.05	Sandy Soil	17.94b	3.99	1.03	9.16	22.28
	Clay loam	12.39a	0.33	0.19	12.00	12.58
<0.05	Sandy Soil	1.87a	0.25	0.07	1.49	2.29
	Clay loam	10.59b	1.65	0.95	8.78	12.00

*Means followed by the same letter are not significantly different at the 0.05 probability level.

**Average of triplicate samples.

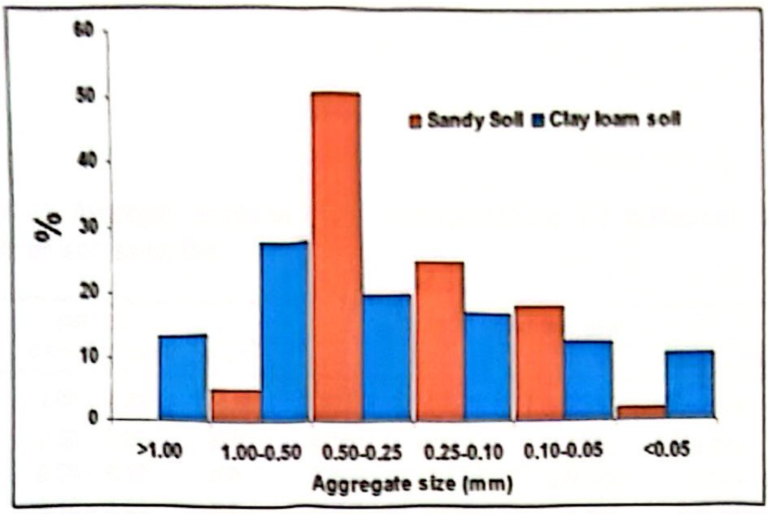


Fig 4.1 **Average soil composition of dry-separated aggregate-sizes in (0-to 20cm) layer.**

to 0.25-mm, 93.05% of the 0.25-to 0.10-mm, and 82.77% of the 0.10- to 0.05-mm particles, respectively. The sandy soil samples showed that the sand, silt and clay contents among 1.00-to 0.05mm aggregate-sizes were significantly distributed (*Table 4.4*). The contents increased as the particle size decreased in the order of < 0.05, 0.10-to 0.05, 0.25-to 0.10, 0.5-to 0.25 and 1.00-to 0.50mm fraction, whereas the sand and silt content increased in the opposite direction.

Zhang *et al.* (2003) reported that the Differences in sand, silt, and clay contents among 1.0-to 0.50, 0.50-to 0.25, and 0.25-to 0.10-mm aggregate-sizes were not significant, whereas significant differences in clay, silt, and, sand contents found between the < 0.05,

(*Table 4.4*) **Average particle size compositions of different aggregate fractions of soil samples**

Soils	particle composition	aggregate fractions mm (gkg-1)					
		2 – 1	1 -0 .5	0.5 – 0.25	0.25 – 0.1	0.1– 0.05	< 0.05
sandy soils n=15	1.00 – 0 .50	NA∞	923.2b	0.00a	0.00a	0.00a	0.00a
	0.50 – 0.25	NA	6.53b	938.01c	0.00a	0.00a	0.00a
	0.25 – 0.10	NA	8.80b	8.21b	930.49c	0.00a	0.00a
	0.10 – 0.05	NA	10.35b	10.98b	15.68c	827.69d	0.00a
	< 0.05	NA	51.13b	42.81a	53.75c	172.31d	1000.00e
	sand	NA	960.80e	951.29d	943.05c	844.34b	0.00a
	silt	NA	26.60a	34.21b	38.69c	132.95d	918.01e
	clay	NA	12.60a	14.50b	18.26c	22.71d	81.99e
clay ‟ loam Soil (n=1)	2.00 – 1.00	134.25b	0.00a *	0.00a	0.00a	0.00a	0.00a
	1.00 – 0 .5	109.00b	145.00c	0.00a	0.00a	0.00a	0.00a
	0.5 0– 0.25	104.00b	126.50c	150.50d	0.00a	0.00a	0.00a
	0.25 – 0.10	106.00b	120.50c	149.00d	213.50e	0.00a	0.00a
	0.10– 0.05	168.25c	209.50d	174.50c	300.00e	153.50b	0.00a
	< 0.05	378.50a	398.50b	526.00d	486.50c	846.50e	1000.00f
	sand	488.50e	449.00d	429.50c	490.00f	35.50b	0.00a
	silt	299.00b	318.50d	377.00e	301.00c	575.00f	121.50a
	clay	212.50c	232.50d	193.50a	209.00b	389.50e	878.50f

*Means followed by the same letter within the same row are not significantly different by Duncan's multiple range tests at the 0.05 probability level.

‟Average of triplicate samples.

∞No available sample.

> 0.10, and, 0.1-to 0.05mm aggregate-sizes. Clay content was higher in the < 0.05mm size than in the > 0.10 and 0.10 - 0.05mm fractions, whereas sand and silt contents decreased in the order of < 0.05, 0.05 - 0.10, and >0.10mm size.

In the other hand, the difference distribution of particle composition of different aggregate-sizes of the highly aggregated clay loam soil was almost similar except for the fractions 0.10 - 0.05 and < 0.05mm. The clay content of the aggregate-sizes of the clay loam soil was markedly higher than that of the sandy soils, because of differences in texture, organic matter content, and type of clay minerals, which influences the cohesive forces among particles. Where an aggregate is a group of two or more primary particles cohere to each other more strongly than to surrounding particles. Therefore clay loam soil is highly aggregated and maintained their identity as aggregates.

These results reflect in addition to differences in clay and organic matter content, the differences in geological origin and in the climatic conditions dominating in the two sites.

Linquist *et al.* (1997) found that all aggregate-size fractions except the two smallest fractions (< 0.072 and 0.027mm) from an Ultisol had similar particle-size distribution and clay mineralogical composition.

4.3 Distribution and attachment of P and Heavy Metals in the Aggregate Fractions

Distribution of P, Cd, Ni, Cr, Pb, Cu and Zn in different aggregate-sizes of sandy soils shows that, the large percentage of total concentration presented in the fraction (0.10-to 0.05) followed by, (0.25-to 0.10), (<0.05), (0.50-to 0.25) and (1.00-to 0.5mm), and the content of total on average was, 30.69%, 29.19%, 20.88%, 16.08% and 2.89% respectively.

(*Fig. 4.2* exemplifies the average contents of total P and heavy metals in the bulk aggregate-size of the total in soil samples).

On the other hand, as we compare the soil composition of different aggregate-sizes, with the average contents of total in these fractions, (Table 4.2). I suggest that, even if the coarser aggregate-sizes (1-to 0.05mm) was make up the largest portion of the soil mass (98.14%), its total content of total P, Cd, Ni, Cr, Pb, Cu and, Zn (2.89-to 330.69%) is considered to be relatively low, as compared to the fine fraction which make up only, 1.87% of the soil mass and, its total content of total P, Cd, Ni, Cr, Pb, Cu and, Zn was, 20.88% on average.

Since the smaller aggregate in the sandy soils contained more silt and clay (Table 4.4), The results from sandy soils advocate that pools of P and heavy metals increase with decreasing aggregate-sizes, but it was challenging to identify the same results from the clay loam soil because there was little difference in clay content along with the fractions.

Specific surface area increases with decreasing particle size (Agbenin and Tiessen, 1995).

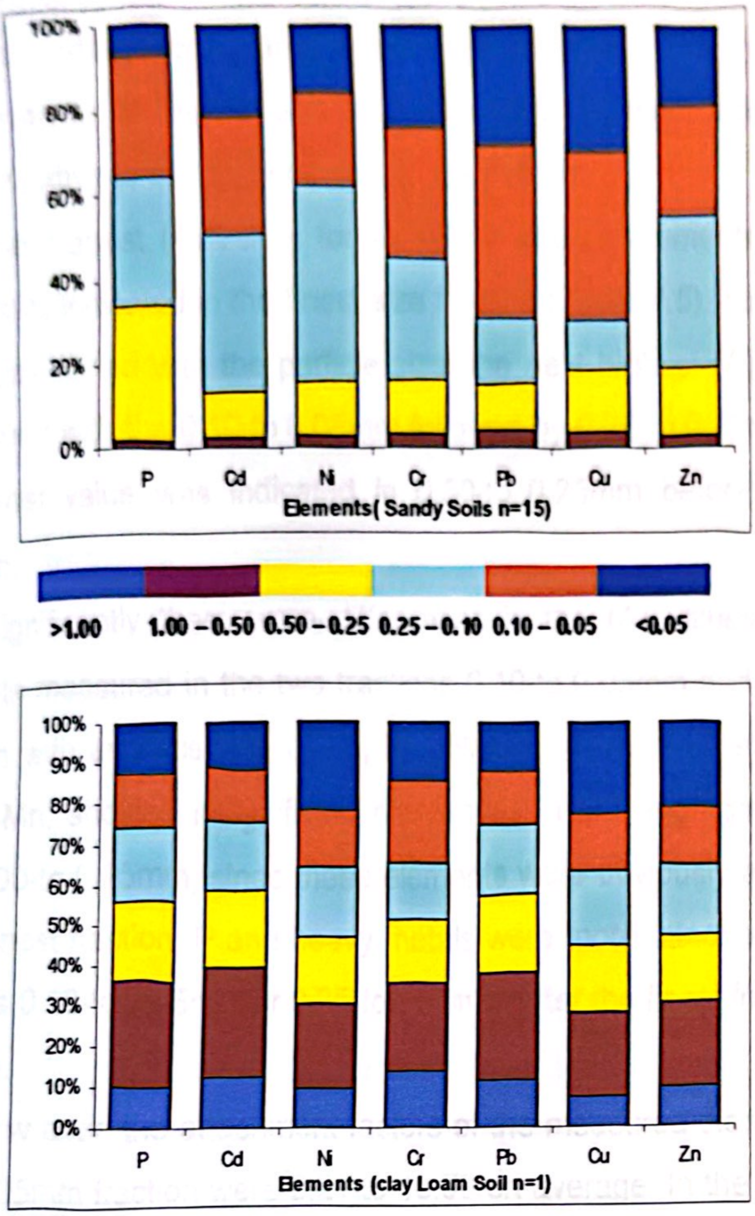


Fig 4.2 **Average distribution of P and heavy Metals, in different aggregate-sizes of soils.**

Zhang *et al.* (2003), increasing the concentration of P and heavy metals with decreasing aggregate-sizes was an indication of surface attachment.

The attachment factor (A), defined as the ratio of concentrations of macro and microelements in each aggregate fraction relative to the concentration in the bulk soil.

The highest (A) value, for all the measured elements in the sandy soils indicated in the finest size fraction (*Table 4.5*). Since this factor was varied with the particle size, the next highest (A) values were found with the 0.10-to 0.05mm followed by 0.25-to 0.10mm and the lowest value was indicated in 0.50-to 0.25mm before 1.00-to 0.50mm.

Significantly there were differences in the (A) values for all elements measured in the two fractions 0.10-to 0.05mm and 0.25-to 0.10mm with an exception of Fe, Mg, Na, Cd and Zn. All elements except Mn, showed insignificant differences in the aggregate-sizes from 1.00-to 0.25mm, since these elements were obviously attached to the finest fraction, P and heavy metals were more attached to the fractions 0.10-to 0.05mm or 0.25-to 0.10mm after the finest fraction < 0.05mm.

How ever, the attachment factors of the measured elements in the < 0.05mm fraction were 3.21-to 16.59 on average. In the case of P attachment factor in the aggregate-sizes was in the following sequence (< 0.05mm) > 0.10-to 0.05mm > 0.25-to 0.10mm or 0.50-to 0.25mm and 1.00-to 0.50mm (*Table 4.5*).

Table 4.5 Attachment factor of total elemental concentrations in different aggregate fractions of soil samples.

Elements	Fraction Size mm					
	>1	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
			Sandy Soils (n=15)			
Al	NA	0.44a*	0.24a	0.84a	1.69b	8.24c
Fe	NA	0.85a	0.45a	1.75b	1.67b	9.81c
P	NA	0.31a	0.55ab	0.93ab	1.32b	3.21c
Ca	NA	2.24b	1.57a	3.48c	4.10d	5.03e
K	NA	0.98a	0.22a	0.75a	3.44b	10.91c
Mg	NA	0.98a	0.44ab	2.09b	1.87b	16.59c
Na	NA	1.01ab	0.47a	1.47bc	1.71c	6.48d
Mn	NA	1.07b	0.33a	1.02b	2.29c	8.40d
Ba	NA	0.52a	0.14a	0.70a	2.15b	12.13c
Cd	NA	0.47a	0.24a	1.60b	1.64b	12.20c
Ni	NA	0.84ab	0.35a	2.57c	1.68b	11.74d
Cr	NA	0.58a	0.24a	1.10ab	1.60c	11.76d
Pb	NA	0.78a	0.21a	0.59a	2.10b	14.19c
Cu	NA	0.62a	0.25a	0.39a	1.89b	13.40c
Zn	NA	0.63a	0.38a	1.72b	1.71b	12.13c
Average		0.82	0.40	1.40	2.06	10.41
			Clay Loam soil (n=1)			
Al	0.96	0.97	1.01	1.01	1.03	1.04
Fe	0.89	0.99	1.02	1.02	1.04	1.05
P	0.80	0.93	1.00	1.09	1.09	1.18
Ca	0.69	1.02	1.04	1.04	1.07	1.10
K	0.96	0.96	0.99	1.03	1.05	1.05
Mg	0.98	0.99	1.00	1.00	1.00	1.03
Na	0.78	0.96	1.05	1.05	1.10	1.10
Mn	0.92	0.96	1.00	1.02	1.05	1.08
Ba	0.86	0.86	0.86	0.86	1.28	1.71
Cd	0.96	0.98	0.99	1.02	1.03	1.05
Ni	0.75	0.76	0.85	1.03	1.14	1.99
Cr	0.74	0.80	0.81	0.84	1.59	1.75
Pb	0.88	0.97	0.98	1.01	1.10	1.11
Cu	0.57	0.76	0.86	1.06	1.17	2.12
Zn	0.75	0.76	0.85	1.03	1.14	1.99
Average	0.83	0.91	0.95	1.01	1.12	1.36

*Means followed by the same letter within the same row are not significantly different by Duncan's multiple range test at the 0.05 probability level.

Attachment factors of heavy metals (Cd, Ni, Cr, Pb, Cu, and Zn) in the < 0.05mm size were (11.74 for Ni -to 14.19 for Pb) on Average, and the lowest (A) values indicated in 0.50-to 0.25mm or 1.00-to 0.50mm fractions.

Comparing with distribution of elements in different aggregate-sizes of sandy soil samples, elements concentrations in the clay loam soil were much similar and smaller, further than that the attachment factors in various fractions were smaller as will and averaged from 0.83-to 1.36.

Zhang *et al.* (2003) found that the next highest (A) values after the smallest aggregate-size > 0.05mm, were indicated with the 1.00 - 0.50mm size otherwise 0.10-to 0.05mm size. Al, Co, Cu, K, Mn, Na, Pb, and, Ba were more attached in the 0.10-to 0.05mm fraction than in the 1.00-to 0.50-mm fractions, whereas other elements were more attached in the 1.00 - 0.50-mm size than in the 0.10-to 0.05-mm aggregate-size.

These results refer to a great dissimilarity in P and heavy metal concentrations among the different aggregate-sizes of sandy soils, along with the similarity in the tendency for attachment factor of P and heavy metals for each fraction.

These finding were in agreement with those reported by (Zhang *et al.* 2003) suggesting that the aggregate-size fractionation is useful tool for identifying different pools of P and heavy metals in sandy soils, excluding this may be not true for highly aggregated soils. Linquist *et al*, (1997) did not find similar results because there was little difference in clay and mineralogy among the aggregate sizes from a highly aggregated soil that they examined.

4.4 Extractability of Phosphorus and Heavy Metals

Zhang *et al.* (2003) referred to (Kuo, 1996 and Mehlich, 1984), both deionized water and Mehlich-III solution are common extractants for testing available P and heavy metals, (Pote *et al.* 1999) soils with higher extractable P and heavy metals are considered more likely to lose P and metals to surface waters by erosion and surface or subsurface runoff, and (Kuo, 1996, Mehlich, 1984 and Pote *et al.* 1999) used the elemental extractability as a means to predict potential release capacity of these elements in soils.

Extractability, defined as the percentages of the total amounts of elements in each aggregate-size extracted by water and Mehlich-3 extraction.

The relative differences in water and Mehlich-III extractability of P and heavy metals from different aggregate fractions of the sandy soils were higher than that of clay loam soil, since the effects of aggregate-size were not distinguishable (*Table 4.6* and *4.7*). Thus, the difference in extractability among aggregates not reflecting only the effect of aggregate-size. However P and heavy metals extracted by Mehlich-3 were much greater than that extracted by water.

In sandy soils water extractability ranged from 0.69-to 8.08% for P and from 0.00-to 5.03% for heavy metals, the highest extractability for all elements was in the 0.50-to 0.25mm fraction, followed by the 1.00-to 0.50 mm, 0.25-to 0.10mm, 0.10-to 0.05mm, and the lowest extractability was in the < 0.05mm fraction.

In clay loam, soil the water extractability ranged from 0.21-to 0.50% for P and from 0.00-to 0.02% for heavy metals.

Table 4.6 Water extractability of P and metals from each aggregate fraction of soils

Elements %	Fraction Size mm					
	>1	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
			Sandy Soils (n=15)			
P	NA	8.08d*	4.47c	3.29b	2.22b	0.69a
Ca	NA	5.93b	7.16c	7.59c	2.58a	5.22b
K	NA	5.00d	7.03e	4.48c	1.76b	0.71a
Mg	NA	3.44d	5.10e	1.51b	2.54c	1.08a
Na	NA	1.02c	1.65d	0.23b	0.03a	0.01a
Mn	NA	0.39d	0.89e	0.27c	0.08b	0.02a
Ba	NA	1.22c	1.89d	0.15b	0.15b	0.10a
Cd	NA	1.20e	0.98d	0.21c	0.05b	0.01a
Ni	NA	2.10d	4.68e	1.02b	1.13c	0.14a
Cr	NA	2.94d	5.03e	0.50b	1.42c	0.10a
Pb	NA	1.07c	1.47d	0.56b	0.01a	0.00a
Cu	NA	1.00c	2.60d	0.64b	0.69b	0.18a
Zn	NA	2.04d	2.30e	0.65b	1.09c	0.06a
			Clay Loam Soil (n=1)			
P	0.50	0.30	0.22	0.23	0.23	0.21
Ca	3.23	3.04	2.95	2.99	2.96	2.76
K	4.80	4.94	3.13	3.28	3.01	2.57
Mg	0.02	0.02	0.01	0.01	0.00	0.00
Na	1.07	1.01	0.98	0.03	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.02	0.02	0.01	0.01	0.01	0.00
Cd	0.01	0.01	0.00	0.00	0.00	0.00
Ni	0.01	0.00	0.00	0.00	0.00	0.00
Cr	0.01	0.01	0.00	0.00	0.00	0.00
Pb	0.01	0.00	0.00	0.00	0.00	0.00
Cu	0.02	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00

*Values within a row followed by the same letter do not differ significantly by Duncan's multiple range test at the (*P* = 0.05) probability level.

Table 4.7 Mehlich-III Extractability of P and Metals from each aggregate fraction of soils

Elements %	Fraction Size mm					
	>1	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
Sandy Soils (n=15)						
Al	NA	40.20d*	42.28e	12.76c	5.26b	2.53a
Fe	NA	13.48d	18.18e	12.35c	4.42b	3.81a
P	NA	72.87d	32.40b	49.88c	20.90a	12.38a
Ca	NA	30.53b	33.24b	58.58d	19.01a	49.06c
K	NA	57.17d	66.28e	25.38c	18.90b	7.48a
Mg	NA	37.28d	55.25e	27.20c	22.95b	17.19a
Na	NA	24.22d	59.86e	21.89c	16.97b	12.12a
Mn	NA	36.54d	57.03e	32.67c	30.84b	18.86a
Ba	NA	29.17d	58.64e	23.63c	9.75b	6.12a
Cd	NA	23.43c	50.44d	4.91b	5.60b	2.20a
Ni	NA	30.20d	52.82e	59.29c	19.46b	2.71a
Cr	NA	19.84d	39.52e	11.49c	8.75b	5.05a
Pb	NA	13.35d	14.26e	11.06c	2.25b	5.06a
Cu	NA	12.53d	14.75e	11.57c	9.78b	6.34a
Zn	NA	15.24d	16.58e	8.85c	11.14b	7.54a
Clay Loam Soil (n=1)						
Al	24.18	12.10	11.00	18.94	12.64	8.43
Fe	6.19	5.54	5.36	6.62	5.69	5.41
P	11.96	11.47	12.86	13.09	10.85	10.12
Ca	16.11	14.53	15.66	16.63	16.06	13.44
K	32.74	31.67	48.21	30.46	22.40	11.90
Mg	15.36	14.45	16.46	15.91	16.02	14.16
Na	5.25	5.19	5.17	4.21	4.18	4.18
Mn	29.33	21.80	20.68	27.77	19.07	19.08
Ba	11.22	10.35	11.34	10.76	10.58	9.36
Cd	12.12	14.28	9.45	10.32	8.36	7.37
Ni	11.53	7.70	7.13	8.11	5.67	5.31
Cr	6.41	5.77	6.65	5.82	5.06	5.63
Pb	6.92	5.47	5.17	4.18	3.97	3.20
Cu	12.83	11.75	13.40	12.72	12.85	10.17
Zn	30.35	23.53	26.93	26.31	23.29	19.90

*Values within the same row followed by the same letter do not differ significantly by Duncan's multiple range test at the (*P* = 0.05) probability level.

Wide-ranging of Mehlich-III extractability for all elements in sandy soils, the extractability was highest in 0.50-to 0.25 and 1.00-to0.50mm aggregate-sizes, ranged from 10.56-to 40.77%, and the lowest was in < 0.05mm followed by 0.10-to 0.05 and 0.25-to 0.10mm.

Anyhow, Mehlich-III extractability for all elements followed approximately the same manner of water extractability. Comparing the results of attachment factor in (*Table 4.5*) with that of extractability in (*Table 4.6* and *4.7*), we suggest that the extractability increase with decreasing concentration of the element in the fractions, the release potential of P and heavy metals is increasing as the aggregate-size increased in sandy soils.

Zhang *et al*. (2003) concluded that the percentages of water-extractable and Mehlich III-extractable P and heavy metals were higher in both the 0.50-to 0.25 and 0.25-to 0.10-mm aggregate-sizes, suggesting that P and heavy metals in these two sizes more readily released to surface runoff or leached to ground water.

4.5 Phosphorus Sorption Capacity

In both soils and size fractions of soils adsorption parameters were calculated using the Langmuir adsorption equation, S_0 (originally sorped P on the solid phase, ($mgKg^{-1}$) was estimated using a least square fit of S' measured at low equilibrium concentrations (<10 $mgPL^{-1}$), (*Fig 4.3*) illustrate the method by using values of soil samples.

The linear portion of the graph used in the calculations had R^2 values of at least 0.95 (Nair *et al*. 1998).

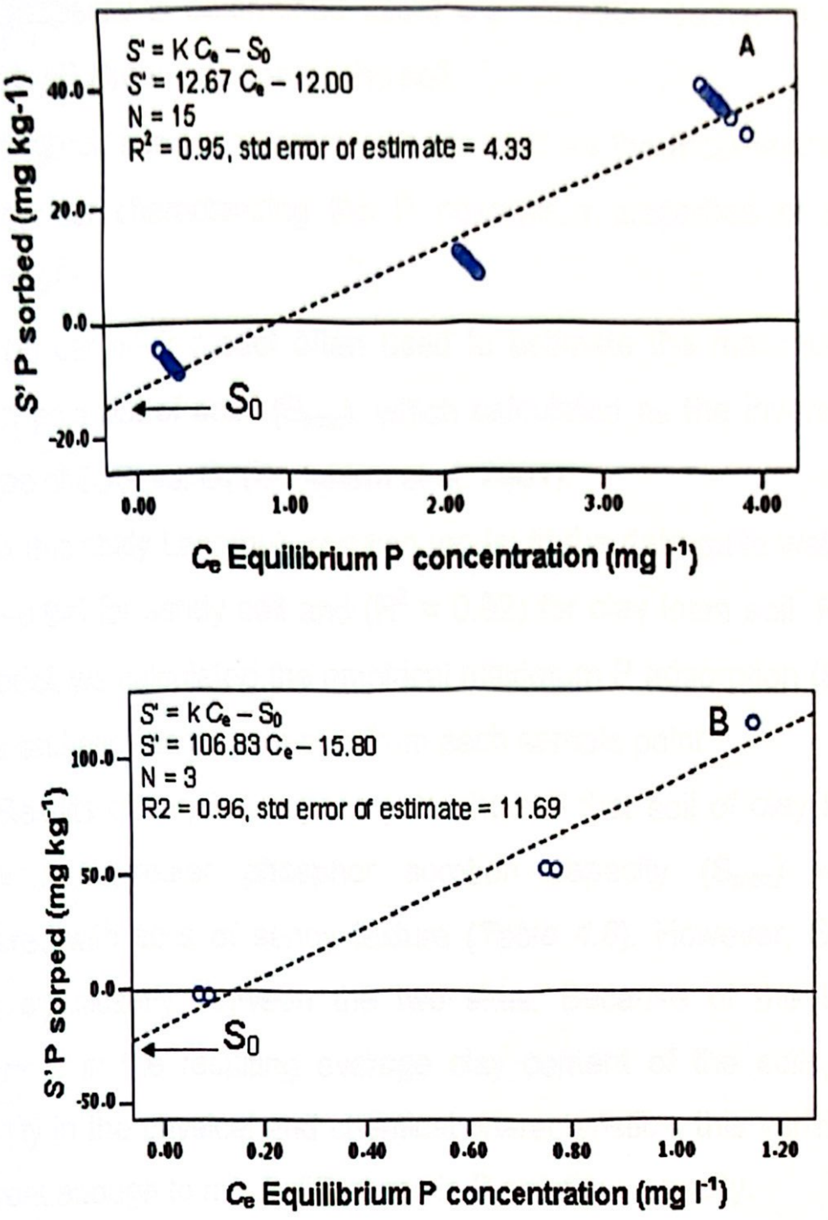


Fig 4.3 **The least square fit of (S') p retained by the solid phase mgkg^{-1} versus (*Ce*) concentration of p in solution after 24h equilibration, mgL^{-1}, (A) sandy soils, (B) clay loam soil.**

Graetz and Nair (2000) the maximum P sorption capacity of a soil is determined by soil properties and not by the P content in the soil. However, soils usually contain some sorbed P, and when P sorption capacity is determined using e.g. sorption isotherms, it is affected by P already sorbed by the soil.

Langmuir adsorption maximum reported as the most important parameter for characterizing the P adsorption properties of soils (Alam, 1999).

The Langmuir model often used to estimate the maximum P sorption potential of soils (S_{max}), which calculated as the inverse of the slope of C_e/S, vs. C_e (Bridgham et al. 2001).

In this study Langmuir sorption model fit the data quite well ($R^2 = 0.85–0.94$) for sandy soil and ($R^2 = 0.92$) for clay loam soil. From this model, we calculated the empirical maximum P adsorption (S_{max}) in soils and each aggregate-size from each sample point.

Results of sorption experiments showed that soil of clay loam texture had greater phosphor sorption capacity (S_{max}) when compared with soils of sandy texture (*Table 4.8*). However, Smax varied significantly between the two sites. Because of the large differences in the resulting average clay content of the soils, the variability in the physical and chemical characteristics, this variability was great enough to make difference in P sorption capacity.

The Langmuir sorption maxima (S_{max}) of the sandy soils ranged from 114.45 to 163.28 mg P kg^{-1}, with a mean value of 137.33mg P kg^{-1}, and from 445.28-to 447.38 mg P kg^{-1}, with a mean value of 445.33 mg P kg^{-1} in clay loam soil. The binding strength constant (K lmg^{-1}), was also higher in the clay loam soil, in which ranged from

0.31-to 0.33 lmg^{-1}, with a mean value of 0.31 lmg^{-1}, and from 0.10-to 0.20 lmg^{-1}, with a mean value of 0.14 lmg $^{-1}$ in sandy soils. This meant that the strength with which the phosphorus was bound to the soil was greatest for the clay loam soil (Table 4.8).

Lower affinity for P by sandy soils and, higher P adsorption maxima with greater clay content of soils has been reported by (Alam, 1999).

Table 4.8 **Langmuir sorption parameters of soil samples.**

Parameters	Soils	N	Mean	Std. D	Std. E	Min.	Max.
S_{max} mgkg^{-1}	sandy soil	15	137.33	14.44	3.73	114.45	163.28
	clay loam	3	445.33	0.07	0.05	445.28	447.38
K Lmg^{-1}	sandy soil	15	0.14	0.03	0.01	0.10	0.20
	clay loam	3	0.31	0.00	0.00	0.31	0.33
R^2	sandy soil	15	0.89	0.03	0.01	0.85	0.94
	clay loam	3	0.92	0.00	0.00	0.92	0.93

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
S_{max} mgkg^{-1}	Between Groups	165378.38	1.00	165378.38	849.52	0.00
	Within Groups	2920.09	15.00	194.67		
K Lmg^{-1}	Between Groups	0.05	1.00	0.05	86.95	0.00
	Within Groups	0.01	15.00	0.00		
R^2	Between Groups	0.00	1.00	0.00	2.02	0.18 *
	Within Groups	0.01	15.00	0.00		

* Values do not differ significantly (*P* = 0.05) one-way ANOVA.
S_{max} = maximum sorption capacity.
K = The binding strength constant.

Using the R^2 values, as a test for goodness to fit, all the aggregate-sizes appeared to conform relatively well to the Langmuir equation in the two different soils. P sorption capacity, (S_{max}) of the aggregate-sizes of sandy soils varied greatly and appeared to be related to the aggregate-size, and tended to decrease with decreasing surface area of particles.

In general the trend in S_{max} values was (< 0.05mm) > 0.050-to 0.10mm > 0.10-to 0.25mm > 0.25-to0.50mm or 0.5-to 1.00mm, the bonding energy was approximately of the same order, (*Table 4.9* and *Fig. 4.4*). Which to be expected in view of differences in the aggregate-sizes properties thus; it appeared that finer fractions situated on sandy soils would probably be the most efficient in retaining P.

These great variations not reflected in the sorption capacity (S_{max}) and binding energy (K) values of the aggregate-sizes from the clay loam soil. In fact, there appeared to be no pattern in (S_{max}) and (K) values among the various aggregate fraction sizes of clay loam soil.

Phosphorus adsorption maximum ratios of aggregate-sizes to the bulk is reflected the difference in P adsorption capacity for various aggregate-sizes in the sandy soils. The P sorption capacities for the 1.00-to 0.50mm, 0.50-to 0.25mm, 0.25-to 0.10mm, and 0.10-to 0.05mm aggregate-sizes, were close to the bulk soils, whereas P sorption capacity for the < 0.053-mm size was much higher than that in the bulk soil (*Fig. 4.5*). On the other hand, values of S_{max} from the various sizes situated in the clay loam soil were almost identical to the bulk soil sample.

Table 4.9 Longmuir sorption parameters of different aggregate-sizes of soils sampled.

	Fraction size mm	N	Mean	Std. Deviation	Std. Error	Min.	Max.
soil texture = sandy soil							
S_{max} mgkg^{-1}	<0.05	15	287.30d*	26.152	6.753	239.788	350.561
	0.1-0.05	15	75.95c	6.943	1.793	66.498	86.895
	0.25-0.1	15	58.69b	6.820	1.761	50.119	69.331
	0.5-0.25	15	29.34a	2.984	0.770	23.589	36.121
	1-0.5	15	23.44a	3.576	0.923	16.926	28.618
K Lmg^{-1}	<0.05	15	0.66c	0.308	0.080	0.284	1.214
	0.1-0.05	15	0.33b	0.048	0.012	0.265	0.472
	0.25-0.1	15	0.31ab	0.047	0.012	0.218	0.392
	0.5-0.25	15	0.24ab	0.033	0.008	0.167	0.281
	1-0.5	15	0.21a	0.038	0.010	0.139	0.263
R^2	<0.05	15	0.97c	0.022	0.006	0.921	0.989
	0.1-0.05	15	0.94c	0.022	0.006	0.889	0.961
	0.25-0.1	15	0.88b	0.063	0.016	0.753	0.951
	0.5-0.25	15	0.88b	0.051	0.013	0.773	0.939
	1-0.5	15	0.73a	0.109	0.028	0.527	0.930
soil texture = clay loam							
S_{max} mgkg^{-1}	<0.05	3	400.120c	0.524	0.370	399.750	400.491
	0.1-0.05	3	299.742ab	0.508	0.359	299.383	300.101
	0.25-0.1	3	416.854c	0.163	0.115	416.739	416.969
	0.5-0.25	3	329.726b	0.296	0.209	329.517	329.935
	1-0.5	3	314.447b	0.521	0.368	314.079	314.816
	>1	3	271.136a	33.959	24.013	247.123	295.149
K Lmg^{-1}	<0.05	3	0.871d	0.043	0.031	0.840	0.901
	0.1-0.05	3	0.421c	0.001	0.001	0.420	0.422
	0.25-0.1	3	0.301b	0.000	0.000	0.301	0.301
	0.5-0.25	3	0.379c	0.000	0.000	0.379	0.379
	1-0.5	3	0.259ab	0.000	0.000	0.259	0.259
	>1	3	0.239a	0.030	0.021	0.218	0.260
R^2	<0.05	3	0.885c	0.001	0.001	0.885	0.886
	0.1-0.05	3	0.722ab	0.001	0.001	0.721	0.723
	0.25-0.1	3	0.715ab	0.000	0.000	0.715	0.715
	0.5-0.25	3	0.788bc	0.000	0.000	0.788	0.789
	1-0.5	3	0.618a	0.003	0.002	0.616	0.621
	>1	3	0.759abc	0.150	0.106	0.652	0.865

* Means followed by the same are not significantly different by Duncan's multiple range test at the 0.05 probability level

This observation agreed to a certain extent with the finding of Zhang *et al.* (2003) that the maximum sorption of P, varied greatly in various aggregate-sizes, and decreased in the order of < 0.05mm, 0.10-to 0.05mm, 0.25-to 0.10mm, 1.00-to 0.25mm and, 0.50-to 0.25mm. Phosphorus adsorption maximum values of the <0.050-mm size in all the sandy soils were much higher than any other size.

From the literature, it is evident that a wide range of associations of soil constituents with P may occur in soils and presumably affect the supply of P to plants.

Zhang *et al.* (2003) attributed the variations in P adsorption capacity among various fractions in the sandy soil samples to differences in Al, Ca, and, Fe contents in different aggregate-sizes. Phosphorus adsorption capacity in various fractions was mainly determined by Al, Ca, and Fe contents, where a Positive correlations occurred between P adsorption capacity and total Al ($R^2 = 0.71$, $P < 0.0001$), Ca ($R^2 = 0.52$, $P < 0.0001$), and Fe ($R^2 = 0.64$, $P < 0.0001$) in all the different aggregate-sizes.

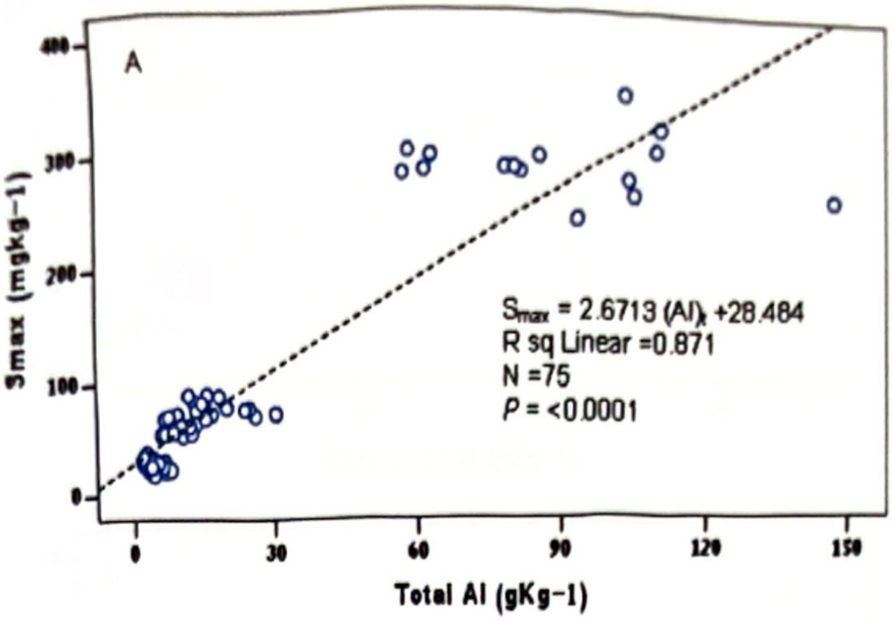
To describe the relationship between phosphorus sorption capacity of various aggregate-sizes of sandy soil and selected physic-chemical properties a linear regression, and correlation analysis were performed (*Fig. 4.4*) between S_{max} and total Al, Ca, Fe, and clay content in all size fractions of the fifteen sandy soil samples.

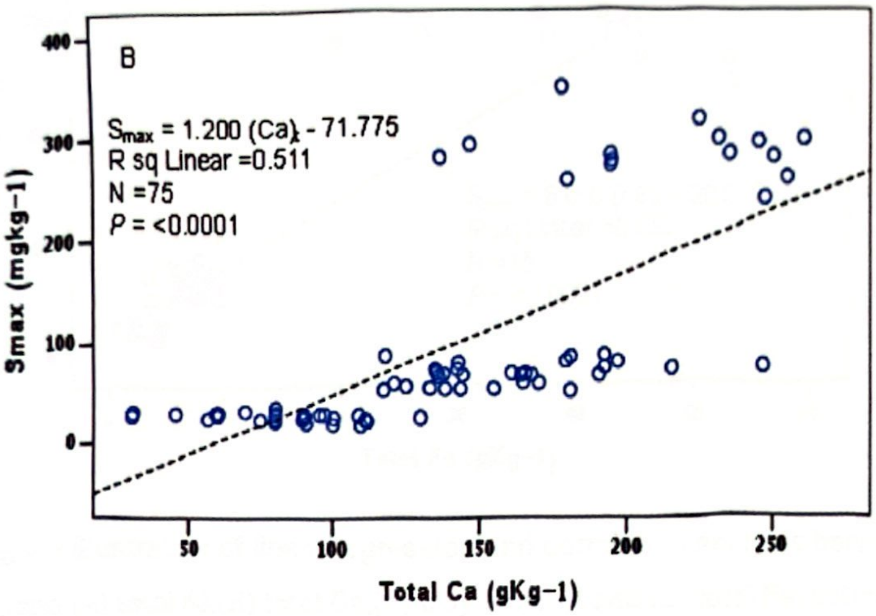
Results of the present study were comparable to that mentioned above of (Zhang *et al.* 2003). A significant linear correlation coefficient indicates the presence of a causal relationship between S_{max} and total Al, Ca, Fe, and clay content in all aggregate-sizes. That results in a linear correlation coefficient (R) being for total

Al ($R_{(75)}$ =0.933, P <0.0001), total Ca ($R_{(75)}$ = 0.715, P <0.0001), total Clay ($R_{(75)}$ = 0.977, P <0.0001) and total Fe ($R_{(75)}$ = 0.945, P <0.0001). These results conform that the variations in P adsorption capacity among various aggregate-sizes in the sandy soil is due to differences in Al, Ca, Fe and clay contents in different aggregate-sizes. Further more Clay content explained 95.5% of the variation in P sorption capacity between different sizes, of which 89.3% of the variation is explained by Fe, 87% explained by Al and, 51.1% is explained by Ca. Thus we can hypothesize that the variations in P adsorption capacity among various aggregate-sizes in the sandy soil is governed by clay content more than Fe or Al and Ca total content.

Samadi, and Gilkes (1999) referred to (Solis and Torrent, 1989) understanding the main governing factors in the recovery of applied P require a knowledge of the P reactive compounds in the soils. These compounds are clay minerals, Fe and Al oxides, and calcite; the first two types of minerals provide most of the active P-adsorbing surfaces, as shown by the positive relationships between P-adsorption capacity at a low equilibrium concentration and clay or Fe content. In contrast, calcite surfaces have a relatively low P-adsorption capacity, but induce slow precipitation of Ca phosphates (Freeman and Rowell, 1981).

Samadi, and Gilkes (1999) reported that it can be assumed that the relative significance of adsorption/precipitation reactions depends largely on the ratio of clay-related (Fe and Al oxides, CEC and clay content) to carbonate-related (active $CaCO_3$ and total $CaCO_3$) properties.


A
Smax (mgkg−1)
400
300
200
100
0
S_{max} = 2.6713 (Al)$_t$ +28.484
R sq Linear =0.871
N =75
P = <0.0001
0
30
60
90
120
150
Total Al (gKg−1)


B
Smax (mgkg−1)
400
300
200
100
0
S_{max} = 1.200 (Ca)$_t$ - 71.775
R sq Linear =0.511
N =75
P = <0.0001
50
100
150
200
250
Total Ca (gKg−1)

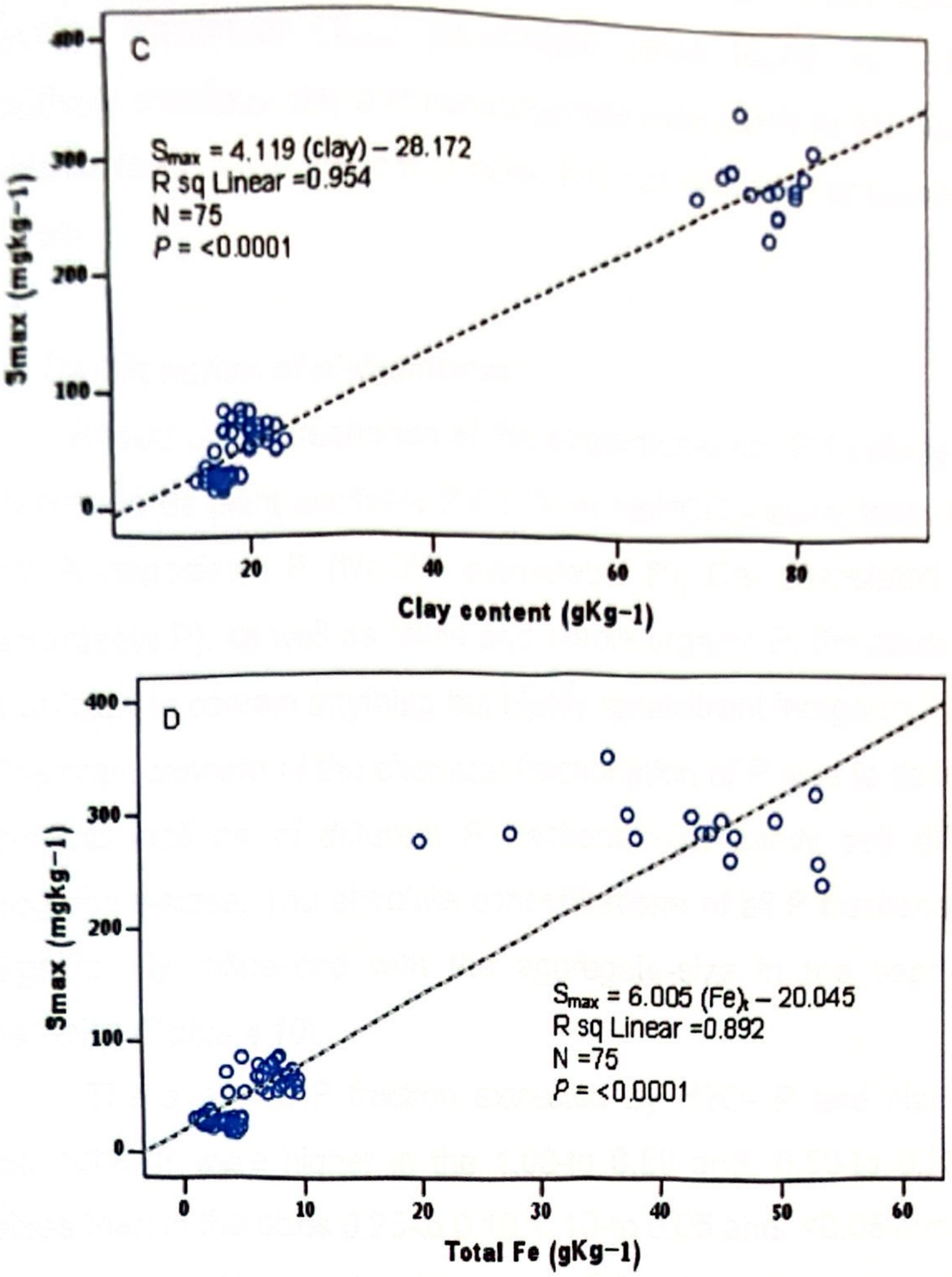


Fig. 4.6 illustration of linear regression and correlation analysis between S_{max} and (A) total Al,(B) total Ca,(C) clay content and (D) total Fe, estimated in the aggregate-sizes (1.00-0.50,0.50-0.25,0.25-0.10, 0.10-0.05 and <0.05mm) in all the fifteen sandy texture soil samples.

Zhou *et al.* (2001) found that The Freundlich K_f and Langmuir sorption maximum (S_{max}) parameters were found to correlate positively with total clay and noncarbonate clay (such as Fe oxide, Al oxide, and Si clays) content of soils, but not with the carbonate clay of soils.

4. 6 fractionation of phosphorus

Based on the sequence of the extractions, soil P fractions were referred to as plant available P (H_2O- or $NaHCO_3$- extractable P), Fe and Al-associated P (NaOH- extractable P), Ca- associated (HCl-extractable P), as well as labile and stable organic P. the residue left is unlikely to contain anything but highly recalcitrant inorganic P.

The main concern of the chemical fractionation of P was to document the associations of different P fractions with sandy soil different aggregate-sizes. The absolute concentrations of all P fractions were significantly influenced with the aggregate-size in the sandy soil samples (*Table 4.10*).

The available P fraction extracted by H2O- P and NaHCO3-inorganic P were higher in the 1.00-to 0.50 and, 0.50-to 0.25 mm sizes than in the sizes 0.25-to 0.10, 0.10-to 0.05 and, <0.05 mm.

Fe and Al- associated inorganic P fraction extracted by NaOH had the opposite order direction which was increases with a decrease of particle size which were lower in the 1.00-to 0.50 and 0.50-to 0.25 mm size than in the finer fractions.

Table 4.10 Distribution of P fractions in various aggregate-sizes of soils sampled.

P fractions		Aggregate-size fractions (mm) of sandy soils *				
		1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
H_2O-P, %	Mean	6.97c	5.84c	4.10b	3.25b	0.85a
	Std. Deviation	1.05	0.34	0.47	0.88	0.09
	Std. Error	0.61	0.20	0.27	0.51	0.05
$NaHCO_3$-IP, %	Mean	14.39c	12.90c	9.18b	8.62ab	6.68a
	Std. Deviation	0.23	0.18	0.54	2.25	0.95
	Std. Error	0.13	0.10	0.31	1.30	0.55
$NaHCO_3$-OP, %	Mean	0.75a	2.46c	2.28c	2.27c	1.24b
	Std. Deviation	0.15	0.50	0.13	0.07	0.13
	Std. Error	0.09	0.29	0.07	0.04	0.08
$NaHCO_3$-TP, %	Mean	15.14c	15.36c	11.47b	10.89b	7.92a
	Std. Deviation	0.20	0.61	0.64	2.29	0.99
	Std. Error	0.12	0.35	0.37	1.32	0.57
NaOH-IP, %	Mean	5.39a	10.14a	15.32b	20.66c	22.12c
	Std. Deviation	1.03	2.56	1.96	3.07	4.32
	Std. Error	0.59	1.48	1.13	1.77	2.49
NaOH-OP, %	Mean	1.60a	2.49b	4.02c	3.37c	3.38c
	Std. Deviation	0.18	0.56	0.41	0.37	0.31
	Std. Error	0.10	0.33	0.24	0.21	0.18
NaOH-TP,%	Mean	6.99a	12.64b	19.33c	24.03cd	24.70d
	Std. Deviation	0.89	2.94	1.69	3.00	4.01
	Std. Error	0.51	1.70	0.98	1.73	2.32
HCl-P, %	Mean	28.46c	18.96b	13.26a	11.55a	13.82a
	Std. Deviation	3.55	2.20	0.50	1.81	3.01
	Std. Error	2.05	1.27	0.29	1.04	1.74
Total extractable P, %	Mean	57.55b	52.79ab	48.16a	49.73a	47.30a
	Std. Deviation	2.20	3.14	2.69	4.16	5.63
	Std. Error	1.27	1.81	1.56	2.40	3.25
Total P, g kg-1	Mean	0.23a	0.12a	0.58c	0.40b	1.10d
	Std. Deviation	0.05	0.02	0.04	0.06	0.16
	Std. Error	0.03	0.01	0.02	0.03	0.09

Table 4.10 continued

P fractions		Aggregate-size fractions (mm) of clay loam soil **					
		2-1	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
H2O-P, %	Mean	0.84ab	0.80ab	0.87ab	0.87ab	0.92b	0.72a
	Std. Deviation	0.04	0.07	0.11	0.04	0.16	0.10
	Std. Error	0.02	0.04	0.06	0.02	0.09	0.06
$NaHCO_3$-IP, %	Mean	7.62a	6.87a	7.28a	7.42a	7.83a	7.11a
	Std. Deviation	1.65	1.68	1.97	1.93	1.72	1.75
	Std. Error	0.95	0.97	1.14	1.11	1.00	1.01
$NaHCO_3$-OP, %	Mean	0.36b	0.34bc	0.30a	0.31a	0.39c	0.36bc
	Std. Deviation	0.02	0.02	0.02	0.02	0.02	0.02
	Std. Error	0.01	0.01	0.01	0.01	0.01	0.01
$NaHCO_3$-TP, %	Mean	7.99a	7.22a	7.57a	7.72a	8.22a	7.48a
	Std. Deviation	1.67	1.69	1.99	1.94	1.74	1.76
	Std. Error	0.96	0.98	1.15	1.12	1.00	1.01
NaOH-IP, %	Mean	21.93a	20.75a	18.83a	18.96a	19.08a	18.00a
	Std. Deviation	1.99	2.17	1.98	1.74	2.27	2.89
	Std. Error	1.15	1.25	1.14	1.00	1.31	1.67
NaOH-OP, %	Mean	1.39c	1.36bc	1.26b	1.46c	1.72d	1.15a
	Std. Deviation	0.07	0.05	0.05	0.06	0.08	0.05
	Std. Error	0.04	0.03	0.03	0.03	0.04	0.03
NaOH-TP,%	Mean	23.32a	22.11a	20.09a	20.42a	20.79a	19.15a
	Std. Deviation	1.99	2.16	1.98	1.74	2.27	2.88
	Std. Error	1.15	1.25	1.14	1.00	1.31	1.66
HCl-P, %	Mean	34.80a	32.94a	31.70a	28.37a	30.14a	31.33a
	Std. Deviation	1.50	1.24	2.88	4.79	3.09	4.48
	Std. Error	0.87	0.72	1.67	2.76	1.78	2.58
Total extractable P, %	Mean	66.95b	63.07ab	60.23ab	57.38a	60.06ab	58.68ab
	Std. Deviation	2.80	2.02	3.70	5.69	4.99	5.87
	Std. Error	1.61	1.17	2.14	3.29	2.88	3.39
Total P, g kg-1	Mean	1.61a	1.89b	2.02c	2.20d	2.20d	2.39e
	Std. Deviation	0.01	0.01	0.01	0.01	0.01	0.00
	Std. Error	0.00	0.00	0.00	0.00	0.00	0.00

Values within a row followed by the same letter do not differ significantly by Duncan's multiple range test ($P = 0.05$) one-way ANOVA.

* Average of three samples.

**Average of triplicate sample.

Ca- associated inorganic P extracted by HCl was higher in the 1.00-to 0.50 and 0.50-to 0.25 mm fractions. Total P increases with a decrease of particle size, and the higher percentage extracted from the fractions of 1.00-to 0.50 and 0.50 -to 0.25mm, Organic P is also concentrated in the finest separates.

Data of the sequential fractionation suggested that, the available P associated with sandy soil aggregate-sizes is relatively low and increase with increasing separates sizes, and a moderately high proportion of the total P is inorganic, mainly Ca- P of primary origin.

Phosphorus associated with the finest fractions is largely of secondary origin, mainly Fe and Al bound P, possibly due to the accumulation of both organic and inorganic P. that can be qualified to the greater surface area and retention capacity. Compared with the sandy soil samples, the clay loam soil had unreliable variations in P fractions among different aggregate-sizes.

Relatively similar results have been reported by (Zhang *et al.* 2003), where they have reported that the 1.00-to 0.50mm fraction contains a larger percentage of Ca-bound P, whereas P in the 0.50-to 0.25, 0.25 -to 0.10 and 0.1-to 0.05mm sizes is more available and readily released into water. Their results were compared with a loam soil sample which had relatively small variations in P fractions among different aggregate-sizes.

Barberis and Withers (2002) referred to (He *et al.* 1995) increase of available P with increasing separates sizes. How ever (Agbenin and Tiessen, 1995) reported contrasting results, where they found an increase of available P with decreasing separates size.

SUMMARY AND CONCLUSION

The results obtained in this study indicate

- Sandy soils were, weakly aggregated due to lack of clay and organic matter. Differences on the relative distribution of the aggregate-sizes separated from sandy soil were higher than those from clay loam soil. The properties and composition of the sandy soil separates were different as well. The 1.00-to 2.00mm aggregate-size was negligible and accounted as 0% and <0.05mm size accounted for 1.49-to 2.29% of the soil air dry weight, and soils were dominated by the 0.50-to 0.25 and 0.25-to 0.10mm these two sizes, accounted on the average for 50.75% and 24.66% of the soil air dry weight respectively.

The sandy soil samples showed that the sand, silt, and clay contents among 1.00-to 0.05mm aggregate-sizes were significantly distributed. The clay and silt contents increased as the particle size decreased in the order of < 0.05, 0.10-to 0.05, 0.25-to 0.10, 0.5-to 0.25, and 1.00-to 0.50mm aggregate-size, whereas the sand content increased in the opposite direction. Clay content of the clay loam soil separates was markedly higher than that of the sandy soils. These variations among the aggregate-sizes of sandy soils influence the concentration and strength of elements binding.

- Distribution and attachment of P and heavy metals in various aggregate-sizes of the sandy soils tended to be controlled by the aggregate-size , concentration and attachment factor of P and heavy metals increase with decreasing aggregate-size, suggesting that P, and heavy metals are readily transported to surface waters through suspended fine particles.
- Mehlich-III and Water-extractability of P and heavy metals from the aggregate-sizes of sandy soils followed approximately the same manner. The highest extractability was in the 0.50-to 0.25mm size, and the lowest extractability was in the <0.05mm size, suggesting that the extractability and the release potential of P and heavy metals is increasing as the aggregate-size increased in sandy soils.
- Phosphorus adsorption capacity (S_{max}) and binding strength constant (K) of the sandy soils was much lower than that of the highly aggregated soil. Sorption maxima (S_{max}) of the sandy soils ranged from 114.45 to 163.28 mg P kg^{-1}, with a mean value of 137.33mg P kg^{-1}, and from 445.28-to 447.38 mg P kg^{-1}, with a mean value of 445.33 mg P kg^{-1} in clay loam soil. The binding strength constant (K lmg^{-1}), was also higher in the clay loam soil in which ranged from 0.31-to 0.33 lmg^{-1}, with a mean value of 0.31 lmg^{-1} and from 0.10-to 0.20 lmg^{-1}, with a mean value of 0.14 lmg^{-1} in sandy soils. This meant that the strength

with which the phosphorus was bound to the soil was greatest for the clay loam soil, because of the large differences in the resulting average clay content of the soils, and the variability in the physical and chemical characteristics.

- P adsorption capacity (S_{max}) and binding strength constant (K) of the aggregate-sizes of sandy soils varied greatly and appeared to be related to the fraction size and tended to decrease with decreasing surface area of particles. In general the trend in S_{max} values was (< 0.05mm) >0.05-to 0.10mm >0.10-to 0.25mm > 0.25-to0.50mm or 0.50-to 1.00mm, S_{max} of the aggregate-sizes of sandy soils was mainly depends to a large extent on their contents of clay, Fe, Al and Ca, This contents is in turn dependent on the surface area of the fractions.
- Results of P sequential fractionation suggested that the concentrations of all P fractions were, aggregate-sizes influenced with the aggregate-size in the sandy soil samples. Available P associated with sandy soil aggregate-sizes is relatively low and increased with increasing separates-size, and a moderately high proportion of the total P was inorganic, mainly Ca- P of primary origin.

The available P fractions extracted by H_2O and, $NaHCO_3$ were higher in the 1.00-to 0.50 and, 0.50-to 0.25 mm aggregate-sizes than in the sizes 0.25-to 0.10, 0.10-to 0.05

and, <0.05 mm. Ca- associated inorganic P extracted by HCl was higher in the 1.00-to 0.50 and, 0.50-to 0.25 mm sizes than any other size. Fe and Al- associated inorganic P fraction extracted by NaOH had the opposite order direction that was increases with a decrease of particle-size, which were lower in the 1.00-to 0.50 and 0.50-to 0.25 mm size than in the finer fractions.

From this study its observable that performance of plant nutrients and heavy metals in soil dependent on properties and composition of the soil matrix; as a result, the variation of composition in the soil matrix lead to significant variation of composition and behavior of nutrients and heavy metals. This reflects the importance of size fractionation to determine labile forms of elements and to evaluate the leaching risk of P and heavy metals from soil to the environment. This is particularly evident for sandy soils, in which attention should be draw for the use of particle-size separation to distinguish pools of different soil compositions.

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الملخص العربي

طاقة التصاق و انطلاق الفوسفور والعناصر الثقيلة وعلاقة ذلك بالأحجام المختلفة لأجزاء الرمل في التربة الرملية

هدفت هذه الدراسة إلى تقدير كل من النقاط التالية:

- فصل الأحجام المختلفة لحبيبات الرمل ومقارنة توزيعها ألحجمي في نوعين من الترب المختلفة القوام (رملية - طينية طمية).
- دراسة توزيع الفوسفور والعناصر الثقيلة بين الأحجام المختلفة لحبيبات الرمل وتقييم مدى إمكانية التصاقها بها وانطلاقها منها في الترب تحت الدراسة.
- تقييم أقصى ادمصاص للفوسفور بواسطة كل من الترب والأحجام المختلفة لأجزاء الرمل فيها.
- التجزيء الكيميائي لصور الفوسفور المرتبطة بالأحجام المختلفة لأجزاء الرمل.

النتائج المتحصل عليها من هذه الدراسة كانت كالتالي:

- التربة الرملية ضعيفة و تتكون من تجمعات (Aggregates) غير تامة التكوين لافتقارها للمادة العضوية والطين و أن الاختلاف في نسب الأحجام المختلفة المفصولة من التربة الرملية كان أعلى منه في التربة الطينية الطمية, حيث افتقرت التربة الرملية للحبيبات حجم (1.00 - 2.00 مم) , بينما شكل الجزء (< 0.05 مم) نسبة (1.49 - 2.29 %) من وزن التربة الجاف, وكانت الأجزاء من (0.50 - 0.25 و 0.25 - 0.10 مم) هي السائدة وشكلت في متوسطها 50.75 % و 24.66 % من وزن التربة الجاف على التوالي، كما أن محتوى ألأحجام المختلفة لحبيبات التربة الرملية (1.00- 0.50 و 0.50 - 0.25 و 0.25 - 0.10 و 0.10 - 0.05 و < 0.05 مم)

من الرمل ، السلت ، الطين أظهر فروق معنوية ، مع تزايد نسبة الطين والسلت وتناقص نسبة الرمل بزيادة المساحة السطحية للحبيبات. كما أن الأحجام المفصولة احتوت على نسبة طين أعلى في التربة الطينية الطميية عنه في التربة الرملية ،

و كان لاختلاف خواص أحجام حبيبات التربة الرملية أثر واضح على قوة ارتباط الفوسفور والعناصر الثقيلة بها.

- أزداد تركيز والتصاق الفوسفور والعناصر الثقيلة بحبيبات التربة الرملية بزيادة المساحة السطحية لهذه الحبيبات مما يشير إلى إمكانية انتقال الفوسفور والعناصر الثقيلة من خلال الجريان السطحي والتحت سطحي للماء باتجاه المياه الجوفية, وذلك بعد ارتباطها بالأجزاء العالقة الدقيقة للتربة.
- استخلاص الفسفور والعناصر الثقيلة بواسطة الماء وطريقة (Mehlich-III) بينت أن أعلى استخلاص كان من الحجم (0.50 – 0.25 مم) وأقله من الحجم (< 0.05 مم) مما يشير إلى إمكانية تزايد انطلاق الفسفور والعناصر الثقيلة بتناقص المساحة السطحية للحبيبات المفصولة من التربة الرملية.
- أقصى ادمصاص للفوسفور (S_{max}) وثابت قوة ارتباط (K) المحسوبة بمعادلة (Langmuir) بعد تحويلها للصورة الخطية بينت أن أقصى ادمصاص للفوسفور كان أعلى في التربة الطينية الطميية (447.38 – 445.28 مج/كج) منه في التربة الرملية (114.45 – 163.28 مج/كج) أيضا أعطت التربة الطينية الطميية ثابت قوة ارتباط أعلى (0.31 – 0.33 لتر/ مج) وذلك نتيجة الفرق الشاسع بين نوعي التربة في محتوى الطين بالإضافة لاختلاف الخواص الفيزيائية والكيميائية ، وتبعا لإحجام الحبيبات المفصولة من التربة الرملية وجد أن أقصى ادمصاص للفوسفور و كذلك ثابت قوة الارتباط يتناسب عكسيا مع أحجام هذه الحبيبات بالإضافة إلى اعتمادها إلى حد كبير جدا على

المحتوى الكلي لهذه الأحجام من الحديد (Fe) والألمونيوم (Al) والكالسيوم (Ca) والطين والتي كانت تزداد بزيادة المساحة السطحية للحبيبات.

- الاستخلاص الكيميائي المتعاقب لصور الفوسفور المرتبطة بالأحجام المختلف لحبيبات التربة الرملية أشار إلى أن الاختلاف في حجم هذه الحبيبات كان له اثر كبير على نسب توزيع الصور المختلفة للفوسفور بينها حيث تبين أن الفوسفور الغير عضوي المستخلص بواسطة (H_2O و $NaHCO_3$) كان أعلى في الأحجام (1.00 – 0.50 ، 0.50 – 0.25 مم) وكذلك بالنسبة للفوسفور الغير عضوي المرتبط بالكالسيوم والمستخلص بواسطة HCl كان أعلى في الأحجام (1.00 – 0.50 ، 0.50 – 0.25 مم) وأن الفسفور الغير عضوي المرتبط بالحديد والالومنيوم والمستخلص بواسطة NaOH كان يزداد بزيادة المساحة السطحية للحبيبات.

مما سبق تبين وجود علاقة واضحة بين الاختلاف في حجم وخواص (الكيميائية و الفيزيائية) أجزاء الرمل المفصولة من التربة الرملية وتوزيع وارتباط الفوسفور و العناصر الثقيلة بلاحجام المختلفة لهذه الحبيبات, وبالتالي التأثير المباشر لهذه الحبيبات (sand particle-sizes) على سلوك هذه العناصر داخل التربة الرملية, الأمر الذي يشير إلى أهمية دراسة هذا السلوك في الأحجام المختلفة لحبيبات هذا النوع من الترب سواء من الناحية الزراعية من حيث تقنين عمليات التسميد وتغذية النبات, وكذلك من الناحية البيئية من حيث إمكانية تلوث المصادر المائية السطحية و الجوفية بهذه العناصر.

فى حين ان هذه العلاقة لم تكن بهذا القدر من الوضوح فيما يخص اجزاء الرمل المفصولة من التربة الطينية الطمية, وذلك لعدم وجود تباين واضح التأثير سواء في الخواص الفيزيائية او الكيميائية بين الاحجام المختلفة لحبيبات الرمل فى هذا النوع من الترب.