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# DEPARMENT OF CROP AND SOIL SCIENCES



SUBSURFACE TRANSPORT OF PHOSPHORUS THROUGH THE SOIL



BY

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# SUBSURFACE TRANSPORT OF PHOSPHORUS THROUGH THE SOIL

 $\mathbf{B}\mathbf{Y}$ 

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MASTER OF SCIENCE

SOIL SCIENCE

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IN

NOVEMBER, 2013

#### CERTIFICATION

I declare that I have personally, under supervision, undertaken the study submitted herein. This thesis has not been submitted in part or whole for any other degree elsewhere.



Signature

November, 2013

# **DEDICATION**

I dedicate this dissertation to my mother, Mrs Eunice Bulley and Rev. Fr. Prof. Mensah Bonsu



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#### ABSTRACT

Phosphorus (P) is critical to the production of crops in agriculture. But the strategies adapted to increase phosphorus capital P capital in the soil tend to neglect subsurface transport of P with the assumption that it is bonded strongly to soil particles and would therefore not be a threat to groundwater contamination. Discovery of high concentrations of P in ground and surface water has inspired investigations into factors that contribute to its transport. The study was conducted to determine the subsurface transport of P through soils under cocoa plantation and arable land. Soil samples were taken at a depth of 0-30 cm from two land-use systems namely, a cocoa plantation and an arable land under cultivation. The samples were air-dried and passed through a 2 mm sieve. The soil particles that passed through the 2 mm sieve were used for the transport experiments. Different rates of P were applied at 0, 69, 137, 206, 274 and 343 ppm. For macropore flow, pores were varied in depth (5, 10 and 15 cm), number (1, 3 and 5) and diameter (2, 4, 6 and 8 mm). The study showed that soil organic carbon (SOC) improved hydraulic conductivity of soils and enhanced their water flux density. The cocoa plantation was more liable to groundwater contamination than the arable land. The concentration of the discharged P effluents increased as the rate of P increased in soils under both land-use systems. This showed that massive application of P to increase "soil phosphorus capital" for plant uptake could increase the risk of subsurface loss of P from agricultural systems into both ground and surface waters. This could lead to environmental problems such as eutrophication of surface water. Macropore depth, number and diameter and their interactions significantly affected preferential flow of P. The contribution of the different macropore parameters to subsurface transport of P in both land-use systems were in the order depth> number> diameter. The impact of soil macropores on preferential flow of P was more profound in soils under the arable land as compared to the cocoa plantation. The study also showed that P solutions moving through the soil profile may enhance more P sorption at the upper horizons than the lower horizons.



#### **CHAPTER ONE**

#### **1.0 INTRODUCTION**

#### 1.1 Background

Studies on phosphorus (P) use have become prevalent in recent times due to its deficiency in soils used for crop production and its related water quality problems. Its use as fertilizer for crops constitutes its largest use in agriculture. Phosphorus build-ups to excessive levels in soils occur when any phosphorus source, including commercial fertilizer, biosolids and manure are over applied (Breeuwsma and Silva, 1992; Mullins, 2009).

Subsurface transport of P to groundwater has received little attention in the past due to the assumption that it is bonded strongly to soil particles and would therefore not be a threat (Kumaragamage *et al.*, 2009; Qian *et al.*, 2011). However excessive concentrations of P in groundwater and surface water have been reported (Kumaragamage, 2009; Havik *et al.*, 2012). This could be attributed to preferential flow (rapid movement of solutes through large pores and cracks) and P equilibrium constants (exchange and dissolution) (Magdoff, 1999; Akay, 2007; Mullins, 2009; Naseri *et al.*, 2011). Also, applying phosphate fertilizers in amounts greater than crop removal could lead to P build-up in soils which can enhance the risk of P loss through leaching and runoff (Breeuwsma and Silva, 1992; Kumaragamage *et al.*, 2009; Nus and Kenna, 2012).

The main processes that move P from agricultural lands into water bodies and increase the possibility of eutrophication are erosion of particulate and dissolved P directly into surface water and leaching of P into groundwater, where the P can reemerge into surface water (Kumaragamage *et al.*, 2009). Ulén *et al.* (2001) reported that losses of P from agricultural (cultivated) fields are very low (0.3 kg total P ha<sup>-1</sup> yr<sup>-1</sup>) compared to its application and uptake by the crops grown, but considering its environmental implications, its risks to ground and surface water may be very high. It has been discovered that coastal waters and lakes in which nitrate is abundant need only minute amount of phosphorus (2  $\mu$ mol/L P) to enhance eutrophication (Dodds *et al.*, 1998).

Macropores play an important role in soils in relation to groundwater contamination by providing preferential pathways from the root zone to the water-table (Wildenschild *et al.*, 1994; Bruggeman, 1997). The reduced retention, combined with small contact area between the flowing water and the soil implies that little removal from physical, chemical and microbiological processes may take place, thus increasing the risk of groundwater contamination (Wildenschild, 1994).

#### **1.2 Problem statement and justification**

Phosphorus deficiency in soil is one of the major problems facing crop production today (Oldham, 2007). However excessive concentration of total P has been found in ground and surface water. For a nutrient known to be strongly sorbed to soil constituents, it is necessary to investigate and understand the processes which influence its transport and then develop methods to minimize its contamination of underground water.

In spite of the progress made to advance the contribution of macropores to preferential flow, information on the interaction effects of depth, number and diameter of macropores on solute transport is inadequate. It is also difficult to quantify the contribution of individual macropore to preferential flow of any chemical of interest. The study seeks to fill in the knowledge gap by providing answers to these compelling deficiencies.

### **1.3 Hypotheses**

- i. Excessive application of phosphorus will influence its transport into groundwater.
- ii. Varying depth, number and diameter of soil macropores and their interactions affect phosphorus transport.
- iii. Different chemical and physical properties of soil affect P transport.

#### **1.4 Objectives**

#### 1.4.1 Main objective

The main objective of the study was to assess the transport of phosphorus through soil columns and its implication on nutrient loss and groundwater quality.

#### 1.4.2 Specific objectives

Working on the stated hypotheses, the specific objectives of the study were to:

- i. assess how different chemical and physical properties of soils affect phosphorus flow through the soil;
- ii. investigate phosphorus transport through soil columns with water flux at different phosphorus rates;
- iii. examine the preferential flow of phosphorus through soil columns containing improvised macropore channels; and
- iv. investigate phosphorus sorption at varying depths of the soil column.

#### **CHAPTER TWO**

#### 2.0 LITERATURE REVIEW

#### 2.1 Phosphorus in agriculture

Phosphorus is an essential macronutrient for plant growth and it is added as fertiliser to increase the physiological efficiency of crops (Idris and Ahmed, 2012). The plant available forms of P in the soil are often not enough to meet plant needs (Borling, 2003). Applications of fertilizer phosphorus are thus needed to overcome this deficiency.

#### 2.1.1 Importance of phosphorus in crop production

Application of phosphorus increases crop growth and yields on soils that are naturally low in P and in soils that have been depleted through crop removal (Mullins, 2009). Most plants need about 0.2 - 0.5 % P (on dry matter basis) for normal growth (Hue and Silva, 2000). Plants do not need to take up new P for every cell function due to the fact that phosphorus existing in plant cells is recycled over and over again (Roper *et al.*, 2004). Early plant growth is dependent on P because of the needs for rapid cell division and expansion (Bolland *et al.*, 2003). The primordial for future roots, stems, leaves, flowers and seeds are produced very early during plant growth (Bolland *et al.*, 2003). Therefore P deficiency during early growth of plants and germinating seedlings can greatly reduce yield potentials of crops and pastures (Bolland *et al.*, 2003). Okeleye and Okelana (1997) recounted that P was critical to cowpea yield because of its multiple effects on nutrition and nodulation. Application of P to soils must be done judiciously since under or over application can lead to some complications in crops. Iron chlorosis may occur if P is greater than

0.15 % in leaves (Hue and Silva, 2000). In cases where P is under supplied, plants are stunted, with limited root systems, thin stems, fewer and shorter new shoots, malformed fruits and seeds (Hue and Silva, 2000).

#### 2.1.2 Soil phosphorus cycle

Phosphorus may be introduced into the soil by chemical weathering, mineralization of organic matter, added fertilizers and through agricultural, municipal and industrial wastes (Figure 1). It may be lost through runoff, erosion and leaching. Soil phosphorus is highly dependent on pH and its deficiency problems are common due to the fact that, it reacts with iron (Fe) and aluminium (Al) to form insoluble Fe and Al phosphates in acid soils and with calcium (Ca) to form insoluble Ca phosphates in alkaline soils (Saleque *et al.*, 2004; Mullins, 2009).



Figure 1: The soil phosphorus cycle (Pierzynski et al., 1994)

#### 2.1.3 Phosphorus forms and amount in soils

The forms of P dissolved in the soil solution under normal pH conditions include the negatively charged primary orthophosphate anion  $(H_2PO_4^-)$  and smaller amounts of the secondary orthophosphate anion  $(HPO_4^{2-})$  (Mullins, 2009). The H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> in solution are always in equilibrium with P sorbed by soil minerals (Mullins, 2009). They are the main inorganic forms of P that are available to plants and can be divided into two forms: labile and occluded P (Bardgett, 2005). The amount of labile P is very low relative to total P and can rapidly be fixed in occluded forms unavailable to plants (Bardgett, 2005). The amount of P contained in most agricultural soils is about 500-1000 ppm of total phosphorus whereas its amount in soil solution ranges from 0.01-1 ppm (Schulte and Kelling, 1996; Mullins, 2009).

The two main categories of P in soils are the organic and inorganic forms (Schulte and Kelling, 1996). The inorganic form includes ammonium polyphosphate  $(NH_4)_3HP_2O_7),$ diammonium phosphate  $(NH_4H_2PO_4)$  $(NH_4)_2HPO_4),$ monoammonium phosphate  $(NH_4H_2PO_4),$ ordinary superphosphate  $(Ca(H_2PO_4)_2+CaSO_4)$  and triple superphosphate  $(Ca(H_2PO_4)_2)$  whereas the organic form includes compost, bone meal, fish meal, wood ash, poultry manure, green manure, rock phosphate and sewage sludge (Schulte and Kelling, 1996). Organic P compounds ranges from readily available plant residues and microbes within the soil to stable compounds that have become part of the soil organic matter (van der Wal et al., 2006).

Organic P is not strongly sorbed as inorganic P (Whitton *et al.*, 1991) and it constitutes a large proportion of the total P transported in leachate (Turner and Haygarth, 2000). The mobility of organic P compared with inorganic P forms makes it an important mechanism by which P could escape from the soil (Curley *et al.*,

2010). Vadas (2006) reported that applying manure slurry to soil columns increased soil P in the top 0-1 cm depth of soil but rarely below 2 cm. He further reported that due to the infiltration behaviour (sorption) of the P, it is rendered less available to transport in surface runoff. According to the author, the results applied only to the infiltration of manure slurry P and before any rain or runoff event. These events could have caused the manure slurry to seep further than the 2 cm.

# 2.1.4 Phosphorus losses and removal from the soil

Phosphorus moves from agriculture production systems by four main mechanisms: removal by harvested product, runoff and erosion, leaching and attachment to sediments (Mullins, 2009). There are increasing concerns that phosphorus losses from agricultural lands contribute to accelerated algae and aquatic plant growth in lakes, rivers and streams (Correll, 1998; Khan and Ansari, 2005).

Losses of P from agricultural soils are generally low (Ulén *et al.*, 2001) but concentrations of P that cause eutrophication can be as low as 2 µmol/L (Dodds *et al.*, 1998). The path taken by water as it carries P off the land describes the P transfer (Curley *et al.*, 2010). Pathways can be broadly divided into surface (overland flow) and subsurface pathways particularly in soil macropores and field drains (Curley *et al.*, 2010). The pathway taken is of critical importance in determining the extent of P loss from agriculture systems (Curley *et al.*, 2010). Heathwaite and Dils (2000) indicated that overland flow (runoff and erosion) and subsurface flow (leaching) are important contributors to the overall P loss. Overland flow is often catastrophic as compared to subsurface flow and is considered to be the most severe in terms of loss, even though subsurface flow is equally important in P transfer (Fraser *et al.*, 1999).

Subsurface pathways include lateral flow through the soil, vertical drainage, preferential flow through macropores and artificial drainage channels (Curley *et al.*, 2010).

Until recently, subsurface losses of P were considered to be negligible due to the tendency of P to be retained in the soil profile. This was aggravated by the fact that measured losses of P in subsurface flow were small compared with the total amount of P in the soil (Schulte and kelling, 1996; Ulén *et al.*, 2001; Curley *et al.*, 2010). The effect of P movement on groundwater quality has drawn attention on subsurface P transfer due to the fact that small concentration of P can cause significant water quality implications.

#### 2.1.5 Phosphorus sorption and kinetics

When P fertilizers are applied to the soil, they are dissolved by soil water. Various reactions occur between the phosphate ions  $(H_2PO_4^- \text{ and } HPO_4^{-2})$  and soil constituents which sorb P from the solution phase and render it less variable. This phenomenon is called P fixation or sorption (Idris and Ahmed, 2012). Bolland *et al.* (2003) simplified the reactions as follows: i) that P is not chemically stable in the water soluble form in the presence of soil, and readily reacts largely with aluminium and iron, to form less soluble and more stable compounds. These reactions according to them mostly take place on the surfaces of soil constituents (clays; oxides of iron and aluminium; organic matter; and aluminium and iron compounds coating surfaces of sands). ii) After the initial surface reaction, the adsorbed P diffuses slowly towards the interior of the soil particles and so becomes less available to plants.

Paini *et al.* (1999) observed that soils differed significantly in their ability to hold P although P sorption was high in all the soils studied. Gichangi *et al.* (2008) studied seven soils and observed that they varied extensively in their abilities to sorb P. Idris and Ahmed (2012) also reported that an entisol sorbed more phosphorus than aridisols and vertisols series studied.

A number of studies indicated that the form of P controls its sorption. Lilienfein *et al.* (2000) found out that inorganic phosphate ( $PQ_4^{3-}$ ) was more strongly adsorbed than dissolved organic phosphorus (DOP) and dissolved organic carbon (DOC). They subsequently suggested that DOP and DOC were thus more susceptible to leaching than  $PO_4^{-3}$ . Comparing triple superphosphate (TSP) to Gafsa phosphate rock (GPR), Gikonyo (2010) reported that more P (threefold) leached from TSP than GPR treatments.

Many authors investigated and reported on the P sorption behaviour of soils with regards to depths. Tilahum (2007) recounted that available P was higher in the subsoils than the topsoils. Borggaard *et al.* (1990) reported that enrichment of Al and Fe in the B horizon of acidic soils of Podzols makes them more efficient in binding P. This corroborates the findings of Vaananen *et al.* (2008) that there was a sharp distinction between horizon O and E which showed lower P retention than horizon B1 and B2. Vaananen *et al.* (2008) further suggested that the low P sorption in the O and E horizon would make them more prone to P leaching as compared to the B horizon. Nonetheless, Tischner (1999) observed that the concentration of P decreased with soil depths.

Using typical sorption experiments to investigate P sorption capabilities in accordance to soil depths poses serious concerns since the reaction of infiltrating P

solution with soil constituents in the upper soil profiles may not be the same as the lower horizon. In these experiments, solution of known P concentration ( $C_o$ ) is applied to known mass of soil and the mixture shaken at known revolution per minutes at specified time interval. After the shaking, the concentration of P in the mixture is determined ( $C_f$ ). The P sorbed by the soils is determined by subtracting concentrations of P obtained from the mixture from the initial concentration of P solution applied. That is,

# P sorbed (soil) = $C_0 - C_f$ KNUST

The contact time for P reactions with the soil constituents may be higher in the upper layers in contrast to lower layers. The contact time between the reacting P and soil constituents can significantly affect the soil's P sorption characteristics.

# 2.1.6 Different application rates of phosphorus and their influence on its transport

Crop production in the future would have to meet the world increasing demand for food in a sustainable way. Soil fertility decline as a result of mismanagement of plant nutrients has made this task more challenging (Gruhn *et al.*, 2000). To avert this problem, strategies have been proposed to intensify sustainable food production. One of such strategies is to replenish "soil phosphorus capital" (Sanchez *et al.*, 1997). Strategic options include massive application of P as against repeated smaller applications and the use of phosphate rock versus soluble P fertilizers (Sanchez *et al.*, 1997). The sorbed P then forms the stock that provides P over a period of 5-10 years and this is termed as "soil capital", while the P available during the annual cropping cycle is called "liquid P" (Sanchez *et al.*, 1997). The P strategies aim at building up the soil phosphorus to a level which would only require maintenance application to replenish P losses owing to plant uptake, removal by erosion or continuing reactions between phosphate and soil (Henry and Smith, 2003).

Seasonal application of P by micro dosing to saturate the sorption sites might be a good initiative but one-time massive dose application of P to achieve this purpose poses future water quality related problems. The possibility of P leaching out of the root zones of crop plant into groundwater has not been critically considered. Application of phosphorus above crop requirement could result in the build-up of soil P (Kumaragamage et al., 2009). Soils that are P saturated due to excessive P fertilizer applications may have a lower capacity to retain more P within the profile (Breeuwsma and Silva, 1992; Kleinman and Sharpley, 2002). Increasing P saturation leads to weaker retention of P, implying that the degree of phosphorus saturation (DPS) appears to govern solution P concentration (Magdoff, 1999). The P retention decreased with increasing number of the adsorption sites being occupied by the P ions (Borggaard, 2002). Consequently, land use systems which receive higher P application rates may lose more of these nutrients through runoff and leaching compared to sites which receive lower application rates. Gikonyo (2010) reported that the amounts of P leached increased with increasing P application rates. He observed that application of TSP at 300, 600 and 900 kg P ha<sup>-1</sup> led to 61, 158, and 289 % loss of P to leaching, respectively in treated soils relative to control. Similar observations were made by Tening et al. (2013) who indicated that phosphorus recovered after applying different P rates increased with added P.

#### 2.1.7 Some soil properties and their influence on solute transport

Soil properties have a wide range of effects on soil nutrients and may affect their stability. Chemicals that are more water soluble at a soil's pH tend to move more easily with water than chemicals that are less water soluble (Hardy et al., 1996). Clay and organic matter are the most chemically active soil solids and are the major soil components to which most chemicals sorb (Hardy et al., 1996). The surface charges of clay minerals (and oxides) are partly pH dependent; hence, anion as pH decreases exchange capacity increases (Idris and Ahmed, 2012). Consequently, clay minerals that possess greater anion exchange capacity tend to have a greater affinity for phosphate ions (Idris and Ahmed, 2012). Soils containing large amounts of kaolinite group clay minerals will retain larger quantities of added phosphate than those containing the 2:1 type clay minerals (Idris and Ahmed, 2012). Lalljee (1997) found out that P fixation was significantly correlated with amorphous Mn, amorphous Fe, organic matter, pH and clay content. D'Angelo (2005) reported that differences in P retention by wetland soils were mainly attributed to the relative amounts of amorphous Al and Fe in the soil which were strongly linked to the amount of soil organic carbon. He specified the role organic carbon plays in controlling Al and Fe chemistry in the wetland soils as follows: Firstly, the carboxylate and phenol groups complexe Al and Fe, thus inhibiting their conversion to low P sorbing crystalline Fe and Al oxides and; secondly, organic matter increases water holding capacity of soil, oxygen consumption, and anaerobic conditions, which inhibit Fe-oxide crystallization. Owusu-Bennoah and Acquaye (1989) observed that P sorption was highly correlated with soil properties in the order:  $Al_2O_3$  > clay content> free Fe<sub>2</sub>O<sub>3</sub> > organic carbon.

Elmahi and Mustafa (1980) noted that P retention in soils increased with increase in concentration of electrolyte or decrease in sodium adsorption ratio (SAR). Exchangeable cations are an indication of the capacity of soils to retain nutrients against leaching (Tilahum, 2007). Soils with higher amount of exchangeable cations will thus retain more nutrients as compared to soils with lower amount of exchangeable cations.

# 2.2 Water eutrophication KNUST

Eutrophication is a plant growth promoting process resulting from accumulation of nutrients in lakes or other water bodies (Khan and Ansari, 2005). It is in fact a very slow, natural process, but can be greatly enhanced by anthropogenic activities that increase the rate of nutrient loads in water bodies (Khan and Ansari, 2005). Water eutrophication is a global environmental problem and understanding the mechanisms that accelerate it will help prevent and remediate it (Yang *et al.*, 2008).

Studies have shown that excessive nutrient loading into surface water is one of the major factors influencing eutrophication (Correll, 1998; Zhao, 2004; Fuchs, 2008). Nitrogen and phosphorus are the nutrients of major interest and concern (Murphy, 2002; D'Angelo, 2005). Zhao (2004) summarized the importance of P in water eutrophication as follows; when P concentration in water is low, it may be the limiting factor for inducing water eutrophication and algal bloom; when its concentration in water increases rapidly, others may become limiting factors (examples include pH, water depth, temperature, light, wave or wind).

Water eutrophication is accelerated by human activities that increase the rate of nutrient input into water bodies due to rapid urbanization, industrialization and intensification of agricultural production (Yang *et al.*, 2008). Detergents, domestic sewage and fertilizers are the three major human made sources of enrichment in eutrophication of natural water bodies (Khan and Ansari, 2005). Khan and Ansari (2005) also noted that water bodies located near large cities are likely to receive more phosphorus from domestic effluents containing detergents while urban water bodies are likely to receive major quantities of phosphorus from fertilizers and other agriculture-related activities. The average concentration of total phosphorus (inorganic and organic forms) in wastewater has been reported to vary in the range of 10-20 ppm (Bitton, 1999). According to Fuchs (2008) the negative effects of eutrophication include polluted drinking water, excessive algal growth, taste and odour issues, and death of fish.

#### 2.3 Preferential flow

Preferential flow is a phenomenon where water and solutes move along certain pathways while by-passing a large fraction of the porous soil matrix (Figure 2). It has both environmental and human health consequences since it favours contaminants transport to groundwater with little interaction with the chemically and biologically reactive upper layers of the soil (Wildenschild, 1994; Allaire *et al.*, 2009). Preferential flow is one of the main routes responsible for the leaching of phosphorus in structured soils (Kleinman *et al.*, 2005).

The study focussed on macropore flow and silent on other types of preferential flow such as fingered flow and funnel flow (Ju and Kung, 1997; De Rooij, 2000). Even under the macropore flow, the P transport phenomena were limited to biopores, that is, pores formed by the soil fauna and plants.



Figure 2: Soil profile showing matrix and preferential flow (Haygarth and Jarvis, 1998)

#### 2.3.1 Soil macropores and solute transport

Classical definition of what constitutes a soil macropore still poses a problem for many researchers today but pores are generally classified based on their equivalent pore sizes (Bruggeman, 1997). Skopp (1981) defined macroporosity as the pore space that provides preferential flow of solutes such that the mixing and transfer between macropores and other pores are limited. He also defined matrix porosity as the pore space that transmits water and solute at a rate slow enough to allow extensive mixing and relatively rapid transfer of molecules between different pores. Luxmoore (1981) defined macropores as pores that channel flow through the profile from surface ponding with an equivalent diameter larger than 1 mm. Allaire *et al.* (2009) defined macropore generally as an opening feature larger than the microscopic scale in the soil that causes non-equilibrium of mass movements and defined macropore flow according to him refers to the mass movements of water and solutes through macropores, leading to non-equilibrium with the soil matrix. The definitions of Allaire *et al.* (2009) on what constitute a macropore and macropore flow are holistic and encompass many other definitions.

Macropores were grouped on the basis of their morphology by Beven and Germann (1982) as pores formed by soil fauna and plants roots which are tubular in shape, and as cracks and fissures formed by shrinking and swelling of clay, freeze/thaw cycles, and cultivation techniques and natural soil pipes formed by the erosive action of subsurface flow.

To achieve greater accuracy in determining the impact of macropores on solute transport, macropores have been morphologically characterized using computed tomography scans, paint injection techniques, hydrometric methods among others. However, substantial reservations regarding the effects of their characteristics still remain, and it may also not be possible to simulate unsaturated flow conditions adequately using undisturbed soil cores (Zhou *et al.*, 2012). On the other hand, interpretation and clarification of results acquired under field conditions has been complicated by the complexity of natural soil systems and difficulties associated with assessing hydraulic properties in the field (Buttle and Leigh, 1997). Therefore, the effects of macropores on solute transport have been investigated in laboratory experiments that have mostly used repacked soil columns with artificial macropores of known dimensions, open at the soil surface and oriented parallel to the direction of water and solute flow (Jarvis, 2007).

Macropore behaviour is site-specific and depends on several factors including experimental boundary and initial soil conditions (Wildenschild, 1994). Soil macropores are ubiquitous, relatively densely distributed, and dynamic, since the soil is exposed to temporal variations in climate, crop development, biological activity and management that strongly affect soil structure (Jarvis, 2007).

Munyankusi et al. (1994) stated that knowing the number and size (diameter) of visible surface macropores are not adequate to model water and solute transport through macroporous soils, but information about the depth and continuity of macropores is also needed. Also, knowledge on the interactive effects of multiple macropores on solute transport is still inadequate (Zhou et al., 2012). Germann and Niggli (1998) posited that flow in macroporous soils increased with soil depth and that preferential flow can linger for a long time and over long distances, once initiated. Akay (2007) and Zhou et al. (2012) also reported that flow of water and solutes increased as the depth of macropore increased. Kluitenberg and Horton (1990) attributed fast breakthrough curves in pulse experiments to larger contribution of continuous channels and voids to the transmission process in which the contact time for diffusion and advection of solute into the soil matrix was minimal. Geohring et al. (2001) recounted that pores of diameter of even 1 mm provides a potential mechanism for transporting P through soil. The number of macropores per unit area of soil also influences macroporous flow (Weiler and Naef, 2003; Zhou et al., 2012). Zhou et al. (2012) reported that surface macropores contribute more to the movement of solutes in solution than buried ones. Akay (2007) observed similar trends and reported that breakthrough time with surface connected macropores was significantly faster compared to buried macropores. All parameters of the macropores stated above affect preferential flow but Perret et al. (1999) noted that the effects of the tortuosity of macropores on solute transport are as important as the depth, diameter and density of macropores.

#### 2.3.2 Biopores

Worms are known to recycle nutrients and improve soil's physical environment. Le Bayon and Milleret (2009) indicated that earthworms regulate nutrient cycling through i) their own metabolism that leads to high availability of carbon and nitrogen from metabolic wastes such as urine, mucus and tissue ii) the dispersal and the stimulation of soil microorganism activity associated with passage through the intestinal tract and iii) the distribution and the mixing of organic matter and soil mineral particles. This improve soil fertility and consequentially affects plant growth. Kemper *et al.* (2011) noted that no tillage favours the development of large populations of *Lumbricus terrestris* L. and their burrows allow many roots to bypass the resistance of compact clay soils (Kemper *et al.*, 2011).

In spite of the numerous benefits obtained from the soil fauna, it has been found out that their burrowing activities in soils contribute to solute transport. Weiler (2005) noted that flows through wormholes are high as compared to the rate in the soil matrix. Even for fairly small earthworm channels, the rate of flow in macropores appears to be always higher than the rainfall intensity (Shipitalo and Gibbs, 2000). Klaus (2013) observed that preferential flow in the vertical macropores formed by the anecic earthworm controls flow to the tile-drain system.

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Figure 3: Burrow characteristics of various earthworm species (Shipitalo and Gibbs, 2005)

Anecic, endogeic, and epigeic earthworms have distinct burrowing characteristics (Figure 3). Not all wormholes can have significant effect on preferential flow like the ones created by the anecic (deep burrowing) earthworms (Jarvis, 2007). For example, the endogeic and epigeic earthworms burrow only within the topsoil and produce burrows that are shorter, branched and more tortuous (Figure 3). The macropores formed by anecic earthworms extends deep into the soil subsurface and can enhance preferential flow of solutes (Figure 3).

Smaller channels created by decaying plant roots also constitute important pathways to non-equilibrium transport (Jarvis, 2007). Mitchell *et al.* (1995) reported that infiltration rates increase where plant roots decay and serve as preferential flow paths.

#### 2.4 Summary of literature review

Phosphorus supply to crops is important especially, at the early stages of growth. Its deficiency in soils used for crop production is more of the soil's inability to supply it than its unavailability. The literature review suggests that the organic forms of P are more liable to leaching than its inorganic forms. Soils differ in their ability to sorb P and also supply it to plants. The literature review suggested that using the typical sorption experiments to investigate P sorption capabilities in accordance to soil depths may be wrong as the contact time for P reactions with the soil constituents may be higher in the upper horizon than lower horizon. The literature indicates that building up soil P through massive applications may cause more of the P to leach. This has the potential of polluting groundwater. P is the major nutrient that control eutrophication in water bodies. There is a gap in literature as to how individual macropores or the interactive effect of multiple macropores affects solute transport. The depth, number and size of soil macropores affect P transport but available information on which of these macropore parameters (depth, number or diameter) contribute more to solute transport is inadequate. Worms are important in soils due to their recycling activities. Their burrowing activities improve aeration and also allow many roots to bypass the resistance posed by compacted zones in the soil. However, their burrowing activities may enhance solute leaching. The observations noted in the literature forms part of the justification of this study and the basis for the formulation of the objective

#### **CHAPTER THREE**

#### **3.0 MATERIALS AND METHODS**

#### **3.1 Experimental site**

The study was carried out at the Soil Science Laboratory of the Department of Crop and Soil Sciences, Faculty of Agriculture, College of Agriculture and Renewable Natural Resources, Kwame Nkrumah University of Science and Technology (KNUST). Soil samples were taken from the Plantation Section of the Department of Crop and Soil Sciences, KNUST from two land-use systems; a cocoa plantation and an arable land under cultivation of cowpea. Geographically, the experimental area stretches from latitudes  $6^0$  40' North and longitude  $1^0$  33' West.

# **3.2 Soil sampling and preparation**

Soil samples were randomly taken at a soil depth of 0-30 cm from the two land-use systems. The soil samples were air-dried and passed through a 2 mm sieve. Soils under each land-use system were then thoroughly mixed to minimise variations. The soil particles that passed through the 2 mm sieve were used for analysis.

# 3.3 Physico-chemical analysis of soil

Particle size distribution of the soils was determined using the hydrometer method (Bouyoucos, 1963) whilst soil bulk density was determined by the metal core sampler method (Blake and Hartge, 1986). Total porosity of soil was calculated using the formula;

where:

f = total porosity

Pb= bulk density and

Ps= particle size density (2.65 g cm<sup>-3</sup>).

Soil pH was determined using a standard pH meter in a soil: water ratio of 1: 2.5. Soil organic carbon (SOC) was determined by the modified Walkley and Black dichromate digestion method (Nelson and Sommers, 1982). Available phosphorus (P) was determined using the Bray P1 method (Olsen and Sommers, 1982). Exchangeable Ca, Mg, K and Na were determined after extracting the soil samples by ammonium acetate (1N NH<sub>4</sub>OAc) at pH 7.0. Exchangeable Ca and Mg in the extracts were analysed using Buck scientific atomic absorption spectrophotometer, while Na and K were analysed by Gallenkamp flame photometer (Chapman, 1965; Rowell, 1994). Iron was determined using Diethylenetriamine penta acetic acid (DTPA) extraction method as described by Lindsay *et al.* (1978) whilst aluminium was determined using the spectrophotometric method (Pritchard, 1967).

#### 3.4 Experimental design and treatments

The treatments considered were P applied at different rates, macropores at different depths, diameter and number, and P sorption as affected by different soil depths.

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#### **3.4.1 Different phosphorus application rates**

Experimental treatments consisted of P source: triple superphosphate (TSP) applied at 0, 20, 40, 60, 80 and 100 kg ha<sup>-1</sup>. The equivalents per the area of soil column were 0, 69, 137, 206, 274 and 343 ppm P respectively. The 0 ppm P served as the control. For the breakthrough curves, only rates at 69, 137, 206, 274 and 343 ppm were considered. Due to the sharp differences between the transit times of P outflow and the complexity of the data collected in soils under both land-use systems, the treatments were analysed separately on each field, For the analysis of variance, the experimental design was complete randomised design (CRD). Each treatment was replicated three times.

#### 3.4.2 Macropore flow

The macroore experiment was factorial arranged in CRD. Three factors plus a control were considered. The three factors were the depth, diameter and number of macropores. The control consisted of soil columns without macropore. The depths of the macropore were at 3 levels (5, 10 and 15 cm); the diameter of macropores at 4 levels (2, 4, 6 and 8 mm) and the number of macropores was at 3 levels (1, 3 and 5). In all, 37 experimental treatments were considered per each replication. Thus for 3 replications, the total number of experimental units were 111 in each land-use type.

The soil under each land-use type was assumed to be homogenous after thorough mixing. However, due to the wide differences in the transit times of the discharged P as affected by the macropores created, analysis of the effect of macropores on preferential flow of P in soils under the arable land was limited to 45 minutes and that of soils under the cocoa plantation to 20 minutes.

Chemical breakthrough curves were also used to ascertain the effects of varying diameter and number of macropores at different soil depths on P transport. Two sided correlation tests were likewise performed to investigate the degree of relationship between the depth, diameter and number of soil macropore and the concentration of P effluents at 5 minutes interval.

# **3.4.3 Sorption of phosphorus as affected by soil depth**

The treatments considered were soils of depth 0-5, 5-10 and 10-15 cm. P sorption in relation to the varying depths of soils within each field was arranged in CRD. In all, 9 experimental units were considered in each land-use system. T-test at 5 % confidence limit was used in separating the means between the land-use systems.

#### 3.5 Experimental setup and column preparation

The experiment was conducted using improvised transparent polyvinyl chloride (PVC) cylinders as shown in plate 1. The cylinders were 45 cm long with internal diameters of 10 cm. The PVC cylinders were attached to a backboard. The rectangular base frame which supports the backboard has four adjustable feet to enable the equipment to be levelled.



The PVC cylinders were removable from the backboard to facilitate filling and cleaning. A tube was fixed to the base of the cylinders to allow flow of effluents into beakers placed underneath. White calico of diameter 10 cm was cut to fit the base of the cylinder. Soil aggregates of diameters 1-2 mm, 2-4 mm and 4-8 mm were also prepared. Both the calicos and the soil aggregates were prepared to filter dirt from the outflow. Also, interception of flow without the calico and the packed aggregates

would have caused more water (or P solutions) to flow through the basal collecting tubes. At the end of each cycle of flow experiment, the calicos and the soil aggregates were washed with 10 ml 0.05 M HCl/ L and then rinsed with distilled water to ensure that any residual P on them was removed.

The column was prepared layer after layer bottom up as follows: the calico was placed at the base of the PVC cylinder and the three soil aggregates packed in succession to the 5 cm mark of the PVC cylinder in the following order: aggregates of diameter 4-8 mm to 0-2 cm layer of the cylinder, 2-4 mm to 2-4 cm and 1-2 mm to 4-5 cm mark. Thereafter, the soil samples were packed to fill the 5-20 cm layer of the PVC cylinder at soil density of 1.3 g cm<sup>-3</sup> (height of soil was 15 cm). White calico was again placed on top of the soil sample and an aluminium mesh fixed on it to hold it firm in place to prevent splashing of soil particles whilst applying solutions to the soil column. This also provided stability of the artificial macropores and prevented soil particles from backfilling and clogging them during the experiment. Effluents discharging from the PVC cylinders were collected using glass beakers at 5 minutes intervals.

#### **3.6 Phosphorus transport initiation**

The soil columns were saturated slowly from the bottom by immersing them in buckets containing distilled water before starting the transport experiments. This was to ensure uniform wetness and to expel air out. Before applying solutions to the soil columns, the plastic tubes from which the effluents flowed were corked to prevent outflow. Water or phosphorus solutions were then applied to the soil columns at a hydraulic head of 20 cm equivalent to a volume of 1571 cm<sup>3</sup>.

Effluents were collected at five (5) minutes interval into beakers. To determine the effects of different P rates on P flow, solutions were applied at 0, 69, 137, 206, 274 and 343 ppm P. For the effects of the depth, number and diameter of macropores on P flow, solutions were applied at 69 ppm P only. Macropores were created at the surface of the soil columns using a 30 cm metallic rod calibrated at 5 cm intervals. The diameters of the four rods were 2, 4, 6 and 8 mm. Macropores were varied in depth (5, 10 and 15 cm), number (1, 3 and 5) and diameter (2, 4, 6 and 8 mm). The macropores were created by pushing the metallic rods into the soil column. The single pores were created at the centre while the others were located diagonally (about 2.5 cm) from the centre.

#### 3.7 Determination of the concentration of phosphorus effluents

Concentrations of the P effluent sampled were determined using the ascorbic acid method (Murphy and Riley, 1962; Edwards *et al.*, 1965; Strickland and Parsons, 1972). The test is largely a measure of the orthophosphates. Because the samples were not filtered, the procedure measured both dissolved and suspended orthophosphate. It is the United States of America Environmental Protection Agency (USEPA) approved method for measuring total orthophosphate. A combined solution (4 mL) consisting of sulphuric acid, potassium antimonyl tartrate, ammonium molybdate, and ascorbic acid was added to 25 mL aliquot of the effluents. Ammonium molybdate and potassium antimonyl tartrate reacts in acid medium with orthophosphates to form phosphomolybdic acid which is reduced to intensity coloured molybdenium blue by ascorbic acid. Absorbance was then measured after 10 minutes at 710 nm using reagent blank as the reference solution.

The intensity of the blue colour is directly proportional to the amount of orthophosphate in the effluents.

#### 3.8 Saturated hydraulic conductivity

Saturated soil hydraulic conductivity was determined using the falling head approach. Soils were packed as in the transport experiment. The hydraulic head of water was 20 cm above the soil column. The time taken for every 2 cm drop in the water level in the tube was recorded. In  $\frac{H0}{Ht}$  was plotted against time (s). H<sub>0</sub> was the initial hydraulic head and Ht, the hydraulic head after each 2 cm drop in the water level.

Slope of graph =  $\frac{Ks}{L}$  .....(2)

Ks = slope of graph x L(3)

Where;

Ks = saturated hydraulic conductivity and L= length of the soil column.

#### 3.9 Determination of water flux density

Quantity of water that flowed through the soil columns was measured using measuring cylinders. The time interval for the flow was also determined.

Water flux density =  $\frac{Q}{t x A}$  .....(4)

where:

Q= Quantity of water per unit time, t and

#### A = area of soil column.

#### 3.10 Sorption of phosphorus at different depths

Phosphorus applied at 69 ppm and used for the transport experiment was allowed to thoroughly drain for 72 hours. Soil samples in the PVC cylinders were then carefully taken out as the cores took the shape of the PVC cylinder. They were then divided at 5 cm interval, that is, 0-5, 5-10 and 10-15 cm. Soil separates were air-dried and the P determined using the Bray P1 method (Olsen and Sommers, 1982).

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#### **3.11 Statistical analysis**

The data collected on the various parameters were subjected to analysis of variance using GenStat statistical package (12<sup>th</sup> Edition). Means were separated using least significant difference (Lsd) at 5 % probability level. Each treatment was replicated three times. Differences between the physico-chemical properties of the two sites were analysed using a two sided T-test at a confidence limit of 95 %.

#### 3.12 Chemical breakthrough curves

Chemical breakthrough curves (BTCs) were used to study the transport phenomenon. The pattern of chemical concentration in the outflow versus time is termed the breakthrough curve. Phosphorus concentrations were normalized (relative concentration) by dividing the measured concentration with the applied concentration such that the concentration values are always between 0 and 1.0. This was plotted against time.

Relative concentration = 
$$\frac{C}{Co}$$
 .....(5)

where:

C= concentration of P in the effluent and

Co= the initial concentration of the solution of interest that was added

Standard deviations of means of the relative concentrations were calculated from which standard deviation of error of means was generated. This was used to separate means in the breakthrough curves. Bars which separated from each other indicated significant differences between curves whiles those which did not easily separate were not significant.



#### **CHAPTER FOUR**

#### 4.0 RESULTS

#### 4.1 Physico-chemical properties of the soils

Selected chemical and physical parameters of the soil from the test sites are presented in Table 1 and 2. The textural class of the two land-use types (arable land under cultivation and cocoa plantation) was loamy sand. Their pH values were low (Table 2). The available phosphorus content was higher (p< 0.03) in soil under the arable land use than that in the cocoa plantation. Field bulk densities of soils under the cocoa plantation and that of the arable land were 1.39 and 1.56 g cm<sup>-3</sup> respectively. The field porosity of both cocoa plantation and arable land were < 0.50. Soil under the arable land contained lower (p< 0.01) amount of organic carbon as compared to soils under the cocoa plantation. The exchangeable cations (except K<sup>+</sup>) were considerably higher in the cocoa plantation than in the arable land (Table 2).

Table 1: Physical properties of the soils

Soil property	Arable land	Cocoa plantation
Particle size distribution (%)	3	
Sand	80.76	84.76
Silt	9.72	5.05
Clay	9.52	10.19
Bulk density (g cm <sup>-3</sup> )	1.56	1.39
Porosity	0.41	0.48
Textural class	Loamy sand	Loamy sand

Water flux density, hydraulic conductivity, iron and aluminium concentrations were significantly (p < 0.01) higher in soils under the cocoa plantation than soils under arable land cultivation (Table 2). The transit time for matrix flow of P in soils under

the arable land was 105 minutes while that of soils under the cocoa plantation was 30 minutes (appendix 1, 2a and 2b).

Soil property	Arable land	Cocoa	p (0.05)	SED
		plantation		
Organic carbon (%)	1.11	1.52	0.002	0.060
Available P (ppm)	3.08	0.36	0.030	0.810
$Ca^+$ (cmol kg <sup>-1</sup> )	2.50	6.07	0.006	0.680
$Mg^+$ (cmol kg <sup>-1</sup> )	1.80	2.40	0.190	0.380
$\mathbf{K}^{+}$ (cmol kg <sup>-1</sup> )	0.15	0.10	0.001	0.003
$Na^+$ (cmol kg <sup>-1</sup> )	0.26	0.32	0.001	0.006
Fe (ppm)	5.61	11.69	0.001	0.120
Al (cmol kg <sup>-1</sup> )	0.80	3.24	0.001	0.080
pH (1: 2.5 soil: H <sub>2</sub> 0)	5.11	5.55	0.070	0.194
Water flux density (m s <sup>-1</sup> )	0.003	0.01	0.001	$4x10^{-5}$
Saturated Hydraulic	0.002	0.01	0.001	$5 \times 10^{-5}$
conductivity (cm s <sup>-1</sup> )	<u>//?</u>			

 Table 2: Some physico-chemical properties of the soils

SED: standard error of difference of means, p: probability

### 4.2 Phosphorus transport as affected by different phosphorus rates

The effects of the different rates of phosphorus applied to the soil columns on P transport are illustrated in Tables 3 and 4, and Figure 4 and 5. Generally, the concentration of P in the effluents (in each rate of P applied) progressively increased as time increased in soils under both land-use types except the control (0 ppm P) where there was fluctuations (Table 3 and 4). The breakthrough times indicated similar trends (Figure 4 and 5). The different rates of P added to the soil column had significant effects (p< 0.01) on P transport. In soils under both land-use systems, the concentrations of P effluents were lowest in the control (0 ppm P) and increased as the rates of P increased (Table 3 and 4). The breakthrough curves (Figure 4 and 5) showed more pronounced trends. Considerable differences in P transport between

the breakthrough times of the different P rates were recorded in both land-use types.

The breakthrough curves showed that the amount of P lost (in terms of their relative

concentrations) was more when the P rates were increased.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Time (minutes)		CV (%)	Lsd					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0	69	137	206	274	343		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			- E	$\langle   \rangle$					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	0.32	0.33	0.37	0.40	0.47	0.47	4.50	0.03
15 $0.53$ $0.45$ $0.68$ $0.81$ $2.87$ $3.12$ $3.50$ $0.09$ 20 $0.54$ $0.62$ $1.49$ $2.77$ $4.99$ $6.71$ $7.00$ $0.35$ 25 $0.46$ $2.09$ $5.70$ $14.81$ $20.93$ $32.07$ $5.00$ $1.14$ 30 $0.44$ $3.68$ $10.98$ $22.30$ $37.09$ $54.62$ $7.10$ $2.73$ 35 $0.47$ $7.22$ $15.77$ $31.19$ $63.23$ $87.19$ $4.60$ $2.79$ 40 $0.55$ $10.10$ $19.79$ $40.23$ $63.23$ $87.19$ $4.20$ $2.78$ 45 $0.58$ $16.41$ $35.53$ $52.69$ $75.93$ $104.64$ $4.30$ $3.68$ 50 $0.65$ $19.64$ $42.97$ $63.74$ $93.96$ $123.00$ $3.50$ $3.56$ 55 $0.97$ $24.18$ $51.55$ $75.93$ $109.28$ $145.77$ $3.30$ $4.02$ 60 $1.00$ $29.21$ $62.02$ $90.50$ $127.46$ $167.94$ $3.70$ $5.31$ 65 $0.81$ $31.75$ $63.42$ $102.86$ $143.81$ $185.85$ $3.10$ $4.90$ 70 $1.59$ $37.06$ $80.66$ $116.04$ $157.73$ $207.46$ $3.10$ $5.48$ 75 $1.00$ $46.00$ $89.90$ $127.10$ $166.20$ $217.70$ $4.20$ $8.10$ 80 $0.96$ $53.54$ $97.44$ $141.23$ $196.35$ $254.06$ $2.80$ $6.19$ <tr< td=""><td>10</td><td>0.41</td><td>0.43</td><td>0.45</td><td>0.46</td><td>0.80</td><td>0.74</td><td>3.40</td><td>0.03</td></tr<>	10	0.41	0.43	0.45	0.46	0.80	0.74	3.40	0.03
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15	0.53	0.45	0.68	0.81	2.87	3.12	3.50	0.09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	0.54	0.62	1.49	2.77	4.99	6.71	7.00	0.35
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25	0.46	2.09	5.70	14.81	20.93	32.07	5.00	1.14
35 $0.47$ $7.22$ $15.77$ $31.19$ $63.23$ $87.19$ $4.60$ $2.79$ $40$ $0.55$ $10.10$ $19.79$ $40.23$ $63.23$ $87.19$ $4.20$ $2.78$ $45$ $0.58$ $16.41$ $35.53$ $52.69$ $75.93$ $104.64$ $4.30$ $3.68$ $50$ $0.65$ $19.64$ $42.97$ $63.74$ $93.96$ $123.00$ $3.50$ $3.56$ $55$ $0.97$ $24.18$ $51.55$ $75.93$ $109.28$ $145.77$ $3.30$ $4.02$ $60$ $1.00$ $29.21$ $62.02$ $90.50$ $127.46$ $167.94$ $3.70$ $5.31$ $65$ $0.81$ $31.75$ $63.42$ $102.86$ $143.81$ $185.85$ $3.10$ $4.90$ $70$ $1.59$ $37.06$ $80.66$ $116.04$ $157.73$ $207.46$ $3.10$ $5.48$ $75$ $1.00$ $46.00$ $89.90$ $127.10$ $166.20$ $217.70$ $4.20$ $8.10$ $80$ $0.96$ $53.54$ $97.44$ $141.23$ $196.35$ $254.06$ $2.80$ $6.19$ $85$ $1.00$ $53.24$ $113.11$ $156.51$ $212.41$ $265.12$ $2.60$ $6.13$ $90$ $1.11$ $53.24$ $115.04$ $188.67$ $224.64$ $284.23$ $2.40$ $5.99$ $95$ $1.10$ $53.24$ $115.04$ $184.39$ $251.91$ $326.95$ $1.70$ $4.70$ $105$ $1.05$ $53.24$ $115.04$ $184.39$ $251.91$ </td <td>30</td> <td>0.44</td> <td>3.68</td> <td>10.98</td> <td>22.30</td> <td>37.09</td> <td>54.62</td> <td>7.10</td> <td>2.73</td>	30	0.44	3.68	10.98	22.30	37.09	54.62	7.10	2.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35	0.47	7.22	15.77	31.19	63.23	87.19	4.60	2.79
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40	0.55	10.10	19.79	40.23	63.23	87.19	4.20	2.78
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	45	0.58	16.41	35.53	52.69	75.93	104.64	4.30	3.68
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	50	0.65	19 <b>.6</b> 4	42.97	63.74	93.96	123.00	3.50	3.56
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	55	0.97	24.18	51.55	75.93	109.28	145.77	3.30	4.02
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	65	0.81	31.75	63.42	102.86	143.81	185.85	3.10	4.90
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	70	1.59	37.06	80.66	116.04	157.73	207.46	3.10	5.48
800.9653.5497.44141.23196.35254.062.806.19851.0053.24113.11156.51212.41265.122.606.13901.1153.24115.04168.67224.64284.232.405.99951.1053.24115.04181.50243.80303.003.208.541001.0853.24115.04184.39251.91326.951.704.701051.0553.24115.04184.39251.91340.260.902.44	75	1.00	46.00	89.90	127.10	166.20	217.70	4.20	8.10
851.0053.24113.11156.51212.41265.122.606.13901.1153.24115.04168.67224.64284.232.405.99951.1053.24115.04181.50243.80303.003.208.541001.0853.24115.04184.39251.91326.951.704.701051.0553.24115.04184.39251.91340.260.902.44	80	0.96	53.54	97.44	141.23	196.35	254.06	2.80	6.19
901.1153.24115.04168.67224.64284.232.405.99951.1053.24115.04181.50243.80303.003.208.541001.0853.24115.04184.39251.91326.951.704.701051.0553.24115.04184.39251.91340.260.902.44	85	1.00	53.24	113.11	156.51	212.41	265.12	2.60	6.13
95       1.10       53.24       115.04       181.50       243.80       303.00       3.20       8.54         100       1.08       53.24       115.04       184.39       251.91       326.95       1.70       4.70         105       1.05       53.24       115.04       184.39       251.91       340.26       0.90       2.44	90	1.11	53.24	115.04	168.67	224.64	284.23	2.40	5.99
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	95	1.10	53.24	115.04	181.50	243.80	303.00	3.20	8.54
105 1.05 53.24 115.04 184.39 251.91 340.26 0.90 2.44	100	1.08	53.24	115.04	184.39	251.91	326.95	1.70	4.70
	105	1.05	53.24	115.04	184.39	251.91	340.26	0.90	2.44

 Table 3: Phosphorus transport as affected by different phosphorus rates in soils under arable land

CV: coefficient of variation, Lsd: least significant difference at 5 %

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Within the first 20 minutes under the arable land, no major differences were observed between the breakthrough times of the different P rates applied. Significant differences were however, recorded subsequently (Figure 4). In soils under the cocoa plantations, significant differences in the breakthrough curves of the different P rates applied were observed from the 5<sup>th</sup> to the 30<sup>th</sup> minutes (Figure 5).

The transit times of P effluent outflow was faster in the soils under the cocoa plantation as compared to soils under the arable land. Also, soils under the cocoa plantation recorded earlier breakthrough times in contrast to soils under the arable land. Generally, the concentrations of the discharging P effluents per time were higher in soils under the cocoa plantation in contrast to soils under the arable land (Table 3 and 4).



 Table 4: Phosphorus transport as affected by different phosphorus rates in soils under cocoa plantation

Time		Phosp	Lsd	CV				
(minutes)	)			1,2	A			(%)
	0.00	69	137	206	274	343		
5	0.51	1.87	20.29	60.14	75.91	84.71	2.46	3.40
10	0.41	17.89	35.48	76.75	136.74	166.60	4.85	3.80
15	0.43	26.30	54.36	112.19	184.43	228.33	5.43	3.00
20	0.45	39.25	83.07	162.74	207.46	265.12	6.31	2.80
25	0.47	51.88	100.12	185.43	242.56	291.99	5.34	2.10
30	0.47	58.82	115.03	196.31	260.58	333.51	5.65	2.00





Figure 4: Breakthrough curves showing phosphorus transport as affected by different rates of phosphorus in soils under arable land



Figure 5: Breakthrough curves showing phosphorus transport as affected by different rates of phosphorus in soils under cocoa plantation

Time (minutes	5)	Phosphorus concentrations (ppm)							
	Control	Ι	Depth (cn	n)		Number	•		
		5	10	15	1	3	5	-	
5	0.33	0.46	9.75	32.31	5.15	13.46	22.79	0.55	3.30
10	0.43	0.99	7.35	31.38	4.38	12.11	22.18	0.56	3.60
15	0.48	7.44	11.02	37.00	6.20	17.39	30.42	1.75	8.10
20	0.62	9.53	14.26	43.46	9.10	22.16	34.23	0.70	2.40
25	2.09	14.04	18.51	48.17	12.48	27.08	39.15	0.76	2.20
30	5.25	18.53	24.06	53.30	17.12	33.02	43.58	0.46	1.60
35	7.22	22.84	29.63	56.23	20.70	38.89	46.75	4.81	10.20
40	10.10	27.50	35.58	60.81	26.91	44.01	50.43	0.82	1.70
45	16.41	32.66	41.17	63.32	32.00	48.12	54.65	0.92	1.70

 Table 5: Contributions of different depths and numbers of soil macropores to preferential flow of phosphorus through soils under arable land

# 4.3 Preferential flow of phosphorus as affected by soil macropores

Preferential flow of phosphorus as affected by varying depths, diameters and numbers of soil macropore are shown in Tables 5, 6, 7 and 8. The transit time of the phosphorus effluents decreased as the depth, diameter and number of soil macropores increased (appendix 1, 2a and 2b). For example, in soils under arable land, the transit time of P effluents outflow in the control (soil column with no macropore) was 105 minutes while that with macropores at depth 15 cm, number 5 and diameter 8 mm was 45 minutes (appendix 2a and 2b). Correspondingly, in soils under the cocoa plantation, the transit time of P outflow took 30 minutes in the control while macropore created at depth 15 cm, number 5 and diameter 8 mm was 20 minutes (see appendix 1). Generally, the concentration of P in the effluents per time increased as the depth, diameter and number of macropores increased (Table 5, 6, 7 and 8). The analysis of variance (ANOVA) revealed that there were significant differences (p < 0.01) in the contribution of depth, diameter and number of macropores to P transport in soils under both land-use systems. As expected, the

influence of varying depths (5, 10 and 15 cm), numbers (1, 3 and 5) and diameters (2, 4, 6 and 8 mm) of macropores on P transport were all higher than the controls (column without macropore) in both land-use types.

Generally, the effects of the different depths, diameters and numbers of macropores on P transport were more pronounced within the 5<sup>th</sup> minute of flow and increased gradually as time elapsed. For example, in soils under the arable land, concentration of P effluent lost within the 5<sup>th</sup> minute was 0.33 ppm in the control, 0.46, 9.75 and 32.31 ppm in depths of 5, 10 and 15 cm respectively. Under the cocoa plantation, the concentration of P leached within the 5<sup>th</sup> minute in the control was 1.87 ppm while that in the macropore created at depths 5, 10 and 15 cm were 6.48, 26.78 and 43.39 ppm respectively (Table 5 and 7).

Table 6: Contributions of different diameters of soil macropores to preferentialflow of phosphorus through soils under arable land

Time (minutes)	Pho	osphorus	pm)	Lsd	CV (%)		
	Control	111.	Diame	eter (mm)			
		2	4	6	8		
5	0.33	11.53	13.05	14.50	16.11	0.25	3.30
10	0.43	10. <mark>4</mark> 5	12.21	13.63	15.28	0.57	3.60
15	0.48	15.10	16.53	<mark>18</mark> .94	21.45	1.78	8.10
20	0.62	18.59	20.93	22.76	25.04	0.85	2.40
25	2.09	23.11	25.42	27.01	29.40	0.94	2.20
30	5.25	28.62	30.12	31.78	34.43	0.80	1.60
35	7.22	33.26	35.01	34.84	38.68	5.89	10.20
40	10.10	37.63	39.19	41.32	43.66	0.83	1.70
45	16.41	42.74	44.25	45.48	47.23	0.93	1.70

CV: coefficient of variation, Lsd: least significant difference at 5 %

The interaction effects between the different combinations of depth and diameter, depth and number, number and diameter and, depth, diameter and number of the macropores created were all significant (p < 0.01) with regards to P transport in soils

under both land-use systems (Tables 9, 10, 11, 12 a/b, 13, 14, 15 and 16; Figures 6, 7, 8, 9, 10 and 11). The interaction results showed that a macropore 5 cm long with varying diameters 2, 4, 6 and 8 mm had little effects on P transport in comparison to the control but as the depth of macropores increased with corresponding increases in numbers and diameters, preferential flow of P increased significantly (Tables 9, 10, 11, 12 a/b, 13, 14, 15 and 16).

 Table 7: Contributions of different depths and numbers of soil macropores to preferential flow of phosphorus through soils under cocoa plantation

Time		Phosp	horus co	Lsd	CV (%)				
(minutes)				10	<u>.</u>				
	Control	Depth	(mm)						
		5	10	15	1	3	5		
5	1.87	6.48	26.78	43.39	16.36	24.67	33.70	0.62	2.10
10	17.89	25.44	34.95	50.30	27.84	36.94	44.38	0.83	1.90
15	26.30	35.82	48.61	60.31	39.54	48.28	55.14	0.78	1.40
20	39.25	50.39	58.45	65.15	52.38	58.21	61.88	0.73	1.10
CV: coeffi	cient of w	oristion	L sd. la	ant cig	aificant	differen	ace at 5	0/2	

CV: coefficient of variation, Lsd: least significant difference at 5

 Table 8: Contributions of different diameters of soil macropores to preferential flow of phosphorus through soils under cocoa plantation

Time (minutes)	Z P	hosphorus	concentra	tions (ppn	n)	Lsd	CV (%)
	Control	× *	Diam	eter (mm)	54	2	
	Ap.	2	4	6	8	_	
5	1.87	22.01	23.74	25.69	28.19	0.63	2.10
10	17.80	33.33	35.14	37.24	39.83	0.84	1.90
15	26.30	45.10	46.64	48.25	50.63	0.78	1.40
20	39.25	55.51	57.18	58.09	59.19	0.74	1.10

Time (minutes)		Phosphorus	concentra	tions (ppn	n)	CV (%)	Lsd
(		Depth (cm)		Numb	er		
	Control		1	3	5	-	
5	0.33	5	0.37	0.46	0.56	3.30	0.37
		10	1.09	7.85	20.31		
		15	15.12	33.18	48.62		
10	0.43	5	0.44	0.71	1.83	3.60	0.60
		10	0.87	5.07	16.10		
		15	12.88	31.60	49.65		
15	0.48	5	_0.49	6.78	15.06	8.10	1.19
		10	1.58	9.67	21.82		
		15	17.98	37.17	55.85		
20	0.62	5	0.63	10.30	17.67	2.40	0.68
		10	4.95	12.92	24.91		
		15	23.48	45.01	61.88		
25	2.09	5	2.281	15.87	23.96	2.20	0.74
		10	8.560	17.36	29.62		
		15	28.61	50.02	65.87		
30	5.25	5	5.495	20.99	29.09	1.60	0.63
		10	13.58	23.06	35.54		
		15	34.46	57.16	68.27		
35	7.22	5	7.36	33.76	27.40	10.20	4.65
		10	19.12	29.19	40.57	-	
		15	37.98	62.43	68.27	7	
40	10.10	5	11.26	32.31	38.94	1.7	0.88
	/	10	24.48	35.65	46.60		
		15	47.53	66.61	68.27		
45	16.64	5	16.64	37.17	44.17	1.7	0.98
		10	28.33	41.30	53.88		
		15	53.418	68.27	68.27		

 Table 9: Interaction effects between the depth and number of soil macropores

 on phosphorus transport in soils under arable land

Breakthrough curves (Figures 6, 7, 8, 9, 10 and 11) were used to demonstrate the interaction effects of macropores on solute transport at constant macropore depths. Faster breakthrough times were obtained as the diameter and number of macropores were increased and as depth of macropore remained constant in soils under both land-use systems. Similarly, as the depths of the macropores were increased faster breakthroughs were obtained. At macropore depth 5 cm, the breakthrough curves diverged (Figure 6 and 9) but tended to converge as the depths of macropore were

varied from 10 to 15 cm (Figure 7, 8, 10 and 11). This further illustrates that earlier breakthrough times are obtained as the depth, diameter and number of macropores increased.

Time		CV (%)	Lsd					
(minutes)				IC	<b>T</b>			
	Control	Depth (cm)		Diamete	r (mm)			
			2	4	6	8		
5	0.33	5	0.43	0.45	0.47	0.50	3.30	0.43
		10	7.29	8.65	10.61	12.45		
		15	28.00	31.17	33.55	36.50		
10	0.43	5	0.85	0.90	1.04	1.18	3.60	0.31
		10	4.68	6.84	8.18	9.69		
		15	26.86	29.93	32.72	36.00		
15	0.48	5	5.25	7.05	8.22	9.26	8.10	1.94
		10	8.40	9.86	11.79	14.04		
		15	33.10	34.12	38.28	42.51		
20	0.62	5	7.46	8.87	10.09	11.72	2.40	0.70
		10	11.47	13.28	15.11	17.19		
	~	15	38.62	42.41	44.85	47.97		
25	2.09	5	12.13	13.39	14.57	16.05	2.20	0.76
		10	15.38	17.78	19.06	21.84		
	/ /	15	43.85	47.09	49.43	52.31		
30	5.25	5	16.44	17.78	19.00	20.88	1.60	0.65
	( )	10	21.16	22.74	24.32	28.03		
	_	15	50.44	52.01	54.191	56.56		
35	7.22	5	21.09	22.29	23.07	<b>24.9</b> 1	10.20	4.81
	EL	10	26.52	28.38	30.02	33.58		
	Sa	15	54.53	56.71	53.76	59.91		
40	10.10	5	25.66	26.22	27.98	30.14	1.7	0.91
		10	31.50	33.77	36.66	40.38		
		15	58.27	60.12	61.83	63.00		
45	16.41	5	30.59	32.02	33.22	34.81	1.7	1.02
		10	37.21	39.83	42.32	45.32		
		15	62.81	63.26	63.26	63.95		

 Table 10: Interaction effects between the depth and diameter of soil macropores

 on phosphorus transport in soils under arable land

Time		Phosph	orus conce	ntrations (p	opm)		CV (%)	Lsd
(minutes)								
	Control	Number		Diameter	(mm)			
			2	4	6	8		
5	0.33	1	3.75	4.49	5.94	6.43	3.30	0.43
		3	10.90	12.60	14.01	16.31		
		5	19.95	22.06	23.56	25.59		
10	0.43	1	3.17	3.73	4.90	5.72	3.60	0.31
		3	9.17	11.14	12.83	15.32		
		5	19.00	_21.77	23.17	24.79		
15	0.48	1	4.55	3.93	6.78	9.54	8.10	1.94
		3	14.01	16.38	18.19	20.97		
		5	26.73	29.27	31.85	33.84		
20	0.62	1	6.84	8.03	10.10	11.43	2.40	0.70
		3	18.71	21.19	22.80	25.92		
		5	30.23	37.75	35.38	33.56		
25	2.09	1	10.68	11.50	12.88	14.86	2.20	0.76
		3	23.10	26.38	28.24	30.59		
		5	35.56	38.37	39.92	42.74		
30	5.25	1	15.39	16.09	17.38	19.64	1.60	0.65
		3	29.47	31.92	33.57	37.10		
		5	41.01	42.35	44.39	46.57	1	
35	7.22	1	19.81	21.21	17.93	23.86	10.20	4.81
		3	35.22	37.92	39.80	42.62		
	-	5	44.76	45.90	46.77	49.57		
40	10.10		24.52	29.96	27.47	25.69	1.7	0.91
		3	40.78	42.94	45.27	47.08		
	/	5	47.61	48.95	51.21	53.95		
45	16.41	1	30.29	31.18	32.33	34.21	1.7	1.02
		3	45.92	47.46	49.22	49.89		
1		5	52.02	54.10	54.87	57.60		

Table 11: Interaction effects between the number and diameter of soil macropores and their influence on phosphorus transport in soils under arable land

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Time	<b>`Phosphorus concentrations (ppm)</b>									
(initiates	Control	Depth (cm)	Number		D	iameter (mm)				
		(em)		2	4	6	8			
5	0.33	5	1	0.34	0.36	0.37	0.40	0.75		
U	0.00	C	3	0.43	0.46	0.47	0.51	0170		
			5	0.53	0.54	0.56	0.60			
		10	1	0.63	0.94	1.24	1.57			
			3	5.46	6.41	8.31	11.21			
			5	15.77	18.59	22.29	24.57			
		15	ZNI	11.41	13.31	17.33	18.44			
			3	27.93	32.06	34.38	38.34			
			5	44.66	48.16	48.95	52.72			
10	0.43	5	1	0.42	0.44	0.44	0.45	0.76		
			3	0.61	0.64	0.73	0.86			
			5	1.51	1.62	1.95	2.23			
		10	1	0.49	0.68	0.97	1.34			
			3	2.32	4.07	0.6.10	7.80			
			5	11.23	15.77	17.47	19.95			
		15	1	9.657	11.12	14.35	16.41			
			3	25.63	29.74	32.70	38.34			
			5	45.29	48.95	51.13	53.24			
15	0.48	5	21	0.47	0.49	0.50	0.51	2.38		
			3	4.07	6.44	7.22	9.40			
		-	5	11.21	14.23	16.93	17.87			
		10	1	0.96	1.26	1.52	2.61			
	/	100	3	7.05	7.91	10.46	13.24			
		1-17	5	17.19	20.42	23.39	26.28			
	( )	15	LATS	13.38	11.49	19.79	26.97			
			3	32.38	36.24	38.34	41.73			
			5	53.24	54.62	56.71	58.82			
20	0.62	5		0.61	0.62	0.62	0.68	0.85		
	121	_	3	7.44	9.31	11.21	13.24			
	135	100	5	14.35	16.66	18.44	21.24			
	1	10	1	3.24	3.83	6.03	6.71			
		W	3	9.75	12.61	13.674	15.65			
		1	255.N	21.41	23.39	25.62	29.21			
		15	1	18.44	21.41	25.41	28.67			
			3	40.71	43.42	45.29	50.65			
			5	56.71	62.40	63.85	64.58			
25	2.09	5	1	2.158	2.25	2.358	2.36	0.94		
			3	12.82	15.28	16.79	18.59			
			5	21.41	22.65	24.57	27.21			
		10	1	7.514	7.99	8.55	10.19			
			3	14.46	16.92	17.46	20.58			
			5	24.17	28.42	31.16	34.74			
		15	1	24.37	26.28	29.74	34.05			
			3	44.04	48.95	52.46	54.62			
			5	63.12	66.05	66.05	68.27			

Table 12a: Interaction effects between depth, diameter and number of macropores on phosphorus transport in soils under arable land

Time		Phosphorus concentrations (ppm)					Lsd	
(IIIIIute	Control	Depth (cm)	Number		Diamete	er (mm)		
		(em)		2	4	6	8	
30	5.25	5	1	5.25	5.46	5.57	5.70	0.80
		-	3	18.02	19.95	21.41	24.57	
			5	26.06	27.93	30.01	32.38	
		10	1	12.50	12.93	13.25	15.65	
			3	20.10	22.28	22.65	27.21	
			5	30.86	33.01	37.06	41.22	
		15	ZK	30.57	32.057	35.48	39.72	
			3	52.46	55.69	58.82	61.67	
			5	68.27	68.27	68.27	68.27	
35	7.22	5	1	7.22	7.36	7.36	7.51	5.89
			3	25.20	26.50	28.17	29.74	
			5	30.86	33.01	33.69	37.49	
		10	1	16.66	18.44	19.63	21.76	
			3	25.41	27.92	29.74	33.69	
			5	37.49	38.78	40.71	45.29	
		15	1	37.90	40.19	29.16	44.66	
			3	57.41	61.67	63.85	66.79	
			5	68.27	68.27	68.27	68.27	
40	10.10	5	-1	10.56	10.74	11.21	12.51	1.12
		5	3	30.57	30.86	33.01	34.79	
	~	-	5	35.86	37.06	39.72	43.12	
		10	I.	22.11	23.58	24.78	27.44	
			3	31.16	33.69	37.06	40.71	
		1-1	5	41.22	44.04	48.16	52.98	
	( )	15	an	43.42	45.39	48.95	52.46	
			3	63.12	66.79	68.27	68.27	
	_		5	68.27	68.27	68.27	68.27	
45	16.41	5		16.16	16.41	16.66	17.33	1.23
	E		3	34.38	36.24	38.34	39.72	
	15	-	5	41.22	43.42	4466	47.37	
	-	10	> 1	25.20	26.28	29.47	32.38	
		ZH	3	37.49	40.23	43.42	44.04	
			5	48.95	52.98	54.06	59.54	
		15	1	51.88	53.24	53.24	55.31	
			3	68.27	68.27	68.27	68.27	
			5	68.27	68.27	68.27	68.27	

 Table 12b: Interaction effects between depth, diameter and number of macropores on phosphorus transport in soils under arable land

Time		Phosphorus concentrations (ppm)CVLsd(a)						
(minutes)	~	<b>D</b>				(%)		
	Contr	Depth (cm)		Number				
	ol							
			1	3	5			
5	1.87	5	2.41	5.08	11.94	2.1	0.67	
		10	16.03	26.69	37.62			
		15	32.55	44.17	53.45			
10	17.89	5	20.19	25.40	30.73	1.9	0.89	
		10	25.65	35.71	43.49			
		15	39.23	51.24	60.44			
15	26.30	5	28.77	35.16	43.54	1.4	0.83	
		10	39.72	48.84	57.25			
		15	51.91	62.61	66.42			
20	39.25	5	43.92	51.10	56.17	1.1	0.79	
		10	51.96	59.00	64.40			
		15	62.79	66.05	66.60			

Table 13: Interaction effects between the depth and number of soil macrope	ores
on phosphorus transport in soils under cocoa plantation	

Table 14: Interaction effects between the depth and diameter of soil macropores
on phosphorus transport in soils under cocoa plantation

				0.5			P	
Time		Phosphor	us concen	trations	(ppm)	1	CV	Lsd
(minutes)		9	Ser.		XX	7	(%)	
	Control	Depth		Diamet	er (mm)	~		
		(cm)	N I	1				
		20	2	4	6	8		
5	1.87	5	4.92	5.81	7.08	8.09	2.1	0.69
		10	23.06	25.22	27.67	31.17		
	Z	15	39.96	42.12	44.25	47.22	7	
10	17.89	5	24.20	24.63	25.67	27.27	1.9	0.92
	15	10	31.17	33.50	35.89	39.24		
	1	15	46.16	48.82	51.72	54.52		
15	26.30	5	33.78	34.91	36.12	38.49	1.4	0.86
		10	45.36	47.15	49.45	52.45		
		15	57.93	59.64	60.96	62.72		
20	39.25	5	47.50	50.74	51.36	51.98	1.1	0.81
		10	56.41	57.48	59.11	60.81		
		15	64.14	64.83	65.31	66.30		

Time (minutes)	)	Phosphorus concentrations (ppm)						Lsd
	Control	number		Diame	ter (mm)			
			2	4	6	8		
5	1.87	1	14.09	15.80	17.18	18.36	2.1	0.69
		3	22.01	23.69	25.22	27.78		
		5	29.93	31.74	34.68	38.43		
10	17.89	1	24.52	26.84	29.08	30.93	1.9	0.92
		3	34.11	35.66	37.98	40.00		
		5	41.35	42.92	44.68	48.56		
15	26.30	1	36.43	38.79	40.63	42.32	1.4	0.86
		3	45.51	46.99	49.09	51.52		
		5	53.36	54.15	55.03	58.04		
20	39.25	1	49.69	51.83	53.41	54.60	1.1	0.81
		3	55.53	58.39	59.34	59.58		
		5	61.31	61.31	61.51	63.40		
		· .· т	1 1	• • • •	11.00			

 Table 15: Interaction effects between the number and diameter of soil

 macropores on phosphorus transport in soils under cocoa plantation

# 4.4 Correlation between the depth, diameter and number of macropores and phosphorus effluents concentration

Tables 18 and 19 showed the degrees of relationship among the depth, diameter and number of macropores and the discharging phosphorus effluents concentrations per time in soils under the two land-use systems. The correlation between the depths as well as the numbers of macropores on preferential flow of P were significant at p< 0.01 while that of the diameters of the macropore were significant at p< 0.01 while that of the diameters of the macropore were significant at p< 0.05 (Table 18 and 19). There was positive correlations between the combinations of macropores created (depth and number; depth and diameter and number and diameter) but none of the combinations were significant in soils under both land-use systems (Table 18 and 19). In soils under the coccoa plantation, the correlation coefficients between the depths of macropores and the concentrations of the discharging P effluents ranged from r = 0.82-0.88 where as that of the number and the diameter of the macropores ranged from r = 0.45-0.56 and 0.20-0.28 respectively (Table 18). Similar trends were

also recorded in soils under the arable land. The correlation coefficients between depths of macropores and the discharging P concentrations ranged from r = 0.70-0.79 whilst that of the number and diameter of macropores ranged from r = 0.46-0.60 and 0.14-0.21, respectively (Table 19). Thus, the correlation coefficient of the depths, diameters and numbers of soil macropores to preferential flow of P in soils under both land-use systems are in the order: depth> number> diameter.

![](_page_59_Figure_1.jpeg)

Figure 6: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropore of varying number and diameter at macropore depth 5 cm in soils under arable land<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> Note: A (B) C means A= depth of macropore (cm), B= number of macropore and C= diameter of macropore (mm). e.g. 5 (1) 2 implies macropore at depth 5 cm, number 1 and diameter 2 mm.

Time (minut	Phosphorus concentrations (ppm)						Lsd	
minuu	Control	Depth (cm)	Number		Diamet	er (mm)		
				2	4	6	8	
5	1.83	5	1	1.90	2.16	2.65	2.92	0.85
-		-	3	4.23	4.80	5.46	5.83	
			5	8.64	10.46	13.13	15.53	
		10	1	13.35	15.41	16.79	18.59	
			3	22.49	24.78	27.44	32.06	
			5	33.35	35.48	38.78	42.86	
		15	1	28.94	31.75	34.03	35.48	
			3	41.22	43.42	44.66	47.37	
			5	49.74	51.20	54.06	58.82	
10	17.89	5		19.48	19.79	20.59	20.91	1.12
			3	24.17	24.37	25.84	27.20	
			5	28.94	29.74	30.57	33.69	
		10	1	21.25	24.37	26.97	30.01	
			3	33.01	34.40	36.65	38.78	
		6. 1	5	39.25	41.73	44.04	48.95	
		15 -	1	34.38	37.90	41.22	43.42	
			3	46.68	49.74	52.98	55.57	
			5	57.41	58.82	60.96	64.58	
15	26.30	5	1	27.44	28.17	29.46	30.01	1.05
		E)	3	32.70	33.69	35.48	38.78	
		FEL	5	41.22	42.86	43.42	46.68	
	X	10	1	35.48	38.78	41.22	43.42	
	/ /	ree.	3	45.29	47.37	49.74	52.98	
		TIM	5	55.31	55.31	57.41	60.96	
		15	1	48.16	51.20	52.98	55.31	
			3	60.32	61.67	63.85	64.58	
			5	65.31	66.05	66.05	68.27	
20	39.25	5		42.30	43.42	44.66	45.29	1.00
	The		3	44.66	53.24	53.24	53.24	
	40	-	5	55.54	55.54	56.17	57.41	
	-	10	1	47.97	51.20	53.24	55.44	
		WJSA	BE NO	57.41	57.41	60.24	60.96	
			5	63.85	63.85	63.85	66.05	
		15	1	60.32	62.40	63.85	64.58	
			3	66.05	66.05	66.05	66.05	
			5	66.05	66.05	66.05	68.27	

 Table 16: Interaction between depth, diameter and number of soil macropores

 on phosphorus transport in soils under cocoa plantation

#### 4.5 Sorption of phosphorus in terms of the vertical distribution of the soil

Table 17 shows how the various depths of soils (0-5, 5-10 and 10-15 cm) in soils under the two land-use systems sorbed P. The amount of P sorbed decreased substantially with soil depths in soils under the arable land (p<0.01) and that of soils under the cocoa plantation (p<0.01). In relation to soils under the cocoa plantation, no significant difference was observed in P sorbed between the depths, 0-5 and 5-10 cm (Table 17). However, significant differences were recorded between soil depth, 0-5 and 10-15 cm, and 5-10 and 10-15 (Table 17). Major differences in P sorption were detected in all depths of soil under the arable land (Table 17). Considerable differences were also recorded between the concentrations of P sorbed at the varying depths of soils between the two land-use systems (Table 17). The amount of P sorbed at the soil depths of 0-5 and 5-10 cm were significantly higher (p<0.05) in soils under the arable land than that of the cocoa plantation (Table 17). The opposite occurred in relation to P sorbed at the soil depth of 10-15 cm (Table 17).

Treatments	0-5 cm	5-10 cm	10-15 cm	Lsd	CV (%)
Arable land	38.15	32.49	12.33	5.42	8.60
Cocoa	23.36	22.03	17.71	2.47	5.20
Р	0.001	0.021	0.016	-	-

Table 17: Sorption of phosphorus at different soil depths

( NT

Note: Lsd values were used to separate between means in terms of the P sorbed at varying soil depths within each land-use type whiles p (T test) values were used to compare P sorption between both land-use systems at each soil depth.

Table 18: Correlation between depth, diameter and number of macropores and concentration of phosphorus at five minutes interval in soil under cocoa plantation

Variables	Depth (cm)	Number	Diameter (mm)
Depth (cm)	-		
Number	0.11	-	
Diameter (mm)	0.13	0.10	-
5 minutes	0.88**	0.45**	0.20*
10 minutes	0.81**	0.56**	0.26*
15 minutes	0.84**	0.56**	0.25*
20 minutes	0.82**	0.56**	0.28*

\*\* = significant at p <0.01, \* = significant at p <0.05 and ns = non significance

Table 19: Correlation between depth, diameter and number of macropores and concentration of phosphorus at five minutes interval in soil under arable land

Variables	Depth (cm)	Number	Diameter (mm)
	Deptil (elli)	Number	Diameter (mm)
Depth (cm)	- A Care A	222	
Number	0.11 <sup>ns</sup>		
Diameter (mm)	0.13 <sup>ns</sup>	0.10 <sup>ns</sup>	-
5 minutes	0.78**	0.46**	$0.14^{ns}$
10 minutes	0.75**	0.46**	$0.15^{ns}$
15 minutes	0.70**	0.59**	0.19 *
20 minutes	0.74**	0.57**	$0.18^{ns}$
25 minutes	0.74**	0.59**	$0.18^{ns}$
30 minutes	0.76**	0.59**	$0.18^{ns}$
35 minutes	0.75**	0.60**	$0.17^{ns}$
40 minutes	0.79**	0.58**	0.21*
45 minutes	0.78**	0.60**	0.19*

\*\* = significant at p <0.001, \* = significant at p <0.05 and ns = non significance

![](_page_63_Figure_0.jpeg)

Figure 7: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropore of varying number and diameter at macropore depth 10 cm in soils under arable land

![](_page_63_Figure_2.jpeg)

Figure 8: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropores of varying number and diameter at macropore depth 15 cm in soils under arable land

![](_page_64_Figure_0.jpeg)

Figure 9: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropores of varying number and diameter at macropore depth 5 cm in soils under cocoa plantation

![](_page_64_Figure_2.jpeg)

Figure 10: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropores of varying number and diameter at macropore depth 10 cm in soils under cocoa plantation

![](_page_65_Figure_0.jpeg)

Figure 11: Breakthrough curves showing preferential flow of phosphorus through soil columns containing macropores of varying number and diameter at macropore depth 15 cm in soils under cocoa plantation

![](_page_65_Picture_2.jpeg)

#### **CHAPTER FIVE**

#### **5.0 DISCUSSION**

#### 5.1 Physico-chemical properties of the soil

The textural class of soils under both land-use systems (arable land under cultivation and cocoa plantation) was loamy sand. The pH values were low indicating acidic conditions in the soils. It was thus expected that P deficiency and fixation problems may be associated with Fe and Al reactions with the P. The lower amount of soil organic carbon observed in the soil under the arable land than the soil under the cocoa plantation may be attributed to land-use changes. Grace *et al.* (1995) indicated that decline in soil organic carbon (SOC) in cultivated fields are intensified due to inadequate input of organic substrates and crop residues removal. Higher exchangeable cations in soils under the cocoa plantation suggest greater capability of these soils to retain more nutrients against leaching although this was not the case with P transport in this study.

The transit time of the matrix flow of P was faster in soils under the cocoa plantation (30 minutes) than soils under the arable land (105 minutes). This can be attributed mainly to the variations in the SOC content between the two land-use systems. Better soil aggregation is associated to soil organic matter and this improves water infiltration and thus reduces runoff (Rawls *et al.*, 2005; Fenton *et al.*, 2008). Organic matter content of soils also greatly affects its hydraulic properties (Lado *et al.*, 2004). Thus, the higher SOC content enhanced the hydraulic conductivity of the soil under the cocoa plantation which further improved its water flux density.

From the reasons stated above, it can be deduced that soil under the cocoa plantations are more prone to groundwater contamination than soils under the arable land especially in areas where the groundwater table is shallow. Soils under the arable land might also be prone to runoff and erosion due to prolong ponding. However, it must be emphasised that soil profiles usually have at least two horizons separated by a horizon interface (Dyck and Kachanoski, 2009). Thus, the rate at which P is transported through soil horizons may not be uniform. Nevertheless, P transport into the lower horizons may still pose threats to groundwater contamination as the lower horizons may act as potential sources or a sinks (Borling, 2003) for further P transport.

## 5.2 Phosphorus transport as affected by different phosphorus rates

Generally, the concentration of the P effluents progressively increased as time elapsed in soils under both land-use systems excluding the control (0 ppm P) where there were fluctuations. Tening *et al.* (2013) observed similar trends when 0 ppm P was applied. He reported that the fluctuations could be due to the fact that sorption in the soils may be mainly adsorption and hence equilibrium could either shift to the left or right depending on the amount of P present at any particular time.

Within the first 20 minutes, no substantial differences were observed in the breakthrough times of the different P rates added to the soils under the arable land. What happened in soils under the arable land may be attributed to the following processes: firstly, as P solution percolated through the soil column, it steadily mixed with and slowly displaced the water initially present in the soil pores; secondly, the P (orthophosphates) in solution reacted extensively with the soil constituents which resulted in much of the P in the solution being sorbed. It is suffice to say from the literature cited on P sorption that the affinity for P sorption was high at these early

stages of flow. The above processes subsequently decreased the concentrations of the effluents at the early stages of flow. Similar processes occurred in soils under the cocoa plantation but its hydraulic conductivity and water flux density were high and the velocity and ease with which the effluents flowed through this system limited their effects. This is in line with observations made by Borling (2003) that P leaching appeared to depend more on inherent soil characteristics, such as water transport mechanisms and P sorption capacity in the profile.

In all land-use systems, the concentrations of P effluents per time were lowest in the control and increased as the rates of P increased. The breakthrough curves illustrating the effects of the different rates of P based on their relative concentrations revealed that the amount of P lost from the soil column was even more when the rates of the P increased. Gikonyo (2010) and Tening et al. (2013) observed similar trends. Del Campillo et al. (1999) recounted that, P (orthophosphates) readily reacts with soil constituents but the capacity of the soil to sorb more of the P remains limited. He further posited that continuous application of P will lead to the eventual loss of the nutrient through leaching. Consequently, landuse systems which receive higher applications of P may lose more of it through leaching compared to sites which receive lower application rates. Furthermore, P losses from agricultural lands to water resources will result in loss of nutrients which may subsequently cause water quality concerns relative to the health of both humans and aquatic systems (Baker et al., 2006). Thus, any strategy designed to replenish "soil phosphorus capital" as indicated by Sanchez (1997) must be considered critically.

The concentrations of the P effluents per time were higher in soils under the cocoa plantation than the soils under arable land. Although most chemical properties of the soil (CEC, Ca, Fe and Al) under the cocoa plantation favoured more P sorption, P leaching was higher in soils under the cocoa plantation in contrast to soil under the arable land. Higher organic carbon content of soil under the cocoa plantation inhibited the capacity of Al and Fe ions to sorb more phosphorus. Bhatti *et al.* (1998) and Ghosal *et al.* (2011) reported that organic molecules released upon decomposition of organic matter reduces P fixation by either competing for sorption sites on Fe and Al oxides or forming complexes with Fe and Al in the soil thereby blocking the sites which are mainly responsible for fixation of phosphorus in the soil. This is similar to the observations made by D'Angelo (2005) who summarised the role of soil organic matter in inhibiting P fixation. Additionally, the velocity and ease with which the P solutions leached out of the soil columns allowed little reactions between the P solutions and soil constituents resulting in lower retention of P in soils under the cocoa plantation.

The soil is the first filter of water bodies and as such it's buffering and filtering capacities determine the quantity and quality of ground and surface water (Clothier *et al.*, 2008). The soil affects plant's uptake of phosphorus in at least three ways: the amount of phosphorus in soil (quantity), the concentration of soil solution phosphorus and the movement of phosphorus to roots (Roper *et al.*, 2004). It can also be inferred from the literature that P unavailability to plants is more of soils problem than its absence from the soils. Care should therefore be taken when deciding on the amount of P to apply to enhance crop growth. Also, in considering the amount of P to apply to enhance crop growth, both the agronomic and environmental impacts of the P must be considered critically.

#### 5.3 Preferential flow of phosphorus as affected by soil macropores

The depth, diameter and number of macropores had considerable effects on the transit time of the P effluents. The transit time of the P effluents reduced as the parameters of the macropores were increased. The effects of macropores on the transit time of P flow were more profound on the arable land where the transit time of P effluents were reduced to more than half with 5 macropores, each of length 15 cm and diameter 8 mm. This shows that soils which have low hydraulic conductivity even with a small increase of macroporosity can enhance their flux densities.

The effects of macroporosity on P transport were more substantial at the early stages of flow. Additionally, subsurface transport of P increased substantially with increasing macropore depth, diameter and number. These phenomena have been reported by several authors. Borling (2003) noted that total P leaching was greatest from soils in which macropore flow dominated water transport. Other researchers have shown that flow through macroporous soils increased with macropore depth (Kluitenberg and Horton, 1990; Germann and Niggli, 1998; Akay, 2007; Zhou *et al.*, 2012), macropore diameter (Geohring *et al.*, 2001) and macropore number (Weiler and Naef, 2003; Zhou *et al.*, 2012).

The results indicate that with all other factors remaining constant, increasing either the depth, diameter or number of soil macropores will result in increasing the preferential flow of P. This further suggests that soils with different macropore numbers, depths and diameters will transport chemicals at different rates through the soil. This tends support to the non-equilibrium movements of solutes as affected by macropores in literature. Soil macropores hardly occur in isolation in nature. Thus, interaction effects of macropores were observed to quantify their effects on the preferential flow of P. The different combinations of depth and diameter; depth and number; number and diameter and, depth, diameter and number of macropores impacted immensely on P transport through the soil columns. Single macropore at a depth of 5 cm and at varying diameters had little effects on P transport in comparison to the control. However, as the depth, diameter and number of macropores increased, preferential flow of P increased considerably. Breakthrough curves used to demonstrate the interactive behaviours of different diameters and numbers of macropores and their continuity on P transport showed faster breakthrough times at constant depths as the parameters were increased.

Macropores thus pose serious threats to groundwater contamination due to their rapid transport of P through the soil profile. This suggests that P transport even in soils with high P sorption capacity may often bypass the bulk of the soil matrix, resulting in substantial loss of P. It should however be recognised that, macropores in the natural systems are tortuous (Perret *et al.*, 1999) indicating that flow rates in this experiment might be faster than what actually happens in nature. Nevertheless, Allaire-Leung *et al.* (2000) and Zhou *et al.* (2012) reported faster breakthrough times in tortuous soils as compared to soils without macropores.

With reference to natural systems, the observations signify that the depth, diameter and number of macropores created by worms and plant roots are essential to P transport in soils. Also, the depths to which the soil fauna (especially the anecic earthworms) burrow are more crucial to groundwater contaminations although the
number and diameter of macropores formed by them are also important to P transport.

Worms in soils can therefore be termed as "necessary evils" as their activities in soils may cause reduction in the amount of wastes sent to landfill. By so doing, the amount of wastes transported to ground and surface water to induce pollution is considerably reduced. But then, their burrowing activities in the soil while trying to achieve the above purpose can contribute to preferential flow of P through the soil. To the agronomist, it may lead to nutrient loss and the environmentalist, pollution. Although their presence in the soil are vital in agronomic and an environmental points of view, strategies must be developed to control their activities in the soils.

## 5.4 Impact of soil depth on P sorption

The concentrations of P sorbed in both land-use systems generally decreased extensively with soils depths. These observations are limited to the topsoils since soil samples were sampled at a depth of 0-30 cm. Tischner (1999) and Tening *et al.* (2013) observed similar trends. They found out that, the amount of P sorbed in the soil profile decreased significantly with soil depths.

With reference to P sorption according to the different land-use systems, more P was sorbed at soil depths 0-5 and 5-10 cm in soils under the arable land than soils under the cocoa plantation. Conversely, more P was sorbed in soils under the cocoa plantation as compared to the arable land at depth 10-15 cm. As reported earlier, chemical properties of soils under the cocoa plantation favoured more P sorption than soils under the arable land. Thus, the differences recorded in P sorption capacities between the two land-use systems cannot be interpreted using reaction of P with aluminium and iron oxides alone. Higher organic matter content of soils under the cocoa plantation might have hindered their ability to sorb more P. The roles of soil organic carbon on P sorption have been stated earlier and apply also to this phenomenon. Furthermore, the contact time between the P solutions and the soil constitutes increased as a result of the prolong ponding in soils under the arable land. These contributed to the high amount of P sorbed under this land-use system at soil depth 0-5 and 5-10 cm. The flow of P in soils under the cocoa plantations was fast and this hindered their sorption capacity.

Soils vary in their ability to sorb P (Paini *et al.*, 1999; Gichangi *et al.*, 2008; Idris and Ahmed, 2012). The differences in the P fixing capacities of soils suggest that the use of blanket phosphate fertilizer recommendations may not be a good strategy as it may lead to under application or over application of P in some areas with the consequence of compromising crop yields or freshwater quality (Gichangi *et al.*, 2008).



### CHAPTER SIX

### 6.0 CONCLUSION AND RECOMMENDATIONS

#### 6.1 Summary and conclusions

The experiments were conducted to investigate the mechanisms that influence subsurface transport of P from agricultural systems. Water quality should be the concern of every human being since its problems are critical to our survival. The summarised objectives of the study were to: investigate the transport of P as affected by different P rates; study P sorption at varying soil depths; study the preferential flow of P through soil columns containing improvised macropore channels and show how some physico-chemical properties of soils affect P transport through the soil. The findings were as follows:

The transit time of matrix flow of P was faster in soils under the cocoa plantation than soils under the arable land. This was attributed mainly to higher SOC content of soils under the cocoa plantation than the soil under the arable land. Higher SOC content in soils under the cocoa plantation enhanced their soil hydraulic conductivity which eventually improved their water flux density. Soils under the cocoa plantation were thus more prone to groundwater contamination than soils under the arable land which may also be prone to runoff and erosion.

It was evident from the experiments that P can be leached out of soil profiles especially when applied at high rates. In the two land-use systems (cocoa plantation and an arable land under cultivation), the concentrations of the discharging P effluents increased as the rates of P increased. Subsurface transport of P was higher in soils under the cocoa plantation in comparison to soil under the arable land. Higher organic carbon content of soil under the cocoa plantation possibly inhibited the capability of Al and Fe ions to fix P. In addition, the speed and ease with which the P solutions leached out of the soil columns allowed limited reactions between the P solutions and soil constituents resulting in lower retention of P in soils under the cocoa plantation. It is therefore important to understand that massive or continuous application of P may lead to P saturation in soils reducing the potential of soils to sorb more P which will eventually result in substantial subsurface loss of it from agricultural systems. This can cause nutrient loss and groundwater pollution. Management strategies are therefore needed to regulate subsurface transport of P for enhanced fertilizer use efficiency and decrease in environmental pollution, particularly, groundwater.

Investigations were also made to quantify the effects of depth, diameter and number of macropores and their interactions on preferential flow of P. The macropores created had significant effects on the transit time of the discharging P effluents. As the depth, diameter and number of soil macropores increased, the transit time of the discharging P effluents reduced considerably. The effects of macropores on the transit time of P flow were more profound on the arable land than that of the cocoa plantation. This further showed that for soils with low hydraulic conductivity, a small increase of macroporosity can enhance their flux density. The effects of macropore depth, number and diameter and, their interactions on P transport were more substantial at the early stages of flow. Furthermore, the subsurface transport of P increased with increasing macropore depth, diameter and number and, their interactions. The contribution of the different parameters of macropores to subsurface transport of P in both land-use systems were in the order depth> number> diameter. This suggests that the depths to which the soil fauna especially the anecic earthworms burrow through the soil are more crucial to groundwater contaminations even though the number and diameters of macropores formed by them are also important to preferential flow of P.

With regards to sorption of P in accordance to soil depths, the vertical distribution of P through the soil column decreased significantly with soil depths in soils under both land-use systems. Also, comparing how each land-use system sorbed P according to soil depths, more P was sorbed by soils under the arable land at soil depths 0-5 and 5-10 cm than the cocoa plantation soils. The contrary occurred at a soil depth of 10-15 cm. The phenomenon which resulted in lower P sorption at soil depth 0-5 and 5-10 cm in soils under the cocoa plantation as compared to the arable land was attributed to higher organic matter content, hydraulic conductivity and faster water flux density in soils under the cocoa plantation. The speed and ease with which the P solutions flowed through the soil matrix of soils under the cocoa plantation hindered their sorption capabilities.

In summary, it can be concluded that, soil organic matter improved hydraulic conductivity of soil and eventually enhanced water flux density in the soil. It subsequently affect subsurface transport of P. Higher application rates of P in amounts greater than crop uptake will enhance its leaching from the soil profile. Furthermore, macropore depth, number and diameter and their interactions affects preferential flow of P. Finally, P solutions moving through the soil profile may enhance more P sorption at the upper horizons than the lower horizons.

The hypotheses for this study as stated in page 3 were therefore accepted based on these observations.

### **6.2 Recommendation**

It can be inferred from the experiments conducted that P losses from agricultural systems are inevitable if massive doses of P are applied to increase the "soil phosphorus capital" as stocks for plant growth. In cases where macropores presence are high, the harm may be devastating. On the other hand, applying P in order to meet the environmental standards set for groundwater and surface water contamination may result in less critical P available for crop uptake. Hence, discrepancies between the agronomic and environmental risks in regards to the amount of P to apply may require critical analysis in the future to ensure judicious use of P especially within the Ghanaian context.

Crop growers must be encouraged to test their soils for available P status in order to determine the right amount of P to apply. The concentration of P in the soil solution and the soil capacity to replenish the soil solution P need to be considered when considering the right amount of P to apply. This has the tendency of reducing the risk of high P soils which may potentially enhance ground and surface water quality. Food production intensification strategies will have to seek a sustainable solution that better addresses integrated soil management while taking cognisance of both the agronomic and environment impacts.

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## APPENDIX

Appendix 1: Detailed Table showing the interaction effects between depth, diameter and number of macropores on phosphorus transport in soils under cocoa plantation (raw data)

Ν	Iacropores	5	<b>Concentrations of phosphorus at 5 minutes interval</b>						
length cm	Number	Size	5 min	10 min	15 min	20 min	25 min	30 min	
0	0	0	1.87	17.89	26.30	39.25	51.88	58.82	
5	1	2	1.90	19.48	27.44	42.30	53.24	66.05	
5	1	4	2.16	19.78	28.17	43.42	53.24	66.05	
5	1	6	2.65	20.58	29.46	44.66	55.54	66.05	
5	1	8	2.92	20.91	30.01	45.29	56.16	66.05	
5	3	2 -	4.23	24.17	32.69	44.66	66.05	*	
5	3	4	33.11	24.37	33.69	53.24	66.05	*	
5	3	6	5.46	25.84	35.48	53.24	66.05	*	
5	3	8	5.83	27.20	38.78	53.24	66.05	*	
5	5	2	8.64	28.94	41.22	55.54	66.05	*	
5	5	4	10.46	29.74	42.86	55.54	66.05	*	
5	5	6	13.13	30.57	43.42	56.16	66.05	*	
5	5	8	15.53	33.69	46.68	57.41	66.05	*	
10	1	2	13.35	21.25	35.48	47.97	63.85	66.05	
10	1	4	15.41	24.37	38.78	51.19	63.85	66.05	
10		6	16.79	26.97	41.22	53.24	63.85	66.05	
10		8	18.59	30.01	43.42	55.44	63.85	66.05	
10	3	2	22.49	33.01	45.29	57.41	66.05	*	
10	3	4	24.78	34.40	47.37	57.41	66.05	*	
10	3	6	27.44	36.65	49.74	60.24	66.05	*	
10	3	8	32.06	38.78	52.98	60.96	66.05	*	
10	5	2	33.35	39.25	55.31	63.85	66.05	*	
10	5	4	35.48	41.73	55.31	63.85	66.05	*	
10	5	6	38.78	44.04	57.41	63.85	66.05	*	
10	5	8	42.86	48.95	60.96	66.05	66.05	*	
15	1	2	28.94	34.38	48.16	60.32	66.05	*	
15	1	4	31.75	37.90	51.19	62.40	66.05	*	
15	1	6	34.03	41.22	52.98	63.85	66.05	*	
15	1	8	35.48	43.42	55.31	64.58	66.05	*	
15	3	2	41.22	46.68	60.32	66.05	*	*	
15	3	4	43.42	49.74	61.67	66.05	*	*	
15	3	6	44.66	52.98	63.85	66.05	*	*	
15	3	8	47.37	55.57	64.58	66.05	*	*	
15	5	2	49.74	57.41	65.31	66.05	*	*	
15	5	4	51.19	58.82	66.05	66.05	*	*	
15	5	6	54.06	60.96	66.05	66.05	*	*	
15	5	8	58.82	64.58	68.27	68.27	*	*	

Note: \* indicates end of transit time for discharging P effluents

# Appendix 2a: Detailed Table showing the interaction effects between depth,

diameter and number of macropores on phosphorus transport in soils under arable

Macropores Concentrations of phosphorus at 5 minutes interval													
De	Ν	Di	5	10	15	20	25	3	35	40	45	50	55
			min	min	min	min	min						
0	0	0	0.33	0.43	0.48	0.62	2.09	5.25	7.22	10.10	16.41	19.64	24.18
5	1	2	0.34	0.42	0.47	0.61	2.16	5.25	7.22	10.56	16.16	19.95	24.17
5	1	4	0.36	0.44	0.49	0.62	2.25	5.46	7.36	10.74	16.40	21.41	24.78
5	1	6	0.37	0.44	0.50	0.62	2.36	5.57	7.36	11.21	16.66	21.93	26.07
5	1	8	0.40	0.45	0.51	0.68	2.36	5.70	7.51	12.51	17.33	23.21	25.63
5	3	2	0.43	0.61	4.07	7.44	12.81	18.02	25.20	30.57	34.38	38.34	42.86
5	3	4	0.46	0.64	6.44	9.31	15.28	19.95	26.50	30.86	36.24	40.71	46.68
5	3	6	0.47	0.73	7.22	11.21	16.79	21.41	28.17	33.01	38.34	43.42	49.74
5	3	8	0.51	0.86	9.40	13.24	18.59	24.57	29.74	34.78	39.72	44.04	51.88
5	5	2	0.53	1.51	11.21	14.35	21.41	26.06	30.86	35.86	41.22	45.29	53.24
5	5	4	0.54	1.62	14.23	16.66	22.65	27.93	33.01	37.06	43.42	48.16	53.24
5	5	6	0.56	1.95	16.93	18.44	24.57	30.01	33.69	39.72	44.66	50.22	55.31
5	5	8	0.60	2.23	17.87	21.24	27.21	32.38	37.49	43.12	47.37	50.71	55.31
10	1	2	0.62	0.49	0.96	3.24	7.51	12.50	16.66	22.11	25.20	30.01	35.48
10	1	4	0.94	0.68	1.26	3.83	7.98	12.92	18.44	23.58	26.28	31.16	36.65
10	1	6	1.24	0.97	1.52	6.03	8.55	13.25	19.63	24.78	29.47	33.35	40.71
10	1	8	1.56	1.33	2.61	6.71	10.19	15.65	21.76	27.44	32.38	37.49	44.04
10	3	2	5.46	2.32	7.05	9.75	14.46	20.10	25.41	31.16	37.49	42.30	48.16
10	3	4	6.41	4.07	7.91	12.61	16.92	22.28	27.92	33.69	40.23	43.42	50.71
10	3	6	8.31	6.10	10.46	13.67	17.46	22.65	<b>29</b> .74	37.06	43.42	48.16	52.30
10	3	8	11.21	7.80	13.24	15.65	20.58	27.21	33.69	40.71	44.04	51.62	58.15
10	5	2	15.77	11.23	17.19	21.41	24.17	30.86	37.49	41.22	48.95	56.01	61.00
10	5	4	18.59	15.77	20.42	23.39	28.42	33.01	38.78	44.04	52.98	57.41	61.67
10	5	6	22.29	17.47	23.39	25.62	31.16	37.06	40.71	48.16	54.06	57.41	63.85
10	5	8	24.57	19.95	26.28	29.21	34.74	41.22	45.29	52.98	59.54	63.85	66.79
15	1	2	11.41	9.66	13.67	18.44	24.37	30.57	37.90	43.42	51.88	57.41	63.85
15	1	4	13.30	11.12	11.49	21.41	26.28	32.06	40.19	45.29	53.24	57.41	63.85
15	1	6	17.32	14.35	19.79	25.41	29.74	35.48	29.16	48.95	53.24	58.15	63.85
15	1	8	18.44	16.40	26.97	28.67	34.05	39.72	44.66	52.46	55.31	61.67	66.05
15	3	2	27.93	25.63	32.38	40.71	44.04	52.46	57.41	63.12	68.27	68.27	68.27
15	3	4	32.06	29.74	36.24	43.42	48.95	55.69	61.67	66.79	68.27	68.27	68.27
15	3	6	34.38	32.69	38.34	45.29	52.46	58.82	63.85	68.27	68.27	68.27	68.27
15	3	8	38.34	38.34	41.73	50.64	54.62	61.67	66.79	68.27	68.27	68.27	68.27
15	5	2	44.66	45.29	53.24	56.71	63.12	68.27	68.27	68.27	68.27	*	*
15	5	4	48.16	48.95	54.62	62.40	66.05	68.27	68.27	68.27	68.27	*	*
15	5	6	48.95	51.13	56.71	63.85	66.05	68.27	68.27	68.27	68.27	*	*
15	5	8	52.72	53.24	58.82	64.58	68.27	68.27	68.27	68.27	68.27	*	*

## land (raw data)

Note: De= depth, N=number, Di=diameter and \* indicates end of transit time for discharging P effluent

Appendix 2b: Detailed Table showing the interaction effects between depth,

diameter and number of macropores on phosphorus transport in soils under

arable land	(raw data)	
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Macropores Concentrations of phosphorus at 5 minutes interval								val				
De	Ν	Di	60	65	70	75	80	85	90	95	100	105
			min									
0	0	0	29.21	31.75	37.06	42.97	52.72	53.24	53.24	53.24	53.24	53.24
5	1	2	26.75	30.01	37.90	45.98	53.24	53.24	53.24	53.24	53.24	53.24
5	1	4	28.94	30.89	39.18	47.97	53.24	53.24	53.24	53.24	53.24	53.24
5	1	6	29.47	31.16	38.75	48.57	53.24	53.24	53.24	53.24	53.24	53.24
5	1	8	30.01	32.69	40.03	49.74	53.24	53.24	53.24	53.24	53.24	53.24
5	3	2	49.43	55.69	61.67	61.67	61.67	61.67	61.67	61.67	61.67	61.67
5	3	4	53.24	57.41	61.67	61.67	61.67	61.67	61.67	61.67	61.67	62.40
5	3	6	53.24	57.41	61.67	61.67	61.67	61.67	61.67	61.67	*	*
5	3	8	55.31	57.41	61.67	61.67	61.67	61.67	61.67	62.40	*	*
5	5	2	55.31	57.41	63.85	63.85	63.85	63.85	*	*	*	*
5	5	4	55.31	61.67	63.85	63.85	63.85	63.85	*	*	*	*
5	5	6	55.31	61.67	63.85	63.85	63.85	63.85	*	*	*	*
5	5	8	57.41	62.40	63.85	63.85	63.85	63.85	*	*	*	*
10	1	2	40.71	45.29	53.24	57.41	61.67	66.05	66.05	*	*	*
10	1	4	41.22	46.68	53.24	57.41	61.67	66.05	66.05	*	*	*
10	1	6	44.66	50.22	56.26	60.32	63.85	66.05	66.05	*	*	*
10	1	8	47.37	53.93	57.41	63.85	66.05	66.05	66.05	*	*	*
10	3	2	55.69	61.67	66.05	66.05	68.27	*	*	*	*	*
10	3	4	55.69	61.67	66.05	68.27	68.27	*	*	*	*	*
10	3	6	57.41	63.85	66.79	68.27	68.27	*	*	*	*	*
10	3	8	62.40	66.79	68.27	68.27	68.27	*	*	*	*	*
10	5	2	66.05	68.27	68.27	68.27	*	*	*	*	*	*
10	5	4	66.79	68.27	68.27	68.27	*	*	*	*	*	*
10	5	6	68.27	68.27	68.27	68.27	*	*	*	*	*	*
10	5	8	68.27	68.27	68.27	68.27	*	*	*	*	*	*
15	1	2	66.05	66.05	68.27	*	*	*	*	*	*	*
15	1	4	66.05	66.05	68.27	*	*	*	*	*	*	*
15	1	6	66.05	66.05	68.27	*	*	*	*	*	*	*
15	1	8	66.05	66.05	66.79	*	*	*	*	*	*	*
15	3	2	68.27	*	*	*	*	*	*	*	*	*
15	3	4	68.27	*	*	*	*	*	*	*	*	*
15	3	6	68.27	*	*	*	*	*	*	*	*	*
15	3	8	68.27	*	*	*	*	*	*	*	*	*
15	5	2	*	*	*	*	*	*	*	*	*	*
15	5	4	*	*	*	*	*	*	*	*	*	*
15	5	6	*	*	*	*	*	*	*	*	*	*
15	5	8	*	*	*	*	*	*	*	*	*	*

Note: De= depth, N=number, Di=diameter and \* indicates end of transit time for discharging P effluents