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**LEACHING OF LEAD (Pb) BY PREFERENTIAL FLOW THROUGH  
AGRICULTURAL SOILS**

**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF CROP  
AND SOIL SCIENCES, FACULTY OF AGRICULTURE IN PARTIAL  
FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER  
OF PHILOSOPHY IN SOIL SCIENCE**

**BY**

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**CERTIFICATION**

I declare that this thesis does not incorporate, without acknowledgement, any material previously submitted for a degree or diploma in any University; and that to the best of my knowledge and belief does not contain any material previously published or written by another person, except where due reference has been made in the text.

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## ABSTRACT

Until recently, scientific studies on lead (Pb) leaching was uncommon owing to the assumption that Pb is strongly bound by soil matrix. Nevertheless, Pb transport in soils has recently received a lot of attention when concentrations beyond permissible limits were detected in groundwater and surface water bodies. A study was conducted to determine Pb leaching by preferential flow through soils under close canopy cocoa, open canopy cocoa, and maize fields. It included three experiments: effect of different Pb concentrations on transport, Pb transport as affected by macropore and matrix flow, and Pb sorption at different soil depth classes. The experimental design was randomized complete block with four replications. Intact soil columns were collected up to soil depths of 0 - 30 cm from the three study sites using polyvinyl chloride (PVC) pipes. Some of the intact soil columns were thoroughly mixed and repacked into other PVC pipes under similar bulk densities such that macropores were virtually disrupted, leaving a maximum proportion of matrix pores. Different concentrations of Pb were then applied at 0, 35, 70 and 105 mg/L to saturated intact soil columns to determine the effect of Pb concentrations on transport. In order to ascertain the effect of macropore flow on Pb transport, 105 mg/L Pb was spiked on other saturated intact and the repacked soil columns. Results from the two soil columns were then compared to determine macropore flow effect on Pb transport. The Pb sorption experiment was conducted by sectioning these intact and repacked soil columns according to the three depth classes (0-10, 10-20, and 20-30 cm) after they had drained for 72 hours. Effluent concentrations of Pb from the two leaching experiments were used to develop breakthrough curves (BTCs) each. Significant differences ( $p < 0.05$ ) were observed among Pb effluent concentrations of intact soil columns under each test site as the concentrations of Pb

applied were increased. Significantly higher ( $p < 0.05$ ) leaching of Pb in terms of relative concentrations were recorded in the order: close canopy cocoa > open canopy cocoa > maize, as the concentrations of Pb applied were increased on the BTCs. In addition, intact soil columns recorded significantly higher ( $p < 0.05$ ) leaching of Pb from the BTCs, than repacked soil columns under each study site. The influence of macropore flow accounted for significantly higher ( $p < 0.05$ ) saturated hydraulic conductivities, Pb fluxes, breakthrough concentrations, and significantly shorter ( $p < 0.05$ ) transit time for Pb transport in intact soil columns than repacked soil columns under each study site. The hydraulic property and transport parameters above were also significantly highest ( $p < 0.05$ ) under close canopy cocoa among the test sites. There were significant positive correlations ( $r = 0.67$  to  $0.99$ ) between the selected physical and hydraulic properties (except bulk density), and transport parameters (except transit time) of both intact and repacked soil columns. Pb sorption generally decreased with depth and increasing macroporosity in the soils under each test site. Significantly higher ( $p < 0.05$ ) Pb sorption were recorded in the corresponding depths of repacked soil columns than intact soil columns under each study site. Soils under maize sorbed the highest amount of Pb at the respective soil depths. From the study, organic matter improved hydraulic conductivity and eventually enhanced water and Pb fluxes in the soils under close canopy cocoa than the two study sites. Generally, soils under close canopy cocoa were more laible to Pb leaching as compared to soils under open canopy cocoa and maize. Macropore flow substancially contributed to Pb leaching in the soils under each study site. The effect of macropore flow on Pb leaching was higher in soils with higher macroporosities. Thus the amount of Pb that leached out from intact soil columns was in the order: close canopy cocoa > open canopy cocoa > maize. Contrastingly, effect of matrix flow on Pb transport

was relatively lower. Hence, applying heavy doses of Pb directly or indirectly by agricultural and industrial activities to soils under close canopy cocoa could leach Pb into the vadoze zone and groundwater. On the other hand, soils under maize are apt to surface transport of Pb into water bodies. The study also showed that percolating Pb solutions in the soils may enhance Pb sorption at the upper layers of the soil profile than the lower layers especially in soils with lower macroporosities and also in the soil matrix.



## DEDICATION

I dedicate this dissertation to my parents, Mr and Mrs Boateng, and my siblings.

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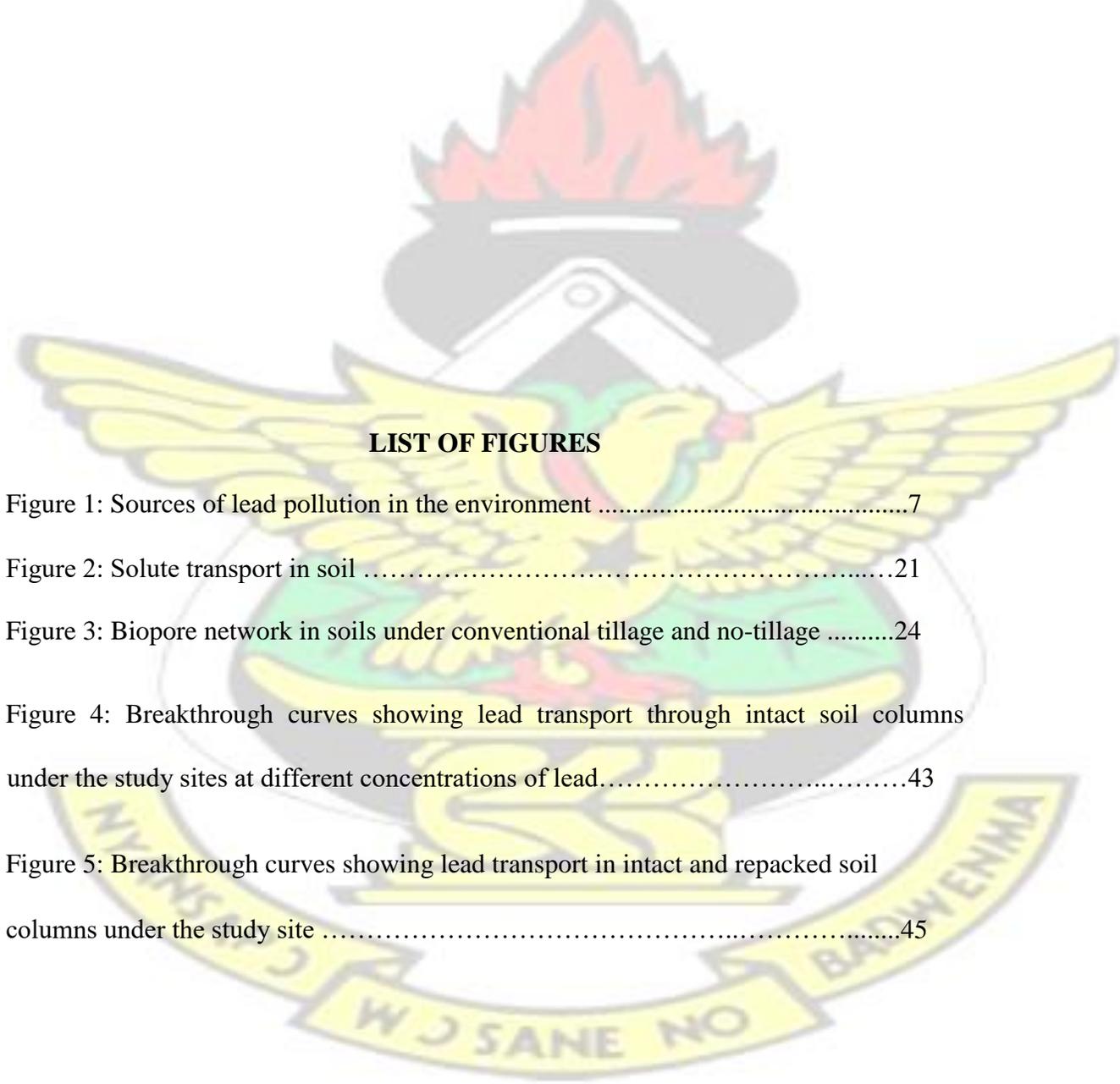
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### CHAPTER ONE

#### 1.0 INTRODUCTION

##### 1.1 Background

Studies on Pb transport in soils received little attention owing to the presumption that it is readily sorbed by soil colloids, until the detection of levels beyond global standards in soils, groundwater and surface water bodies (Kedziorek *et al.*, 1998; Deiss *et al.*, 2004; Sathyanarayana *et al.*, 2011). The dramatic contamination of these resources is dated back to the beginning of the industrial revolution (Voegelan *et al.*, 2003) where point and diffuse contamination of farmlands and water bodies basically resulted from agricultural, industrial and urban activities (Ross, 1994; Nicola *et al.*, 2003; Rashad and Shalaby, 2007; Nicholson *et al.*, 2010). Upon entry into soil, Pb is subjected to a variety of processes including sorption/desorption, precipitation/dissolution, oxidation/reduction, leaching, runoff and erosion (McLean and Bledsoe, 1992; McBride, 1994).

Preferential flow or non-equilibrium transport (rapid solutes movement in preferred routes) has been reported as the major phenomenon responsible for leaching of solutes in

soils (Bruggeman, 1997; Nicholls *et al.*, 2000). Among the three main types, namely: fingering, funnel and macropore flow, the latter is ubiquitous in structured soils (Kung, 1990; Jarvis and Dubus, 2006). It drains freely by gravity (Jarvis *et al.*, 2007). Thus it may transport reactive solutes like Pb and water at higher velocity and flux within short transit time and subsequently, rapid breakthroughs such that there is minimal interaction between solutes and the bulk of soil (Nielsen *et al.*, 1986; McGrath *et al.*, 2009). Hence, in structured soils, macropores could serve as the main route for Pb leaching into the vadose zone and groundwater (Deiss *et al.*, 2004). However, macropore volume to total soil volume ratio (macroporosity) vary among soils and thus its effect on physical transport of Pb may be site-specific (Aubertin, 1971). The influence of chemical equilibrium reactions on Pb dissolution and complexation could contribute substantially to Pb leaching (Deiss *et al.*, 2004; Fifi *et al.*, 2013). Again, influx of higher loads of Pb into soils at a given point in time is known to increase the chances of Pb transport by leaching and runoff and/or erosion into groundwater and surface water bodies severally (Appel and Ma 2002; Rosazlin *et al.*, 2010). In point of fact, soils that have larger macroporosities and high Pb content under favourable transport conditions, may leach significant quantities of Pb into the vadose zone and underground aquifers.

## **1.2 Problem statement and justification**

Urban and peri-urban farms as well as farmlands subjected to mining activities in rural areas get polluted by Pb through the use of untreated wastewater, polluted rivers and streams for irrigation purposes, application of untreated organic fertilizers including sewage sludge as sources of plant nutrients, and spillage from mining incinerators and runoff from mining waste landfills (Ross, 1994; Mensah *et al.*, 2001; Ingwersen and Streck, 2005; Obuobie *et al.*, 2014). The contribution of the various sources of Pb to total

soil Pb, coupled with the fate of mobile forms of Pb, have been found to cause groundwater and surface water pollution. Therefore Pb transport is worth studying in order to critically understand the processes that governs it and then develop possible means to minimise contamination of water resources and its adverse effects on agriculture and human health.

Again, in spite of the substantial evidence of Pb leaching, there is little on the subject of influence of macroporosity variability on preferential flow of Pb in soils under different land-use systems and land covers. The study therefore seeks to provide relevant information to help fill the knowledge gap.

### **1.3 Hypothesis**

- i. Macropores have greater influence on Pb transport in structured soils than the soil matrix.
- ii. Soil chemical, physical and hydraulic properties under different land-use systems and land covers vary and these affect Pb transport and sorption.
- iii. Increasing Pb concentrations in soil will influence its transport into groundwater.

### **1.4 Objectives**

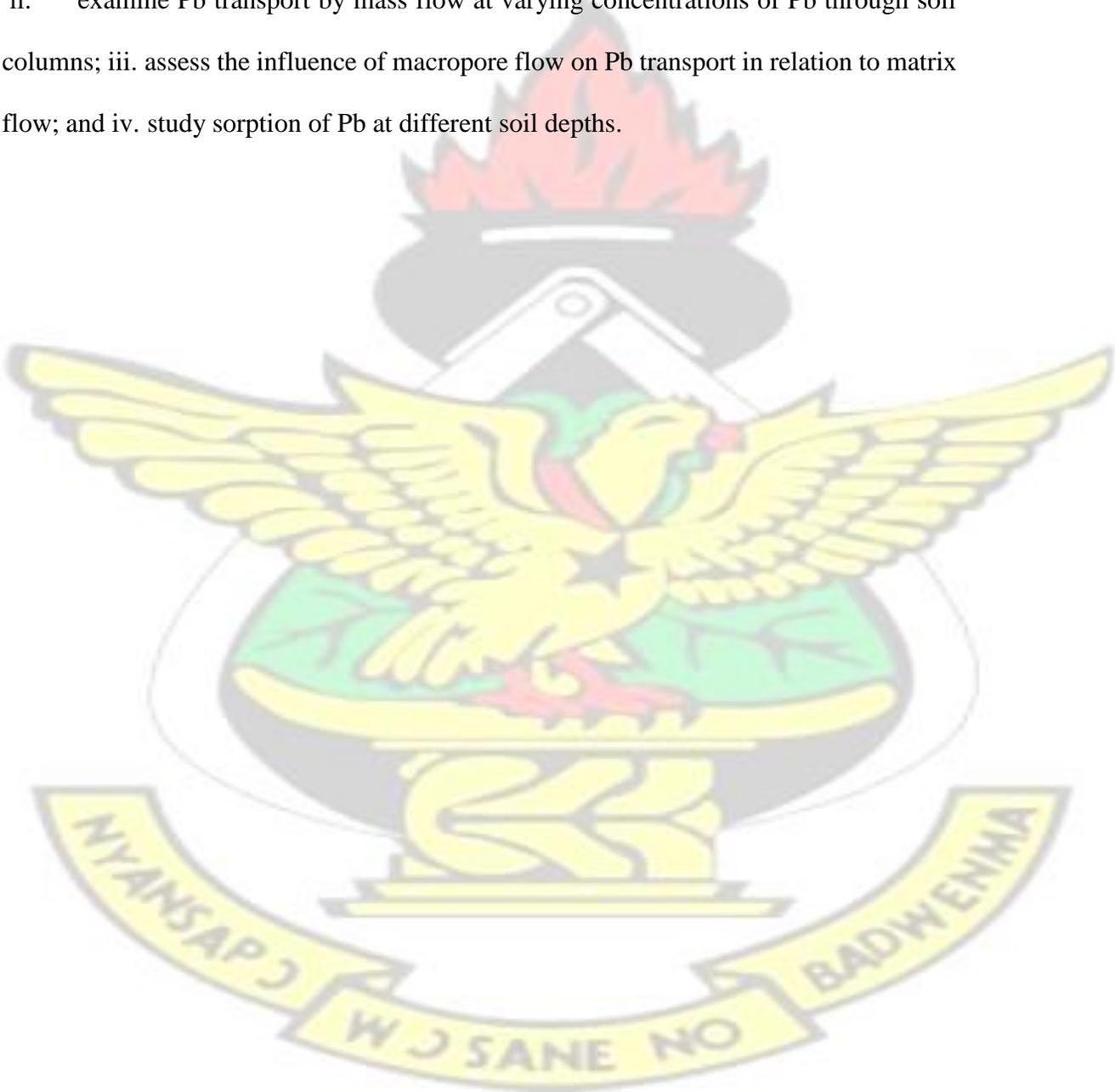
#### **Main Objective**

The main objective of the study was to assess and quantify Pb leaching in soil columns and its implications on vadose zone contamination, groundwater and surface water quality.

## Specific Objectives

The specific objective were to:

- i. determine the effect of some soil chemical, physical and hydraulic properties on Pb transport;
- ii. examine Pb transport by mass flow at varying concentrations of Pb through soil columns;
- iii. assess the influence of macropore flow on Pb transport in relation to matrix flow; and
- iv. study sorption of Pb at different soil depths.



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## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Lead as a heavy metal

Generally, heavy metals are known as elements in the periodic table having atomic numbers more than twenty and densities more than  $5\text{g/cm}^3$  excluding alkali metals and alkaline earth metals (Sherene, 2010). The term heavy metals normally, is used for nonessential metals among this periodic group including: Pb, Cadmium, Mercury and the metalloid, Arsenic (Rauser, 1995; Sharma and Dubey, 2005). Thus they are nonnutrient and hence, do not play any major role in the physiology of plants, animals and man but rather tend to be toxic when they bioaccumulate in living tissues over time upon absorption (Rauser, 1995; Sharma and Dubey, 2005; Madyiwa, 2006).

Among all heavy metals, Pb stands out to be one of the most hazardous pollutants in the environment since it is readily available in air, water resources and soils and this poses a lot of ecological concerns as a result of its impact on the environment (Shahmohammadi-Kalalagh *et al.*, 2011; Malar *et al.*, 2014).

However, the stable silver-grey metallic Pb which is rarely found in its elemental form is combined with other elements to form a variety of complexes, compounds and alloys which are further used in products such as electric storage batteries, radiation shields, pigments, paints, glassware, sheaths for electric cables and rubber compounds (Juberg,

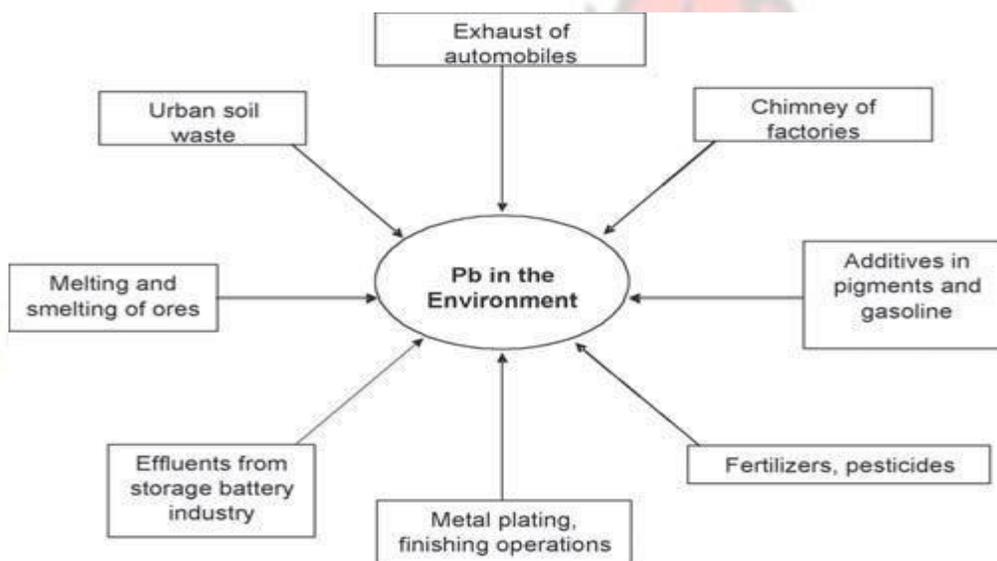
2000; Tukker *et al.*, 2001).

### 2.2.1 Sources of lead in agricultural soils

Sources of Pb in agricultural soils has been reported to be site specific depending on the major environmental or anthropogenic impacts on a given soil (Juberg, 2000; Tardy *et al.*, 2003). Apart from natural weathering processes, global outlets of Pb into the environment include: metal plating and finishing operations, effluents from storage battery industry, melting and smelting of ores, urban waste, exhaust of automobiles, chimney of factories, fertilizers and pesticides, and additives in pigments and gasoline (Figure 1).

Chrastny *et al.*, (2010) generally imputed Pb build-up in agricultural soils to point sources such as wastewater irrigation and the application of inorganic phosphorus fertilizers and sewage sludge especially in urban and peri-urban farming in developing countries. Asante and Ntow, (2009) posited emphatically that in Ghana, mining and agriculture remain the major localized sources of chemical pollution in general. Thus urban and peri-urban farming systems is currently reported as one of the major sources of heavy metals including Pb in agricultural soils, due to repetitive use of economical but contaminated sewage sludge and waste water as fertilizer and irrigation water respectively (Cornish and Lawrence, 2001; Obuobie *et al.*, 2014). Despite mild contamination in the cities, this situation is worse in rural mining areas where mining activities increased without proper regulations of treatment and disposal of discharges (Obuobie *et al.*, 2014).

Other major point and non-point sources of Pb are known to be atmospheric deposition, mining, incineration, production of plastics, nuclear radiation, shooting ranges, fossil fuel burning from vehicles and power generating plants in developed countries (He and Singh, 1993). Out of these sources, Nicola *et al.* (2003) found atmospheric deposition to be the major source of Pb in agricultural lands. They assigned livestock manures and sewage sludge to be locally important sources.



**Figure 1: Sources of Pb pollution in the environment** (Sharma and Dubey, 2005).

### 2.1.2 Amounts and permissible limits of lead in soils

Lead is one of the commonest naturally occurring heavy metals in the environment. It has an estimated concentration of 13 mg/kg in the earth crust (Asklund and Eldvall, 2005). It is rarely found naturally as a metal but rather accumulates in sulphurcontaining minerals (e.g. galena) and also fix in mineral lattice (e.g. feldspar) whilst replacing sodium, potassium and calcium (Olive, 2006). The average concentration of

Pb in most soils ranges between 10 – 30 mg/kg (Craigmail, 2010). Different levels of Pb contamination in soils have been reported by many authors. Maldonado *et al.* (2008) reported very high concentrations ranging between 4.48 mg/kg to 20,313 mg/kg within 0 – 50 cm depth of four Mexican farmlands irrigated with industrial wastewater. In Ghana, Nartey *et al.* (2012) recorded Pb concentrations ranging from 1.12 mg/kg to 2.60 mg/kg in fertilizer amended soils under cocoa plantations. Also, Boadu (2004) reported point Pb contamination levels between 642.27 mg/kg to 1,392.67 mg/kg in soils of a scrap metal company in Ghana which were far beyond Dutch intervention levels (530 mg/kg).

There are different permissible limits of total soil Pb in different locations. However, literature suggests that foreign and international permissible limits have been adopted in Ghana (EPA-G, 1996; Boadu 2004; Tiimub *et al.*, 2012). Some of these are as follows:

Dutch desirable maximum and intervention values in unpolluted soils are 85 mg/kg and 530 mg/kg respectively (MH-N, 1994) and FAO/WHO permissible limit in soils is 50 mg/kg (FAO/WHO, 2001). Hence a modest of 70 mg/L of Pb was considered under this study.

### **2.1.3 Fate and forms of lead in soils**

The fate of Pb in soils is mainly controlled by inherent soil chemical and physical processes such as dissolution into soil solution, precipitation as pure or mixed solids, oxidation and reduction reactions, surface adsorption by exchangeable sites, specific adsorption by soluble and insoluble organic and inorganic ligands, leaching by mass flow, and surface transport by runoff and erosion (McLean and Bledsoe, 1992; Tardy *et al.*, 2003). Native Pb may be fixed in lattice of primary and secondary minerals or be subjected to any of the above processes depending on the geological history of a given

area (Olive, 2006). Hence fate determines the various forms, amounts and movement of Pb in soils.

Lead in soils may exist as aqueous Pb or solid Pb (McLean and Bledsoe, 1992; Chen and Daroub, 2002). Aqueous forms in the soil solution generally consist of the following. Dissolved, desorbed, and oxidized Pb ions ( $\text{Pb}^{2+}$ ) that result from dissolution of discrete minerals of Pb in acidic to near neutral environments, desorption from exchange sites, and oxidation of elemental Pb. Organic and inorganic complexes of Pb (e.g.  $\text{PbHCO}_3^+$ ,  $\text{PbCO}_3$ ,  $\text{PbBr}^+$ ) and Pb associated with soluble colloidal materials (e.g.  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb-DOM}^+$ ) which also result from specific adsorption of Pb by organic and inorganic ligands in the soil solution. Aqueous Pb is noted as the main source that contribute to Pb bioaccumulation in plant tissues and transport by leaching, runoff and erosion (Tardy *et al.*, 2003). By comparison, Pb associated with mobile colloids are easily transported by water followed by cationic Pb and Pb complexes severally. This is because the resultant complex species may have negative, positive or neutral net charge and hence, may be weakly adsorbed or more strongly adsorbed to solid particles relative to free Pb ions (McLean and Bledsoe, 1992). There is therefore a large consensus among scientist that the amount and type of aqueous Pb in soil determines to a greater extent, the risk of plant toxicity, groundwater and surface water contamination rather than total Pb (Chen and Daroub, 2002).

Lead leaching is broadly defined as the process where aqueous Pb move with water by mass flow via soil matrix pores or preferential paths into deeper soil horizons and underground water and it is known to threaten human health (Park *et al.*, 2013). Also, chemoautotrophic bacteria induced bioleaching of Pb has been reported in literature

(Falciglia and Vagliasindi, 2013). The route of Pb leaching is of great concern as it directly affects the extent of leaching and risk of contamination (Deiss *et al.*, 2004). Preferential paths for Pb leaching over a long period of time may be detrimental to animal and human health relative to soil matrix pores (Deiss *et al.*, 2004). Chemical removal of Pb in soils with low buffering capacities by acidic runoff and detachment of Pb-containing sediments in bare soils by erosion are the basic surface transport phenomena that contribute to Pb contamination of surface water bodies from soils (Wang *et al.*, 1980).

Solid compounds of Pb in soils contaminated by industrial and agricultural activities, among others, include Pb soluble salts {e.g.  $\text{Pb}(\text{NO}_3)_2$ , galena ( $\text{PbS}$ ), anglesite ( $\text{PbSO}_4$ ), cerussite ( $\text{PbCO}_3$ ), litharge ( $\text{PbO}$ ), crocoite ( $\text{PbCrO}_4$ )} and Pb phosphates {e.g. pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ }. They are mainly formed from precipitation and reduction of aqueous forms into pure or mixed solids, complexation by insoluble organic and inorganic ligands, and specific adsorption by colloidal particles (Tardy *et al.*, 2003; Olive, 2006). The reduction of aqueous Pb by reducing agents such as phosphates ( $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ ) and apatite  $\{\text{Ca}_5(\text{PO}_4)_3\text{X}\}$  groups and specific adsorption into inner spheres of soil colloids such as Iron (Fe) and Manganese (Mn) compounds produces solids that are geochemically stable under wide range of soil pH (Traina and Laperche, 1999; Ma and Rao, 1999; Chen and Daroub, 2002). Nonetheless, the rest are highly soluble and may easily leach under acidic pH conditions (Traina and Laperche, 1999; Shen *et al.*, 2006).

Solid organic complexation of Pb in soils is not as well defined as inorganic complexation due to difficulty in identifying organic ligands (McLean and Bledsoe, 1992). However, complexation of Pb and fulvic acids as well as humic acids in sewage sludge is noted to

be a primary source of organic Pb complexes in agricultural soils (Baham and Sposito, 1986). This form increases the risk of Pb leaching and transport by runoff and erosion in soils since it is soluble at slightly acid pH (Strawn and Sparks 2000).

#### **2.1.4 Impacts of lead to agriculture and human health**

Over the years, there has been substantial studies on the negative impact of Pb on agriculture and human health. Concern over human health and plant physiology has still not waned due to its high toxicity and lack of known biological benefits (Juberg, 2000; Sharma and Dubey, 2005).

Lead is known to bind to sulphur-containing ligands in cells due to its high affinity to the latter, and hence bioaccumulate in living tissues and later inactivate many enzymes and disturb lots of metabolic processes (Seregin and Ivanov, 2001). In acidic soils, it is bound by the carboxy group of root mucilage uronic acids at the root surface but released later and absorbed passively by plants when these acids biodegrade (Salt *et al.*, 1995; Sharma and Dubey, 2005). This serves as the primary route of Pb entry into food chain with the other secondary route being via the leaf stomata (Salt *et al.*, 1995). Generally, toxic levels of Pb in plants cause chlorosis and rapid inhibition of root and shoot growth (Malar *et al.*, 2014). Specific symptoms include upsets in mineral nutrition and water balance, changes in hormonal status, inhibition of photosynthesis and poor membrane structure and permeability, death of cells and reduction in yield at very high toxic concentrations (Seregin and Ivanov, 2001; Malar *et al.*, 2014). Mishra and Choudhari (1998), reported that Pb toxicity inhibited germination and retarded seedling growth as it reduced germination percentage, tolerance index, dry mass and length of root and shoot. Verma

and Dubey (2003) reported similar findings that higher concentrations of Pb (1 mM) caused 14 - 10 % reduction the germination of rice seeds and decreased seedlings growth by 13 - 14 %. Nevertheless, Malar *et al.* (2014) observed that water hyacinth plants, *Eichhornia crassipes* can tolerate higher Pb concentrations in surface water bodies due to increased levels of antioxidative enzymes but higher levels of 100 mg/L Pb concentration significantly inhibited growth by 50 %.

Human and animal exposure to Pb may occur directly through the environmental outlets, through ingestion of food and water containing detectable amounts of Pb, and from the use of Pb-containing consumer products (Hutton, 1987; Juberg, 2000). Pb intoxication in farm animals is common in ruminants that graze by road sides (Hutton, 1987). Byrne (2011) outlined symptoms of Pb poisoning in ruminants as paralysis of the tongue, circling and “star-gazing”, nervous signs and hypomagnesaemia. Pb can be passed on in the milk of farm animals and may reduce substantially, the quantity and quality of milk in dairy cows (Hutton, 1987). Martinez *et al.* (2004) upon their investigations on effect of Pb on morphology and physiology of the neotropical fish, *Prochilodus lineatus*, observed that exposure of the latter to Pb for long period of time caused histopathological lesions in the gills including: epithelial lifting, hyperplasia and lamella aneurism, and significant decrease in sodium plasma concentration.

According to Juberg (2000), the major effects of chronic or acute exposure of Pb in human manifests in four different system namely: the renal, reproductive, neurological and haematological. Mainly acute exposure to Pb may cause encephalopathy, anaemia, peripheral neuropathy, and renal failure whilst lower-level chronic exposure (bioaccumulation) is associated with subtle effects, including hypertension, dental caries, osteoporosis, reproductive dysfunction, developmental defects, abnormal vitamin D

metabolism, and in some situations death (USEPA, 1992; ATSDR, 2007). Pb poisoning in children and pregnant women have been reported to be fatal than in adults (Tong *et al.*, 2000). In children, it is known to cause decreases in IQ scores, retardation of physical growth, hearing problems, impaired learning, and in pregnant women, decrease in birth weight and shortening of gravidity during prenatal stages (ATSDR, 2007).

### **2.1.5 Lead sorption and kinetics in soils**

Free metallic Pb ions, soluble organic and inorganic Pb complexes, and Pb associated with mobile colloidal materials available in the soil solution undergo one of the physico-chemical reactions termed as sorption, with the soil matrix thus organic matter, clay minerals, oxides and hydroxides of Fe and Mn, carbonates and amorphous aluminosilicates (McLean and Bledsoe, 1992).

Sathyanarayana *et al.* (2011) broadly categorised these reactions under alkaline soil conditions into two: first, cation exchange, which is characterized by a rapid, stoichiometric, reversible and diffusion controlled equilibrium reaction that occurs on the outer-sphere of adsorption sites by means of electrostatic interactions; and secondly, specific adsorption of Pb through an inner-sphere reactions at higher bonding energy that would not be available for leaching or bioaccumulation in plants. The former controls the amount of Pb in the soil solution through cation exchange reactions whilst the latter increases the tendency for the formation of hydroxo-complexes, organic Pb complexes, and hydroxides of Pb (Schwertmann and Taylor, 1989; Olive, 2006).

Lead sorption in soils is highly variable depending on integral physicochemical properties and the occurrence of anthropogenic sources of Pb (Elbana, 2013). Dutta and Singh (2011)

reported different sorption behaviours of Pb in four soils with diverse sorption capacities. In the soil, the pH dependent equilibrium reactions (dissolution/precipitation) affects Pb solubility which subsequently influence Pb sorption (McLean and Bledsoe, 1992). The solubility of organic and inorganic compounds of Pb added to soils from various sources are different (Freeman *et al.*, 1996). Thus soils that receive readily soluble forms of Pb such as Pb nitrate {Pb(NO<sub>3</sub>)<sub>2</sub>}, Pb chloride {Pb(Cl)<sub>2</sub>}, Pb acetate {Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>}, as well as sparingly soluble forms including Pb iodate {Pb(IO<sub>3</sub>)<sub>2</sub>}, Pb selenide (PbSe) and Pb tellurite {Pb(TeO)<sub>3</sub>} (Clever and Johnston, 1980), may have higher levels of aqueous Pb available for sorption or transport depending on soil pH (McLean and Bledsoe, 1992).

A number of authors have investigated Pb sorption with respect to soil depths. In most cases, it accumulated in the upper horizons due to high organic matter content and additional deposits from anthropogenic sources, and reduced significantly with depth depending on clay mineralogy (Barriquelo *et al.*, 2003; Sipos *et al.*, 2005). Sipos *et al.* (2005) stated categorically that in the underlying soil layers, Pb distribution content is best explained by the differences in carbonate, oxides and hydroxides content as well as the mineralogical characteristics of the various soil horizons of a given soil profile.

Length of contact time that is how long a solute interacts with the adsorption sites, has tremendous effect on sorption of contaminants. Increasing contact time may increase amount of solutes sorbed. However the amount sorbed decreases with time once the sorption capacity of a given soil is exceeded (Strawn and Sparks, 2000; Tardy *et al.*, 2003; Fonseca *et al.*, 2009)

Matini *et al.* (2011), made conclusions that corroborated Pb sorption and vertical distribution in soils of spoil heap in the vicinity of an abandoned treatment plant of Pb ore. They reported that the amount of Pb sorbed by the soil decreased from 11,800 mg/kg within 15-45 cm depth of soil to 2,000 mg/kg within 35-150 cm soil depth. They attributed this to the length of contact time for Pb and the soil constituents within each layer and its strong relationship with organic matter and clay fractions. Eventhough talc was present in greater amount, followed by kaolinite, chlorite and smectite, kaolinite was the dominant clay mineral responsible of the vertical migration of Pb in the soil profile. The upper layers had longer contact time than the underlying soil layers because it received Pb first and hence, had longer time to interact with Pb than subsurface layers.

According to literature, varoius Pb sortpion studies have mostly been conducted using batch equilibrium experiments (Sherene, 2010). Usually, Pb solutions are added to equal mass of soils from different soil layers. The differences between initial and final amount of Pb in solution after a common contact time for Pb sorption, gives the amount of Pb sorbed by a particular soil layer (Strawn and Sparks, 2000). This clearly shows that using batch equilibrium experiments to study Pb sorption at different soil layers would either overestimate or underestimate the amounts of Pb sorbed by each layer of the soil profile since a common contact time is used. Soil column leaching experiments on the other hand allow respective contact times for Pb sorption at the various soil layers.

### 2.1.6 Effect of increasing lead loads on its transport in different soils

Despite the awareness that Pb and other heavy metals are highly toxic, various activities which directly or indirectly increase total Pb contents of agricultural soils are still ongoing especially in developing countries (Voegelan *et al.*, 2003; Asklund and Eldvall, 2005; Asante and Ntow, 2009). Lack of proper chemical assessment of organic fertilizers, rampant use of urban waste water for irrigation by poor farmers in urban and peri-urban farming, as well as reckless spilling and disposal of industrial and mining effluents, attest to this (Forstner, 1995; Mensah *et al.*, 2001; Fodor and Szabo, 2004).

Decades ago many researchers assumed virtually no effect of Pb build-up on transport since it readily reacted with the soil matrix to form geochemically stable compounds. However current studies have confirmed excessive Pb leaching in soils under heavy loads of Pb (Richards *et al.*, 2000; Bundt *et al.*, 2001). Garcia-Miragaya *et al.* (1986) explained how this occurs. At low concentrations, aqueous Pb is adsorbed by specific adsorption and exchangeable sites. However, increasing the concentration of Pb in soil will cause saturation at the sorption sites, and hence increase Pb mobility. Consequently, soils that receive heavy loads of Pb may end up polluting groundwater or surface water bodies. Several authors have confirmed this (Fodor and Szabo, 2004; Rosazlin *et al.*, 2010). Nonetheless, the effect of increasing Pb loads may be site specific (Diatta, 2006; Elbana, 2013)

Dutta and Singh (2011), demonstrated the effect of increasing Pb concentration on transport using batch equilibrium reaction of Pb sorption in three different soils. They concluded that Pb sorption increased at a decreasing rate when more Pb was added to the soils until further addition, increased Pb concentration in solution for all the three

different soils. Diatta (2006) used sorption densities to evaluate direct impact of additional Pb inputs on four different agricultural soils. He ascertained that among the four soils, one could leach significant quantities of Pb since only 27 % of the initial Pb applied ( $2.0 \text{ mmol/dm}^3$ ) was adsorbed when the cation exchange capacity (CEC) ( $5.97 \text{ cmol}^+/\text{kg}$ ) was exceeded. However the effect of increasing Pb concentration on the remaining three soils types was minimal.

### **2.1.7 Some soil properties and their influence on lead transport**

Lead mobility in soils is affected by a wide range of soil properties as well as their interactions (Prasad and Freitas, 2003; Gadd, 2004). Generally, colloidal materials serve as the most active binding sites for Pb and their ability to bind Pb is mainly dependent on point of zero charge (PZC) i.e., the pH at which the sum of negative charges on a surface equals the sum of positive charges (Olive, 2006). Therefore at pH values higher than the PZC, the net charge on colloidal surfaces is negative and sorption of Pb by organic matter, clay, hydroxides and oxides of Fe and Mn, and carbonates, is favoured (Nessner and Esposito, 2010). On the other hand, soils with low pH values relative to PZC have low cation exchange capacity and rate of insoluble Pb complexation but dissolution of Pb-bearing compounds may be higher (Wei and Yang, 2010). This increases amount of Pb in soil solution and hence, favours easy transport to the vadose zone by mass flow (Schwertmann and Taylor, 1989). As a rule, there is negative correlation between soil pH and Pb mobility. Tardy *et al.* (2003) observed that Pb leaching from small arms firing range soils increased by 100 to 200 % (i.e. 60 % of the original Pb content in soil) when pH was lowered from between 5.38 to 7.5, to 3.0. Soil redox potential indirectly influences metal mobility. Olive (2006) recounted that at low redox potential, reductive

dissolution of Mn and Fe oxides, favours Pb sorbed on their surface to dissolve into solution, facilitating easy transport of Pb. Contrarily, Pb may co-precipitate with Mn and Fe oxides in soils with higher redox potential.

Many authors have given detailed relationship between Pb and soil organic carbon (SOC) content in terms of sorption and leaching. Sipos *et al.* (2005) studied Pb sorption using stirred-flow experiments. They reported that the clay fractions of forest luvisols could adsorb 20-30 % more Pb than the bulk soil but this adsorption capacity decreased by 50 % upon removal of SOC. Nevertheless, the different clay mineralogy adsorbed Pb in different amounts: vermiculite dominated fractions adsorb more Pb than the chlorite dominated ones.

Strawn and Sparks (2000) reported a contradictory effect of SOC on Pb leaching in soils under slightly acid pH conditions. They concluded from Pb sorption kinetics study that formation of soluble organic Pb complexes at this pH from the interactions of soluble organic matter (humic and fulvic acids) and Pb by specific adsorption could guarantee Pb leaching from soils. Rooney (2002) further reported that the risk could be higher in soils where SOC content was high. Again, SOC improves infiltration capacity, hydraulic conductivity and water flux densities as a result of good structure development and formation of abundant macropores (Brady and Weil, 1990; Clothier *et al.*, 2008). This may increase mass movement of reactive solutes like Pb from the upper soil layers through the matrix pores and macropores into underlying soil horizons (Brady and Weil, 1990; Clothier *et al.*, 2008). Hence soils in land-use systems and land covers which has high SOC content and slightly acid pH conditions may be apt to Pb leaching into underground aquifers especially when larger quantities of Pb are added in a pulse.

## 2.2 Solute transport in soils

Solute transport by water through the soil is mainly controlled by matrix flow and preferential flow. Matrix flow is the movement of water and solutes through soil matrix pores such that there is uniform wetting front (Kordel *et al.*, 2008). Preferential flow however, refers to the flow mechanism where dissolved or suspended matter is transported by water at faster rates through certain pathways whilst by-passing the chemically and biologically active porous soil matrix (Kung, 1990; Bruggeman, 1997). Even though matrix flow in sandy textured soils may be dominant due to higher proportion of larger matrix pores (Kordel *et al.*, 2008), it is observably low in structured soils as a result of larger proportion of finer pores (Jarvis and Dubs, 2006; Kordel *et al.*, 2008). On the other hand, the characteristic solute transport features of preferential pathways in structured soils poses environmental and human related problems since it causes contaminant transport to vadose zone and underground aquifers (Merdun, 2005; Allaire, *et al.*, 2009). Among the three main types of preferential flow: macropore flow, funnel flow and fingering, the former is deemed significant in structured soils due to the abundance of macropores (Bruggeman, 1997).

### 2.2.1 Soil macropore and solute transport

There is no general definition for soil macropores. For example, various authors have used pore diameter limits to define what they considered macropores (Chen and Wagenet, 1992; Jarvis *et al.*, 1999; Greco, 2002). Beven and Germann (1982), earlier defined macropores as pores having a size of more than 1 mm. However most experimental work

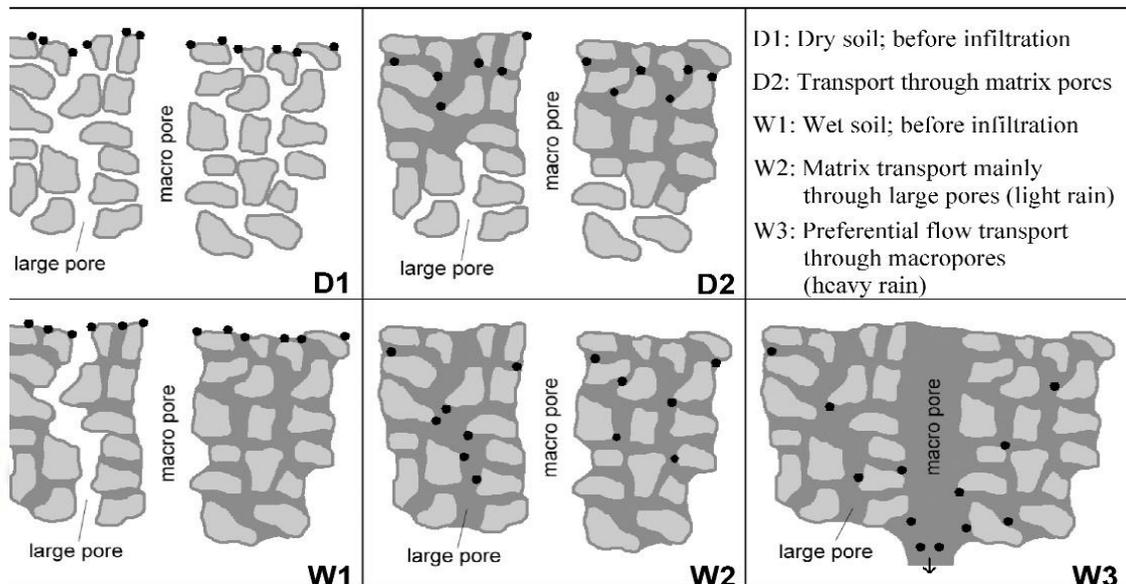
suggested that pores that were at least 0.3 mm in diameter were able to cause preferential flow of water and solutes if they were continuous (Jarvis and Dubus, 2006).

Jarvis (2007), further defined macropores as pores with diameter of 0.3 mm to 0.5 mm that allow non-equilibrium flow of water and solutes at water entry pressure of at least -10 cm (near atmospheric pressure). Rowell (2014), also defined macropores using soil water relations as pores that drain freely by gravity at field capacity moisture content.

Macropore flow definition according to literature are many but all highlights the importance of rapid mass movement. Beven and German (1982) defined macropore flow as the vertical flow of water in macropores into the vadose zone that prevented lateral distribution from the soil matrix. Allaire *et al.* (2009) gave a wholistic definition of macropore flow as movement by mass flow through macropores that leads to physical and chemical non-equilibrium with the soil matrix.

Generally, macropore flow occurs when water at pressures close to atmospheric pressure (i.e. under surface ponding condition or near saturation), move through macropores by gravity when the soil is not fully wet (Jarvis, 1999). Thus macropores transport solutes through advection by water (Figure 2). Fine pores, large pores and macropores become activated when they are water-saturated but differences in hydraulic conductivities triggers uneven solute distribution in the soil profile. If rain reached a wet soil, macropore solute transport is much faster since flow proceeds directly through them whilst bypassing matrix pores already filled with immobile water (Figure 2). Merdun (2005), morphologically classified macropores as biopores formed by soil fauna and plant roots which are tubular and continuous, and as fissures or cracks formed by swelling and shrinking of clay as a result of wetting/drying and/or freezing/thawing cycles, and as

natural soil pipes formed by erosive action of subsurface flow. Biopores are formed in soils with high silt and low clay contents (Merdun, 2005; Kordel *et al.*, 2008). Hence the study mainly focused on Pb transport through biopores and natural soil pipes excluding cracks since the texture of soils under this study was loamy sand.



**Figure 2: Solute transport in soil** (Kordel *et al.*, 2008).

Macropore flow of solutes is by far the most important transport process in structured soils (Shougrakpam *et al.*, 2010), hence different laboratory and field procedures for quantifying macroporosity and macropore flow with their associated merits and demerits have been developed. Expensive but accurate methods such as X-ray computer tomography scanners, dye staining techniques, models and fractal geometry among other methods have been employed to characterise and quantify macropores and macropore flow at various scales including the soil microscale, column scale, profile scale and landscape scale (Allaire *et al.*, 2009; Gantzer and Anderson, 2002). Nevertheless, the high

heterogeneity of macropores in soils still warrants the need for site-specific studies on reactive solute transport (Bruggeman, 1997; Shougrakpam *et al.*, 2010).

Determination of macroporosity by regression and pedotransfer models usually requires a collection of larger data, and the models, after their development may tend to be site specific (Stolf *et al.*, 2011). Beven and Germann (1981) reported that macropores could be estimated using soil water relations. Thus a simple and site specific method base on the volume of water that drains by gravity from a saturated soil column for a period of 48 hours (field capacity moisture condition) may be used to estimate soil macroporosity (Rowell, 2014).

Again, (Kordel *et al.*, 2008) posited that methods that require simple instrumentation including solute breakthrough curves, measurement of soil hydraulic properties and transport parameters may be used to quantify macropore flow. Thus at the soil column scale, solute breakthrough curves of intact soil columns under saturated conditions could be compared with that of homogeneously repacked soil columns under similar initial conditions (bulk density and moisture condition) to quantify macropore flow (Lang, 2004; Allaire *et al.*, 2009).

Aubertin (1971) indicated that there are variabilities in macropore formation and subsequently macroporosities in soils. Generally, the variability is highly dependent on soil type, land use and management practices, as well as climatic conditions (Jarvis, 2007; Kordel *et al.*, 2008). Shougrakpam *et al.* (2010), further reported that though the inherent physical properties of soil may be responsible for structural voids of a soil, the vegetation dynamics as influenced by land use system and land cover is the most critical factor which determines the extent of water and solute movement in macropores. Malone *et al.* (2003)

reported that solute transport can be attributed to macropore flow but the direct and indirect effect of land management practice such as tillage on macropore transport is uncertain. Therefore there is the need for further studies on macropore flow in different land use systems and land covers.

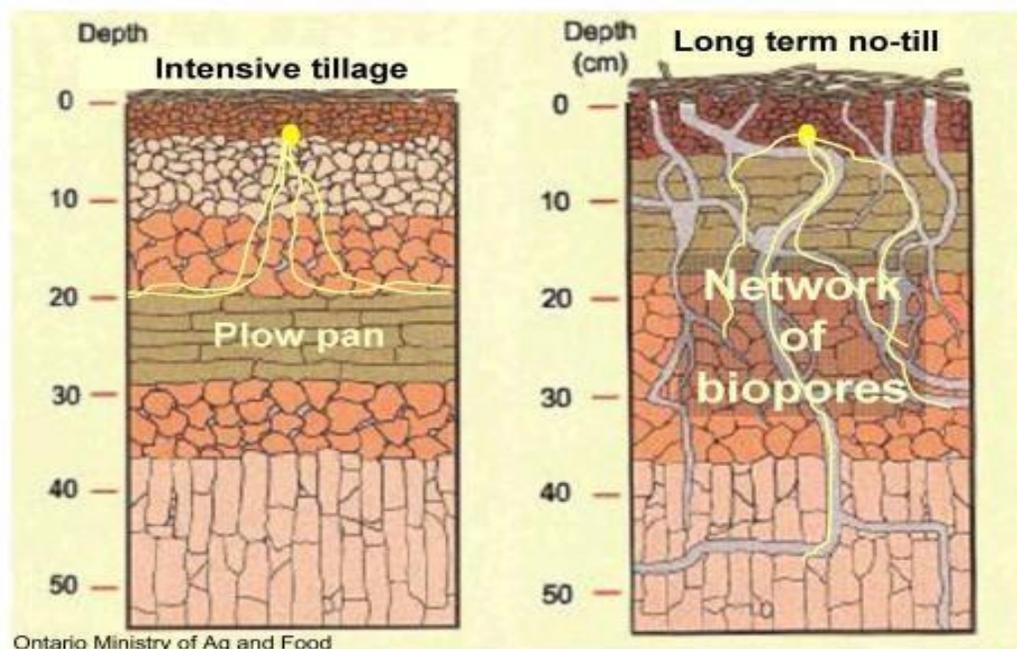
### **2.2.2 Biopores**

Earthworms are known to play beneficial role in soil. Oades, (1993) grouped these into two: firstly, improvement in soil fertility by shredding crop residue, stimulating microbial decomposition and nutrient release, and production of nutrient-rich casts; and secondly, structure development by promoting aggregation, plant root growth, and improving water infiltration and flux through the formation of biopores. Conventional tillage speeds up litter decomposition, reduces biological activities of earthworms, destroys biopores and increases soil compaction (Figure 3). Lachnicht *et al.* (1997) observed from X-ray image analysis that macropore network and macroporosities in terms of number and area of pores greater than 16 mm<sup>2</sup> increased significantly (124.18 m<sup>-2</sup>; 0.98 %) within the upper soil layers (10 cm) in earthworm-addition fields under thick litter of close canopy forest plants and no tillage than the other treatments.

Irrespective of the importance of worms to soil fertility and structural development, their burrows can be potential routes for solutes transport. Peres *et al.* (1998) noted that water and solute flux through smaller wormholes in no-till is higher than the soil matrix. Normally the rate of flow in smaller but stable macropores seemed to be higher than rainfall intensities (Kordel *et al.*, 2008). Shipitalo and Butt (1999) observed that deepburrowing night crawlers (*Lumbricus terrestris* L.) can produce numerous deep and stable biopores which transport solutes into deeper soil layers. Nonetheless, not all

communities of earthworm have this burrowing capacity (Peres *et al.*, 1998). Epigeic and endogeic earthworm unlike anacic earthworms as stated above, mix and feed on litter at the soil surface, and create shallow and tortuous burrows within 20 – 30 cm depth with impaired effects on water and solute flow (Peres *et al.*, 1998; Capowiez *et al.*, 2001).

Channels created by dead plant roots also constitute important pathways for nonequilibrium solute transport (Jarvis, 2007). Tippkötter (1983) made conclusions that hydraulic properties of dead plant root channels enhance mass movement of water and solutes.

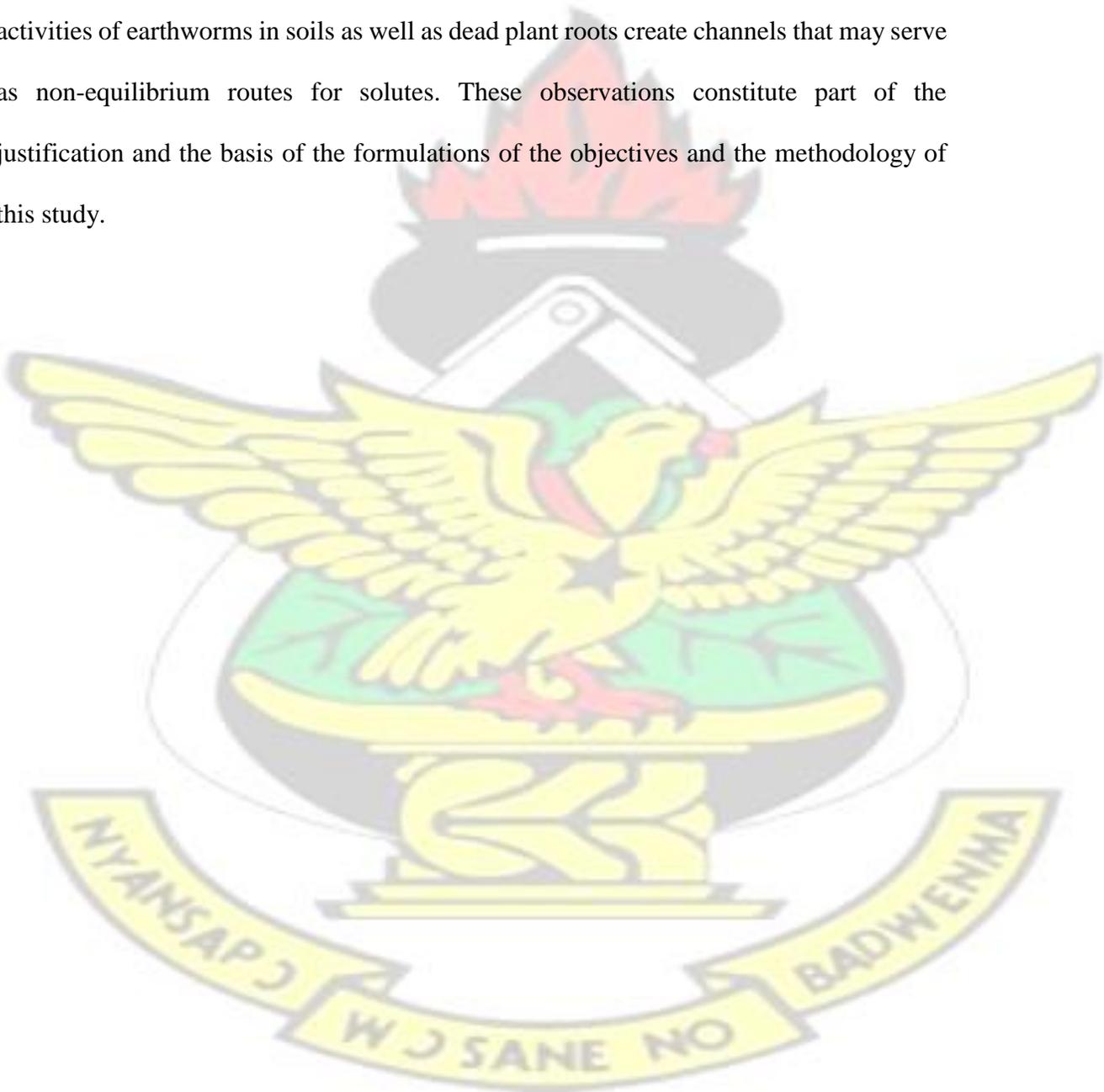


**Figure 3: Biopore network in soils under conventional tillage and no-tillage (OMFA, 2008).**

### 2.3 Summary of literature

Lead as a non-essential heavy metal does not play any significant role in the physiology of plants, animals and human beings. It rather interrupts relevant cellular processes. At high concentrations, it adversely affects growth and yield in plants. In human and animals, it affects vital organ systems and exposure to very high toxic concentrations could result in death. The literature review suggests that the main sources of Pb in agricultural soils is anthropogenic activities, and other sources include *in situ* weathering of Pb-containing minerals depending on soil geochemistry. The literature review indicated that in soils, Pb naturally occurs in lower quantities but high levels beyond permissible limits were recorded in contaminated soils. Pb readily reacts with soil matrix by several chemical processes to form insoluble precipitates and complexes at soil pH > 7. However in slightly acid to moderately acid soils, formation of soluble organic Pb complexes and dissolution of other Pb-bearing compounds into soil solution, facilitates transport by leaching and runoff into groundwater and surface water bodies respectively. The solubility of forms of Pb in soils is highly variable depending on pH and redox potential. Soils differ in their ability to sorb Pb. The literature shows that higher loads of Pb in soils at a given time can influence Pb leaching and movement by runoff since excess Pb may be added to soil solution once sorption capacity is exceeded. This could potentially contaminate underground aquifers and surface water bodies. The literature review suggests that batch equilibrium experiments cannot be used to assess Pb sorption with respect to soil depths since the contact time for Pb-matrix interaction at the upper soil layers is longer than the remaining layers. Macropores provide pathways for faster transport of solutes in soil. Soil moisture characteristics provides simple and site-specific approach to quantify macroporosity. According to the literature review, the heterogeneity of macropores leaves

uncertainties in preferential transport of solutes and hence knowledge gap, precisely under different land use systems and land covers. Earthworms are known to improve soil fertility and structure. They feed on residue and facilitate decomposition reactions and nutrient release. They improve aggregation and enhance root growth into deeper soil layers. However, their activities are impaired by conventional tillage. Burrowing activities of earthworms in soils as well as dead plant roots create channels that may serve as non-equilibrium routes for solutes. These observations constitute part of the justification and the basis of the formulations of the objectives and the methodology of this study.



# KNUST

## 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 Natural Resources, Kwame Nkrumah University of Science and Technology (KNUST). Soils were sampled from the Plantation Section, Department of Crop and Soil Sciences, KNUST from three study sites: close canopy cocoa plantation, open canopy cocoa plantation, and maize fields. The soils belong to Kumasi series (Adu, 1992), and are classified as Plinthi Ferric Acrisol (FAO/UNESCO, 1990) or Typic Plinthustult (Soil Survey Staff, 1998). The experimental site is geographically located at latitude 6° 40' North and longitude 1° 33' West.

#### 3.2 Experimental treatments and design

The study included three experiments namely: effect of Pb concentration on transport at four Pb concentrations (0, 35, 70 and 105 mg/L), Pb transport as affected by two types of transport processes (macropore and matrix flow), and Pb sorption at three depth classes

(0 – 10, 10 – 20, and 20 – 30 cm). The experimental design was randomized complete block with 4 replications.

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### **3.3 Soil sampling and preparation**

Intact soil columns were sampled within a soil depth of 0 - 30 cm for the two Pb transport experiments, sorption experiment, and the determination of physical, hydraulic, and chemical properties. At each study area, at least 38 intact soil columns were sampled using PVC pipes of internal diameter , 10.5 cm and height, 60 cm, leaving half (30 cm) of the height of each PVC pipe.

Some of the intact soil columns at each study site were bulked and thoroughly mixed to form a homogenous mixture in nylon sacs and later repacked at similar bulk densities of 4 intact soil columns into 4 other PVC pipes of the same dimensions in the Soil Science Laboratory. Before the two transport experiments, all intact and repacked soil columns were saturated with distil water to attain same moisture condition. After saturation, 16 intact soil columns from each study site were used to study the effect of different Pb concentrations on transport. The 4 sets of comparable soil columns (intact and repacked) from each test site were also used to study Pb transport as affected by macropore and matrix flow.

In addition, some of the intact soil columns that remained were also repacked at similar bulk density of their respective intact soil columns. These repacked soil columns and the

intact soil columns that finally remained were used for the determination of physical and hydraulic properties in the Soil Science Laboratory.

After conducting the experiment of Pb transport as affected by macropore and matrix flow as discussed below (3.5.2), the intact and repacked soil columns were allowed to drain for 72 hours and sectioned into three depth classes (0 -10, 10 - 20, and 20 - 30 cm). The remaining bulked soil samples from the study sites as well as soils of the different depths of the intact and repacked soil columns after the leaching experiment, were air-dried and passed through the 2 mm sieve, and were later used for soil physical and chemical analysis, and sorption experiment respectively in the Soil Science Laboratory.

### **3.4 Physical and chemical analysis of soil sample**

The selected physical and chemical soil properties considered include: bulk density, total porosity, macroporosity, saturated hydraulic conductivity, soil pH, SOC content, initial Pb, Mn and Fe and CEC.

#### **3.4.1 Determination of selected soil physical properties**

Particle size distribution of the soils was determined using the hydrometer method (Bouyoucos, 1963). Soil bulk density up to depth of 0 - 30 cm was determined by the column sampler method (Blake and Hartge, 1986). Total porosity of soil was calculated as:

$$f = 1 - \frac{\rho_b}{\rho_s} \quad (1)$$

where:

$f$  = total porosity,  $\rho_b$  = bulk density, and  $\rho_s$  = particle size density (2.65 g/cm<sup>3</sup>).

The soil macroporosity of each study site was determined using soil moisture relations (Beven and Germann, 1981; Rowell, 2014). Intact soil columns were saturated by immersing them into plastic buckets containing distilled water to reduce air entrapment until they were fully saturated. The top of each soil column was covered with wax to reduce moisture loss by evaporation. Calico was tied at the bottom of the column and funnel was fixed on it to allow water outflow (Plate 1). The soil column was allowed to drain by gravity into reagent bottles through the funnel that fitted the mouth of the reagent bottles for a period of 48 hours (Plate 1). Soil macroporosity was then estimated by:

$$f_m = \frac{V_g}{V_c} \quad (2)$$

Where:

$f_m$  = macroporosity of the soil column,  $V_g$  = volume of water that drained by gravity after 48 hours, and  $V_c$  = total volume of soil column.

Saturated hydraulic conductivity for intact and repacked soil columns were determined using the falling head method. The hydraulic head of water was 30 cm above the soil column. The time taken for every 2 cm drop in the water level in the tube was recorded.

$\frac{H_0}{H_t}$  was plotted against time (s).  $H_0$  and  $H_t$  were the initial hydraulic head and the hydraulic head after each 2 cm drop in the water level respectively. The saturated hydraulic conductivity was determined by:

$K_s$

$$M = \dots \dots \dots (3) L$$

$$K_s = M \times L \dots \dots \dots (4)$$

Where:

M = slope of graph, L= length of the soil column, and  $K_s$ = saturated hydraulic conductivity.



**Plate 1: Experimental setup (columns covered with wax) for the determination of**

## **macroporosity**

### **3.4.1 Determination of selected soil chemical properties**

Soil pH was determined using a standard pH-meter in a soil: water ratio of 1: 2.5. SOC was determined by the modified Walkley and Black dichromate digestion method (Nelson and Sommers, 1982). Initial Pb, Mn and Fe were determined after extraction by Diethylenetriamine pentaacetic acid (DTPA) solution at pH 7.3 (Motsara and Roy, 2008). They were later analysed using Atomic Absorption Spectroscopy (AAS) (Motsara and Roy, 2008). The CEC was determined by the amount of Na<sup>+</sup> that occupied the exchangeable sites of the soils after rigorous shaking of 5 g of soil in sodium acetate solution (1.0 M NaOAc at pH 8.2) on a reciprocating shaker. Afterwards, the soil was thoroughly washed with 95 % ethanol to enhance the removal of all the exchangeable cations and bases. The adsorbed Na<sup>+</sup> occupying the exchangeable sites were then extracted by ammonium acetate solution (1.0 M NH<sub>4</sub>OAc at pH 7.0). The CEC was later obtained from Na analysis in the supernatant solution after centrifuging, by Gallenkamp flame photometer (Chapman, 1965; Rowell, 1994).

## **3.5 Study Experiments**

### **3.5.1 Application of different concentrations of lead**

Intact soil columns from soils under the three study sites were used to determine effect of different Pb concentrations on transport. The experimental treatments considered were 0, 35, 70, and 105 mg/L of Pb from lead nitrate salt {Pb(NO<sub>3</sub>)<sub>2</sub>}. Calculations for the various concentrations are outlined in Appendix 1. The 0 mg/L served as a control. All the

treatments with the exception of the control were used to develop breakthrough curves. In order to make comparison between the effects of different Pb concentrations on Pb transport at the various study sites easier, analysis of Pb effluent concentrations was limited to an arbitrary time of 80 minutes.

Breakthrough curves of Pb transport through the intact soil columns from each study site were developed and least significant difference (LSD) bars at 5 % probability level were used to separate the treatment means. Differences between means of absolute concentrations of Pb effluents were also separated using LSD at 5 % probability level.

### **3.5.2 Macropore and matrix flow effects on lead transport**

The effect of macropore and matrix flow on Pb transport was achieved using Pb transport through the sets of comparable soil columns (intact and repacked) from the study sites. It was assumed that repacking the bulked homogeneous soil samples in the PVC pipes virtually disrupted many macropores leaving fairly large proportion of matrix pores. On the contrary, the intact soil columns had macropores *in situ* and also matrix pores. Hence, matrix flow was dominant in the repacked soil columns. However both macropore flow and matrix flow occurred in the intact soil columns. The effect of macropore flow alone was then attained by direct comparison of Pb transport in intact soil columns with repacked soil columns. Thus Pb transport was studied at two levels: macropore flow and matrix flow.

For a convenient comparison of the effect of macropore flow and matrix flow on Pb transport, analysis of BTCs of Pb effluent concentrations were limited to an arbitrary time of 80 minutes. BTCs of Pb transport through the test soils were developed and LSD bars were used to separate the treatment means at 5 % probability level. Differences between means of transport parameters, hydraulic and physical properties of intact and repacked soil columns were analysed using two sided t-test at 95 % confidence limit.

### **3.5.3 Lead sorption as affected by soil depths**

In order to study Pb sorption as affected by soil depths classes, intact and repacked soil columns that received 105 mg/L of Pb solution for the second transport experiment were allowed to thoroughly drain for 72 hours. The soil depth classes that were considered were 0 – 10, 10 – 20, and 20 – 30 cm. Soil samples in the PVC cylinders were carefully removed after the 72-hour period as the columns took the shape of the PVC cylinder. They were divided at 10 cm interval, thus 0 - 10 cm, 10 - 20 cm and 20 - 30 cm. Soils from each section was air-dried, and the Pb was extracted using DTPA solution at pH 7.3 (Motsara and Roy, 2008). The supernatant obtained after centrifuging the extract, was filtered with Whiteman No. 42 filter paper, and analysed for Pb by AAS (Motsara and Roy, 2008). Differences between means of Pb sorbed by the different depths of intact and repacked soil columns were compared using two sided t-test at 95 % confidence limit. Differences among means of Pb sorbed by corresponding soil depths were separated using LSD at 5 % probability level.

### **3.6 Lead transport experimental setup**

The Pb transport experiments were conducted using improvised opaque PVC cylinders of the same dimensions (Plate 2). The PVC cylinders were held and supported by a backboard and a rectangular base frame with two legs to maintain its balance. The PVC cylinders were removable from the backboard to facilitate cleaning and sampling of other soil columns. Composite soil samples were repacked into the PVC cylinders. White calico of diameter 20 cm was tied around the base of the cylinder to hold the soil and filter the effluent. A plastic funnel was fixed to the base of the cylinders to allow flow of effluents into 250 ml conical flasks placed underneath. At the end of each cycle of flow experiment, the PVC cylinders were washed thoroughly with detergents and water, and the calicos were replaced with new ones to prevent the effect of residual accumulation. Effluents discharging from the PVC cylinders were collected using conical flasks and reagent bottles at 10 minutes intervals.

#### **3.6.1 Lead leaching experiments**

The Pb leaching experiments were conducted using both intact and repacked soil columns. Before applying solutions to the soil columns, the plastic funnels from which the effluents flowed were corked to prevent outflow.  $\text{Pb}(\text{NO}_3)_2$  solutions were then applied to the remaining height of the soil columns at a hydraulic head of 30 cm equivalent to a volume of 2.6 L (Plate 2). Based on preliminary study on the flow rates of the soil columns from each study site, effluents were collected at ten minutes interval into conical flasks. To determine the effects of different Pb rates on Pb flow, solutions were applied at 0, 35, 70,

and 105 mg/L. The effect of macropores on Pb flow was achieved by using intact and repacked soil columns. The Pb effluents collected were then filtered with Whiteman No. 42 filter paper to further remove soil particles and analysed for Pb by AAS (Motsara and Roy, 2008).



**Plate 2: Experimental setup for Pb transport.**

### **3.7 Determination of some transport parameters of lead**

The transport parameters that were considered were transit time of Pb transport, breakthrough concentration of Pb, and Pb flux. Transit time for each study site was taken

to be the time that elapsed for the total period for the flow of Pb solutions in a given soil column. The breakthrough concentration was measured as the highest absolute concentration of Pb within a given transit time. The Pb flux by mass flow was determined as:

$$q_c = q \times C_b \quad (5)$$

Under saturated conditions,  $q = K_s$  Therefore:

$$q_c = K_s \times C_b \quad (6)$$

Where:

$q_c$  = Pb flux by mass flow,  $K_s$  = saturated hydraulic conductivity,  $q$  = water flux density, and  $C_b$  = breakthrough concentration of Pb in the effluent.

### 3.9 Analysis of results

#### 3.8.1 Statistical Analysis

The data collected on the various parameters were subjected to analysis of variance using GenStat statistical package (12<sup>th</sup> Edition). Differences between treatment means were compared using two sided t-test at 95 % confidence interval, and differences among treatment means were separated using LSD at 5 % probability level.

### 3.8.2 Chemical breakthrough curves

Chemical breakthrough curves (BTCs) were used to study the Pb transport phenomena. Thus effect of Pb concentration on transport, and the effect of macropore flow and matrix flow on Pb transport. BTCs describes the variation in solute relative concentration over time in effluents. Pb concentrations were normalized (relative concentration) by dividing the measured concentration with the applied concentration such that the concentration values are always between the ranges of 0 to 1.0.

$$\text{Relative concentration} = \frac{C}{C_0} \quad (7)$$

where:

$C$  = concentration of Pb in the effluent, and  $C_0$  = the initial concentration of the Pb solution.

The mean relative concentration of Pb were plotted against time. Lsd bars at 5 % probability level were used to separate means on the breakthrough curves.

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## CHAPTER FOUR

### 4.0 RESULTS

#### 4.1 Physical and chemical properties of the soils

The selected physical and chemical properties of the soils from the study sites are presented in Tables 1 and 2. The textural class of soils under the three study sites was loamy sand (Table 1). Field bulk density of soils under maize was significantly higher ( $p < 0.05$ ) than soils under close canopy cocoa and open canopy cocoa (Table 2). Total porosity of soils under close canopy cocoa was significantly higher ( $p < 0.05$ ) than soils under open canopy cocoa and maize (Table 2). The degree of macroporosities were in the order: close canopy cocoa > open canopy cocoa > maize, and were significantly different ( $p < 0.05$ ).

**Table 1: Particle size distribution of the fine earth (< 2mm) fraction**

Soil property	Study site		
	Close canopy cocoa	Open canopy cocoa	Maize
Particle size distribution			
Sand (%)	81.6	81.5	79.6
Silt (%)	12.8	13.7	4.8
Clay (%)	5.6	Loamy sand	15.6
Textural class	Loamy sand		Loamy sand

The pH was moderately acid under maize and slightly acid under both close canopy cocoa and open canopy cocoa (Table 2). Saturated hydraulic conductivity and SOC were significantly higher ( $p < 0.05$ ) in soils under close canopy cocoa than soils under open

canopy cocoa and maize. The CEC, Fe and Mn content of soils under close canopy cocoa were significantly higher ( $p < 0.05$ ) than soils under open canopy cocoa and maize. However, there were non-significant differences ( $p < 0.05$ ) in Fe and Mn content in soils under open canopy cocoa and maize. The initial Pb concentrations at the three test sites were low and there were non-significant differences ( $p < 0.05$ ) among the study sites except close canopy cocoa and maize.

**Table 2: Some Physical and chemical properties of the soils**

Soil property	Close canopy cocoa	Open canopy cocoa	Maize	CV (%)	LSD (0.05)
$K_s$ (cm/h)	88.80	43.20	10.20	18.80	20.15
$\rho_b$ (g/cm <sup>3</sup> )		1.47	1.59	0.70	0.02
$f$ (cm <sup>3</sup> /cm <sup>3</sup> )		0.45	0.40	0.90	0.009
$f_m$ (cm <sup>3</sup> /cm <sup>3</sup> )		0.19	0.15	6.60	0.03
		0.93	0.56	16.60	0.37
/kg soil)					
O)		0.81	0.49	24.50	0.91
		7.11	5.33	0.07	2.09
	1.43				
	0.46				
	0.23				
<b>SOC (%)</b>	1.43				
<b>CEC (cmol<sup>+</sup>)</b>	11.48	8.39	4.39	10.80	1.98
<b>pH (1: 2.5 soil:H<sub>2</sub>O)</b>	6.33	6.26	5.77	1.40	0.19
<b>Initial Pb (mg/L)</b>	0.06	0.07	0.10	23.20	0.04
<b>Mn (mg/L)</b>	3.63				
<b>Fe (mg/L)</b>	12.07				

CV is coefficient of variation, LSD is least significant difference at 5 %,  $K_s$  is saturated hydraulic conductivity, SOC is soil organic carbon, CEC is cation exchange capacity,  $f$  is total porosity,  $f_m$  is macroporosity, and  $\rho_b$  is bulk density.

#### 4.2 Transport of lead by mass flow through intact soil columns at different lead concentrations

The effects of Pb concentration on Pb transport by mass flow through the intact soil columns from soils under close canopy cocoa, open canopy cocoa and maize are presented in Table 3. Generally, the Pb concentration in the percolates of the control (0 mg/L) under each study site fluctuated with time (Table 3). Although the effluent concentrations of 35, 70, and 105 mg/L in the soil columns from each study site also fluctuated, there was relatively higher net increase with time. Besides, significant differences ( $p < 0.05$ ) were observed between the Pb effluent concentrations of the different concentrations of Pb applied at a given time under each study site (Table 3).

**Table 3: Effect of different concentrations of lead with time on lead transport through intact soil columns under each study site.**

Time	Study Site		Lead Concentration (mg/L)			CV	LSD	(minutes)	0
	70	105	(%)	(0.05)					
10			0.02	8.31	19.08	21.02	5.60	1.35	
20			0.03	4.74	14.17	17.56	9.20	1.67	
30			0.08	4.83	11.66	40.57	6.60	1.88	
40	Close canopy cocoa		0.07	15.31	25.08	45.69	3.50	1.52	
50			0.10	18.45	24.63	43.25	1.60	0.68	
60			0.15	19.68	50.17	73.09	8.10	5.77	
70			0.03	25.71	49.55	80.90	2.30	1.76	
80			0.03	25.89	56.36	86.42	2.00	1.66	

10		0.07	8.23	12.58	23.02	14.60	3.21
20		0.05	5.64	9.41	18.04	10.80	1.78
30		0.18	4.59	12.91	19.82	17.00	3.19
40		0.09	9.65	16.21	19.62	9.70	2.22
50		0.14	9.78	13.81	33.30	11.30	3.22
60		0.04	11.37	19.83	39.32	3.80	1.33
70	Open canopy	0.10	16.20	28.21	46.84	4.00	1.83
80	cocoa	0.16	17.67	27.39	47.21	8.30	3.83
90		0.11	18.72	35.06	49.21	4.40	2.29
100		0.21	18.91	40.98	64.36	1.90	1.21
110		0.17	20.38	41.96	68.52	1.70	1.09
120		0.16	21.12	45.80	71.05	1.30	0.88
130		0.11	21.60	46.90	73.61	1.60	1.12
10		0.08	2.47	4.18	6.37	7.60	0.50
20		0.05	1.94	3.92	7.32	9.80	0.65
30		0.07	1.77	3.21	5.82	7.10	0.39
40		0.09	1.13	3.88	8.55	10.60	0.73
50		0.20	2.33	5.83	11.95	12.70	1.29
60		0.16	5.12	8.65	13.48	8.90	1.21
70		0.30	6.43	12.54	22.35	7.50	1.56
80	Maize	0.29	7.95	14.21	25.63	6.80	1.64
90		0.06	6.79	16.06	27.08	5.80	1.45
100		0.18	7.87	19.62	31.30	6.70	1.97
110		0.20	9.21	22.54	37.73	4.10	1.42
120		0.15	11.49	20.58	35.78	4.60	1.57
130		0.35	12.51	25.43	42.35	7.50	3.02
140		0.28	13.50	28.18	45.37	6.10	2.66
150		0.10	13.92	31.68	49.06	3.80	1.80
160		0.07	13.89	32.13	49.37	2.40	1.13
170		0.03	15.00	32.12	49.96	4.90	2.38
180		0.09	15.08	32.33	50.51	2.00	1.72
190		0.08	15.21	34.01	53.48	3.50	1.01

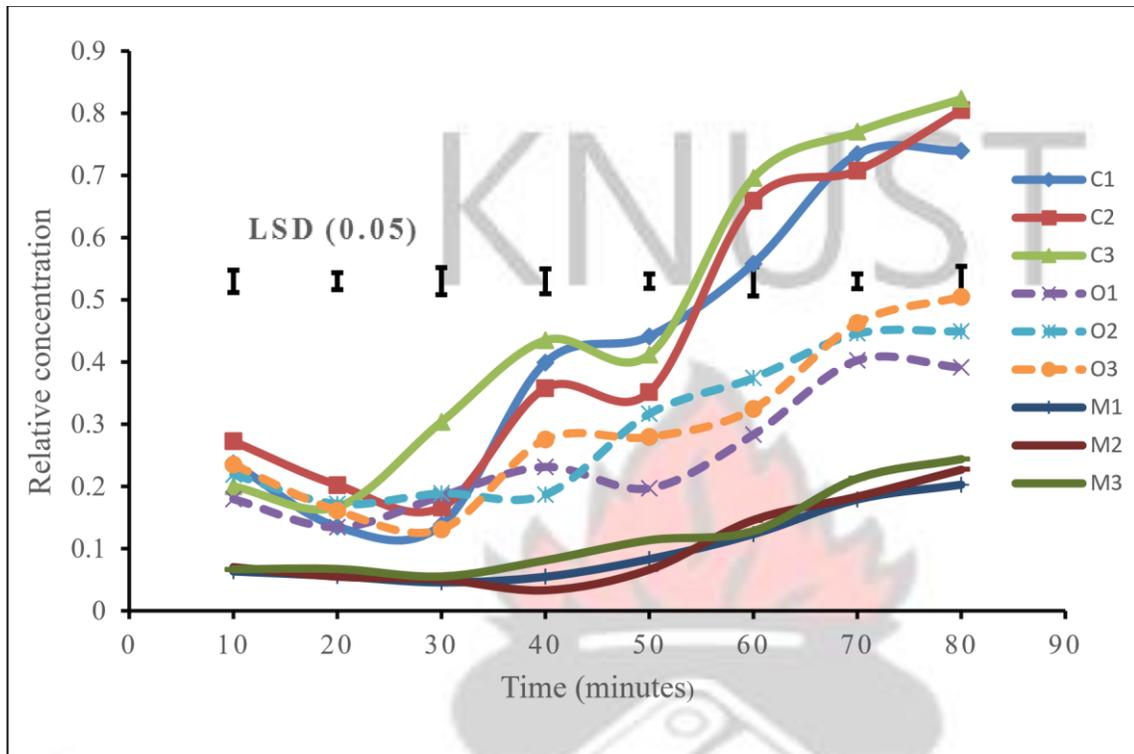
CV is coefficient of variation, LSD is least significant difference at 5 %

The breakthrough curves (BTCs) of relative concentration against time of the three different concentrations (35, 70, and 105 mg/L) for the three test sites are shown in Figure 4. Pb transport was limited to the first 80 minutes on the BTCs of each study site for easy comparison. The breakthrough curves showed net increase in relative concentrations for the different chemical concentrations. Although there were significant differences in the relative concentrations at the initial times on the BTCs with the exception of soils from

the maize field, there was a general decrease in effluent concentrations in terms of relative concentrations from high values at the 10<sup>th</sup> minute up to the 20<sup>th</sup>, and 30<sup>th</sup> minute.

In addition, at the early times on the BTCs of the 105 mg/L chemical concentration for the three study sites, the relative concentrations were at least, lower than one of the remaining concentrations (35 mg/L and 70 mg/L). However, their respective relative concentrations increased with increasing time. The increase in relative concentration occurred first in close canopy cocoa, but was very early in open canopy cocoa than maize. Higher differences among the relative concentrations of the three concentrations applied at a given time on the breakthrough curves was observed in soils under close canopy cocoa and open canopy cocoa than maize (Figure 4).

The amount of Pb leached by mass flow at the different concentrations as determined from the relative concentrations (Figure 4), showed higher and significant ( $p < 0.05$ ) leaching of Pb when concentrations of Pb were increased. This observation was much pronounced in soils under close canopy cocoa, open canopy cocoa and maize, respectively.



**Figure 4: Breakthrough curves showing lead transport through intact soil columns under the study sites at different concentrations of lead**

C1 is 35 mg/L under close canopy cocoa, C2 is 70 mg/L under close canopy cocoa, C3 is 105 mg/L under close canopy, O1 is 35 mg/L under open canopy cocoa, O2 is 70 mg/L under open canopy cocoa, O3 is 105 mg/L under open canopy, M1 is 30 mg/L under maize, M2 is 70 mg/L under maize, M3 is 105 mg/L under maize, and LSD is least significant difference at 5% probability.

#### **4.3 Macropore transport of lead in relation to matrix transport.**

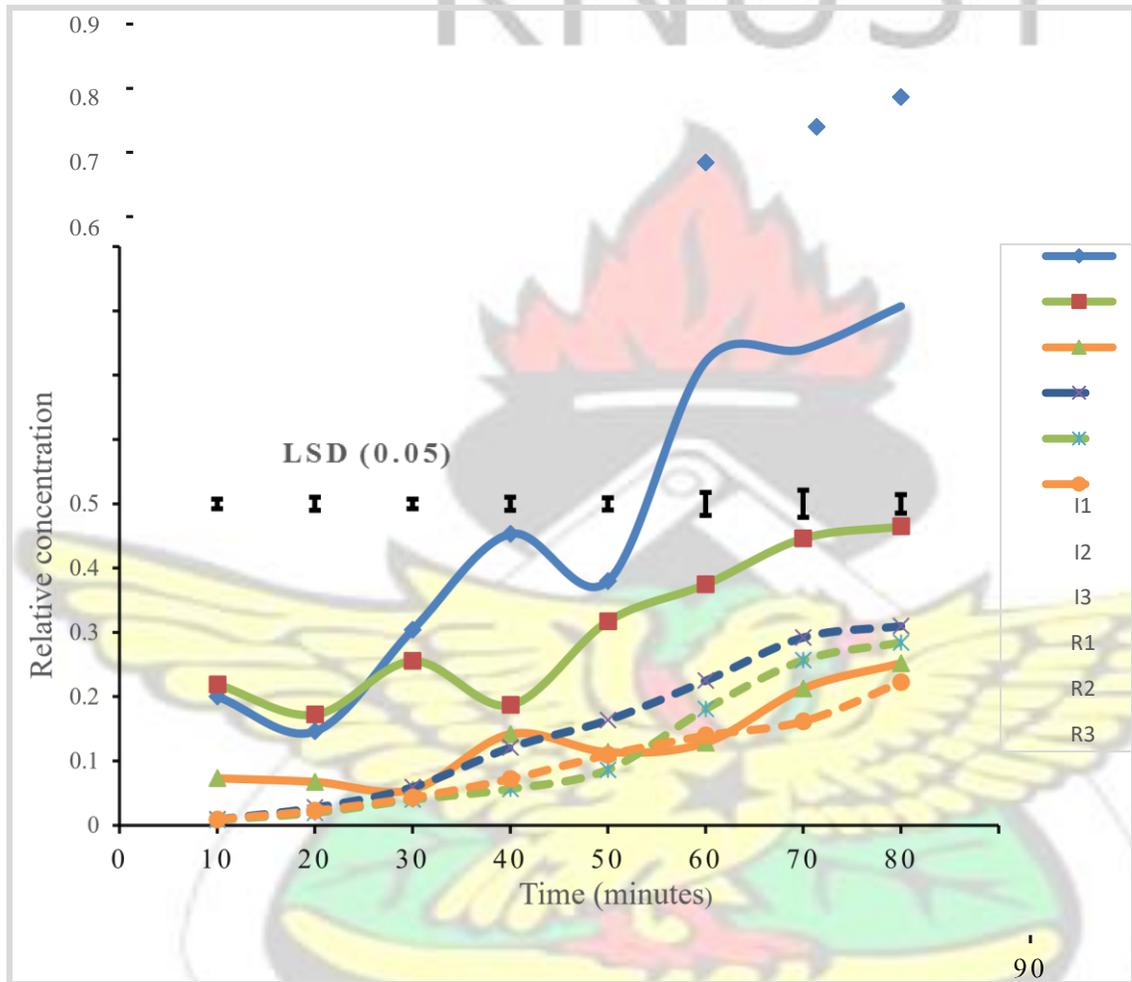
Comparison of Pb transport in intact soil columns and repacked soil columns were used to achieve the effect of macropore flow on Pb transport. Transport of Pb through intact and repacked soil columns from soils under close canopy cocoa, open canopy cocoa, and

maize at 105 mg/L are presented in Figure 5. For easy comparison of Pb transport in both soil columns, a transit time of 80 minutes was used for each study site. The BTC of intact soil columns under close canopy cocoa was marked by two distinct peaks with the highest height, whilst those of both open-canopy cocoa and maize were also marked by one distinct peak. However the peak was higher in open canopy cocoa than maize. On the other hand, the BTCs of repacked soil columns were not marked by peaks and hence were relatively smooth (Figure 5). There were non-significant differences in the relative concentrations of repacked soil columns from the three study sites within the initial 30 minutes as evidenced by the BTCs. Contrarily, significant differences were recorded for the given transit time period in intact soil columns under the three study sites. The initial 30 minutes of the transport process in intact soil columns was marked with higher effluent concentrations of Pb and subsequently, lower and fluctuating relative concentrations of effluents.

From the BTCs, there were significant differences between relative concentrations of intact soil columns under close canopy cocoa and open canopy cocoa, and the repacked soil columns under the three study sites. Generally, significant differences ( $p < 0.05$ ) were recorded among the relative concentrations of intact soil columns under maize and the repacked soil columns under the three study sites up to the 30<sup>th</sup> minute, whereas non-significant differences ( $p < 0.05$ ) were recorded from the 30<sup>th</sup> minute up to the 80<sup>th</sup> minute.

Lead leaching in terms of relative concentrations from the BTCs showed that more Pb leached out from the intact soil columns at a faster rate than the repacked soil columns of

the three study sites. This was also observed in the intact soil columns in the order: close canopy cocoa > open canopy cocoa > maize.



**Figure 5: Breakthrough curves showing Pb transport in intact and repacked soil columns under the study sites**

I1 is intact soil columns under close canopy cocoa, I2 is intact soil columns under open canopy cocoa, I3 is intact soil columns under maize, R1 is repacked soil columns under close canopy cocoa, R2 is repacked soil columns under open canopy cocoa, R3 is repacked soil columns under maize, and LSD is least significant difference at 5% probability

#### **4.4 Selected transport parameters, hydraulic and physical properties of intact and repacked soil columns under the test sites and their interrelationships**

Saturated hydraulic conductivity, Pb flux, breakthrough concentrations, and transit time of both intact and repacked soil columns are shown in Table 4. There were significant differences ( $p < 0.05$ ) between the soil properties of the different soil columns (i.e., intact and repacked) for the various study sites. Significant differences ( $p < 0.05$ ) were recorded among the soil properties of intact soil columns from the various study sites. Saturated hydraulic conductivities of the intact soil columns were 41, 76, and 73 % higher than the repacked columns under close canopy cocoa, open canopy cocoa and maize, respectively (Table 4). Pb fluxes in the intact columns were 54, 85, and 84 % higher than the repacked soil columns under close canopy cocoa, open canopy cocoa and maize respectively. Breakthrough concentrations of the intact columns were 23, 40, 38 % higher than the repacked columns under close canopy cocoa, open canopy cocoa, and maize, respectively. Transit time of Pb transport through the intact soil columns under close canopy cocoa, open canopy cocoa and maize were 88, 54, and 42 % faster than the respective transit times through the repacked columns.

Saturated hydraulic conductivity of intact soil columns was 51 % higher under close canopy cocoa than open canopy cocoa, 89 % higher under close canopy cocoa than maize, and 76 % higher under open canopy cocoa than maize. Pb flux of intact soil columns recorded higher differences of 57 % under close canopy cocoa than open copy cocoa, 93 % under close canopy cocoa than maize, and 83 % higher under open canopy cocoa than maize. Breakthrough concentrations of the intact soil columns was 12 % higher under close canopy cocoa than open canopy cocoa, 35 % higher under close canopy cocoa than maize, and 26 % higher under open canopy cocoa than maize. Transit time of intact soil

columns was 63 % faster under close canopy cocoa than open canopy cocoa, 138 % faster under close canopy cocoa than maize, and 46 % faster under open canopy cocoa than maize.

Lead leaching as determined by Pb flux and breakthrough concentrations showed that more Pb leached out from the intact columns at a faster rate than the repacked columns of soils from the various study sites. Similar observations were made in the intact columns in the order: close canopy cocoa > open canopy cocoa > maize.

**Table 4: Selected saturated hydraulic property and transport parameters of intact soil columns and repacked soil columns at the study sites.**

Study site	Hydraulic Property	Transport parameter			
		$K_s$ (cm/h)	$q_c$ (mg/cm <sup>2</sup> /h)	$C_b$ (mg/L)	t (minutes)
CCC	Intact soil columns	88.80	7.51	84.76	80
	Repacked soil columns	52.80	3.46	65.08	150
	P (0.05)	0.03	0.01	0.001	0.04
	SED	10.73	0.83	1.18	23.09
OCC	Intact soil core	43.20	3.22	74.61	130
	Repacked soil columns	10.80	0.47	45.02	200
	P (0.05)	0.02	0.01	0.001	0.01
	SED	4.18	0.31	1.83	14.40
M	Intact soil columns	10.20	0.56	55.22	190
	Repacked soil columns	2.80	0.09	34.06	270
	P (0.05)	0.001	0.001	0.001	0.003
	SED	0.33	0.03	1.67	12.91
	CV (%)	18.60	18.40	3.70	10.60
	LSD (0.05)	20.15	1.57	5.95	32.06

SED is t-test standard error of difference of means, p is t-test probability, CV is coefficient of variation, LSD is least significant difference at 5 %, CCC is close canopy cocoa, OCC is open canopy cocoa, M is maize,  $K_s$  is saturated hydraulic conductivity, t is transit time,  $q_c$  is Pb flux, and  $C_b$  is breakthrough concentration.

Note: the SED values were used to compare differences between means of intact and repacked soil columns, and the Lsd values were used to separate means of intact soil columns.

Tables 5a and 5b represent the degrees and types of relationships between the selected soil physical and hydraulic properties, and selected transport parameters of both intact and repacked soil columns from the study sites. Correlations between Pb flux, breakthrough concentrations and transit times, and saturated hydraulic conductivity, total porosity, macroporosity, bulk densities of both soil columns were significant ( $p < 0.05$ ).

There was positive correlation between transit time and bulk density of both soil columns but negative correlations were observed between transit time and saturated hydraulic conductivity in both soil columns, and macroporosity and total porosity in intact soil columns. Macroporosity and total porosity of intact soil columns correlated positively with Pb flux and breakthrough concentration. Negative correlations were recorded between bulk density and Pb flux, and breakthrough concentration in both soil columns. The correlation coefficients for all correlations between soil physical and hydraulic properties, and transport parameters of intact and repacked soil columns ranged from  $r = 0.67$  to  $0.99$ .

**Table 5a: Correlation between selected hydraulic and physical properties, and selected transport parameters of intact soil columns under the study sites**

	$K_s$	$f$	$f_m$	$\rho_b$
$q_c$	0.99**	0.90**	0.94**	-0.90**
$C_b$	0.95**	0.96**	0.90**	-0.96**
$t$	-0.88*	-0.84*	-0.76*	0.84*

\*\* = significant at  $p < 0.01$ , \* = significant at  $p < 0.05$ .

$K_s$  is saturated hydraulic conductivity,  $\rho_b$  is bulk density,  $q_c$  is Pb flux,  $C_b$  is breakthrough concentration,  $t$  is transit time,  $f$  is total porosity, and  $f_m$  is macroporosity.

**Table 5b: Correlation between selected hydraulic and physical properties, and selected transport parameters of repacked soil columns under the study sites**

	$K_s$	$\rho_b$
$q_c$	0.99**	-0.67**
$C_b$	0.97**	-0.85**
$t$	-0.84*	0.93**

\*\* = significant at  $p < 0.01$ , \* = significant at  $p < 0.05$ .

$K_s$  is saturated hydraulic conductivity,  $\rho_b$  is bulk density,  $q_c$  is Pb flux,  $C_b$  is breakthrough concentration, and  $t$  is transit time.

#### 4.5 Sorption of lead at different soil depths

Sorption of Pb in the intact and repacked soil columns at varying depths (0-10, 10-20, and 20-30 cm) of soils under close canopy cocoa, open canopy cocoa and maize are presented in Tables 6a and 6b. Comparisons of Pb sorption by intact and repacked soil columns at the different soil depths are also shown in Table 6c. The overall Pb sorption behavior followed a trend of significantly higher ( $p < 0.05$ ) sorption within the 0-10 cm depth and a decreasing succession with increase in depth in the intact and repacked soil columns from each study site (Tables 6a, 6b, and 6c).

Generally, the amounts of Pb sorbed by repacked soil columns were significantly higher ( $p < 0.05$ ) than those of the intact soil columns under the three study sites (Table 6c).

There was non-significant difference between the amounts of Pb sorbed at soil depth of 10-20 cm in repacked soil columns under close canopy cocoa and open canopy cocoa (Table 6b). Moreover, there was non-significant difference between the amounts of Pb sorbed at 10-20 cm and 20-30 cm soil depths in repacked soil columns under open canopy cocoa (Table 6b). With the exception of these, Pb sorption at the soil depth of 0-10 cm of both intact and repacked soil columns were significantly higher ( $p < 0.05$ ) than the amount sorbed by 10-20 cm which was also successively higher than the amount sorbed by 20-30

cm (Tables 6a and 6b). Sorption within the corresponding soil depths of both soil columns under the three study sites, was significantly higher ( $p < 0.05$ ) under close canopy cocoa, followed by open canopy cocoa and maize, in the order given

(Tables 6a and 6b).

**Table 6a: Lead sorption at different depths of intact soil columns from the study sites**

Study site	Soil depth (cm)			CV (%)	LSD 0.05)
	0-10	10-20	20-30		
CCC	50.36	41.99	37.11	2.70	2.60
OCC	57.32	48.75	41.63	3.50	3.85
M	63.06	55.75	44.91	1.20	1.45
CV (%)	2.62	2.90	2.40	-	-
LSD (0.05)	3.80	3.18	2.28	-	-

CV is coefficient of variation, LSD is least significant difference at 5 % probability, CCC is close canopy cocoa, OCC is open canopy cocoa, and M is maize.

**Table 6b: Lead sorption at different depths of repacked soil columns from the study sites**

Study site	Soil depth (cm)			CV (%)	LSD (0.05)
	0-10	10-20	20-30		
CCC	60.69	55.78	51.53	2.90	3.71
OCC	67.81	58.68	56.30	1.60	2.56
M	76.56	70.68	59.89	2.70	4.29
CV (%)	2.50	2.20	2.60	-	-
LSD (0.05)	3.84	3.12	3.24	-	-

CV is coefficient of variation, LSD is least significant difference at 5 % probability, CCC is close canopy cocoa, OCC is open canopy cocoa, and M is maize.

**Table 6c: Comparison of Pb sorption at different depths of intact and repacked soil columns from the study sites.**

Study site		Soil depth (cm)		
		0-10	10-20	20-30
CCC	Intact soil columns	50.36	41.99	37.11
	Repacked soil columns	60.69	55.78	51.53
	P (0.05)	0.004	0.001	0.001
	SED	1.79	1.50	1.28
OCC	Intact soil columns	57.32	48.75	41.63
	Repacked soil columns	67.81	58.68	56.30
	P (0.05)	0.001	0.001	0.001
	SED	1.29	1.17	1.19
M	Intact soil columns	63.06	55.75	44.91
	Repacked soil columns	76.56	70.68	59.89
	P (0.05)	0.001	0.001	0.001
	SED	1.32	0.90	0.55

SED is t-test standard error of difference of means, p is t-test probability, CCC is close canopy cocoa, OCC is open canopy cocoa, and M is maize.

## CHAPTER FIVE

### 5.0 DISCUSSION

#### 5.1 Physical and chemical properties of the soils

The textural class of the study sites was loamy sand. The pH values were moderately acid and slightly acid (Horneck *et al.*, 2011) which indicated slightly acid conditions in the soils. The relatively high CEC, SOC, Fe and Mn contents (Boerma *et al.*, 1995; Horneck *et al.*, 2011) in the soils under close canopy cocoa favour more Pb sorption (Olive, 2006) but this was not the case in this study.

The initial Pb concentrations of the three study sites were far below the permissible limit of Pb in soils indicating negligible anthropogenic influences (MH, 1994; FAO/WHO, 2001). The main source of Pb in the soils could have been the result of the application of organic and inorganic fertilizers, which inherently have lower quantities of Pb. Variations

in macroporosity, total porosity, SOC content, and bulk density were mainly attributed to the land-use systems and land covers. Vegetation cover and accumulation of litter under the close canopy cocoa over time, and the absence of tillage practices, subsequently increased the organic matter content. It eventually favoured the burrowing activities of earthworms, and extensive root growth by the cocoa plants

(Jarvis, 2007). This explains the highest macroporosity and total porosity, and the lowest bulk density in the field as compared to the soils under open canopy cocoa and maize fields. Soils under maize, on the other hand, had relatively higher bulk density, and lower total porosity and macroporosity due to the continuous use of tillage implements. This may have possibly enhanced the rate of organic matter decomposition, as well as the destruction of bulk of the macropores within the upper soil layer. This consequently resulted in compaction, which is responsible for the reduced macroporosity and total porosity, and higher bulk density.

Among the different land management practices, Bot and Benites (2005) identified tillage as one major practice that reduced organic matter levels in soils under different land-use systems and soil covers. They described the contrasting effect of no-till and conventional tillage on organic matter contents severally as faster rate of organic matter decomposition and pile up of crop residue and litter on soil surfaces, accompanied with reduced rate of decomposition due to fewer micro-organisms that are exposed to it. Shougrakpam *et al.* (2010) posited that macroporosity varies, even in the same soil series; Jarvis (2007) linked this with differences in organic matter content and soil water regime which are strongly influenced by weather conditions, plant cover and land management practices. Thus, from the results, high organic matter content in the close canopy cocoa increased the burrowing activities of worms and extensive root growth, which eventually resulted in increased total

porosity and reduced bulk density (Bot and Benites, 2005; Hugar and Soraganvi, 2014). Malone *et al.* (2003) made contributions on the direct effect of tillage on macroporosity, total porosity, and bulk density. They concluded that repetitive tillage destroyed many macropores in the upper layers of the soil and also reduced total porosity and increased bulk density through soil compaction.

The saturated hydraulic conductivity of the soils under close canopy cocoa was highly influenced by the high SOC content recorded in the field. Thus SOC enhanced hydraulic properties of soils by increasing total soil porosity through the enhancement of the formation and stability of soil aggregates (Rawls *et al.*, 1991; Benjamin *et al.*, 2007). The contribution of SOC to physical and hydraulic properties was responsible for the faster transport of Pb through the soils under the close canopy cocoa. Again, the influence of SOC on transit time was observed to be significant in soils under open canopy cocoa than maize fields. Thus, more often than not, soils from close canopy cocoa is liable to Pb leaching than soils under open canopy cocoa fields. However, Pb transport through runoff and erosion is more likely to occur in soils in the maize field.

## **5.2 Transport of lead by mass flow at different concentrations**

Lead transport through intact columns were used to determine effect of different concentrations on transport through the soils. Generally, effluent concentrations of Pb at the applied concentrations were higher than their respective controls, which suggested that, the applied concentration greatly contributed to Pb transport. Deiss *et al.* (2004)

observed similar trends after comparing results from the controls with the spiked Pb concentrations.

From the BTCs (Figure 4), there were fairly large differences in the relative concentrations of Pb in intact soil columns from close canopy field at the varying concentrations. The differences were however, not comparatively pronounced in soils from open canopy cocoa and maize fields. The behaviour of the BTCs (Figure 4) at the initial stages of the transport process is due to macropore flow which will be discussed in section 5.3. Generally, the effluent concentrations of intact soil columns also increased with time, probably due to high macroporosity and SOC content. These improved matrix hydraulic conductivity and Pb flux in general, through the interactions of dissolved organic matter at the slightly acid pH (6.33 and 6.26). Contrarily, the lowest macroporosity and SOC content, and lower hydraulic conductivity of the soils from the maize field did not favour Pb transport as reported in the literature (Malone *et al.*, 2003; Shougrakpam *et al.*, 2010). Lead transport was, therefore, mainly controlled by soil macroporosity, SOC content, and hydraulic properties. Consequently, soils with high macroporosity and SOC content will consequently, facilitate transport of larger quantities of Pb through the soil. Since macropore and matrix flow occurred simultaneously, the largest differences in breakthrough times and effluent concentrations with time were observed in the order: close canopy cocoa>open canopy cocoa>maize.

These observations are in line with the findings of Deiss *et al.* (2004). They reported that the combined effects of macropores and soluble organic Pb complexes in a soil enabled high levels of Pb to move through undisturbed soil columns. Jarvis and Dubus (2006)

posited that solute-matrix interactions is weak during macropore flow. This happens as a result of small surface areas and significant kinetic effects in macropores, especially, when they have high connectivity, continuity and large sizes. According to Aubertin (1971), increasing macropore number, size and depth is associated with increasing macroporosity. Hence, soils with higher macroporosities tended to leach larger quantities of Pb as observed in soils from the close canopy cocoa field. Additionally, Sauve *et al.* (1998) reported that soil organic matter dissolves into soluble compounds at slightly acid pH and further bind to soluble Pb forms to form organic-lead complexes, thereby inhibiting Pb sorption and enhancing its vertical movement by mass flow. They further observed that this event increased with increasing soil organic matter content. Again, increasing SOC content increases the hydraulic and transport properties of a soil (Horn *et al.*, 1994). Therefore, the findings of this study buttress the conclusions made by Kordel *et al.* (2009) that solute transport in intact soil columns is mainly controlled by inherent soil properties such as soil macroporosity and SOC.

In the three study sites, the concentration of Pb effluents in the control was the least and increased dramatically with increasing concentrations of Pb (Table 3). The BTCs (Figure 4) showing the loss of Pb in terms of relative concentrations also depicted more losses of Pb when the concentrations of Pb applied were increased. The effect was largest in soils under close canopy cocoa followed by open canopy cocoa and maize, respectively. Again, relative concentration of the highest Pb concentration (105 mg/L) applied was always lower than the rest in the initial stages of Pb transport (Figure 4).

These were attributed to Pb sorption behavior as reported by Scanlon (1992). Sherene (2010) reported that mobility of heavy metals including Pb in the soil is mainly controlled by sorption processes. Thus, the adsorption sites of a soil, continue to sorb Pb until its

sorption capacity is exceeded as a result of high Pb loadings (Diatta, 2006). Therefore the relative concentrations of 105 mg/L Pb were always lower due to higher initial sorption. Fodor and Szabo (2004) further postulated that additional Pb input would result in Pb bioavailability or transport by leaching and/or run-off depending on type of soil and solute concentration. This suggests that soils that receive heavy doses of Pb by agricultural and industrial activities may cause Pb pollution in underground aquifers and surface water bodies. It, therefore, suggests that soils from the close canopy cocoa and open canopy cocoa sites are more prone to Pb leaching at higher concentrations, which may pollute the underlying groundwater system, however, the risk associated with the open canopy fields may be relatively lower, and it would be lowest in soils from the maize field. On the contrary, soils under maize is likely to cause Pb pollution of surface water bodies through runoff in erosion prone areas (soils with poor structure) and Pb bioavailability in the soil solution for plant root absorption.

### **5.3 Transport of lead by soil macropore flow in relation to matrix flow**

Lead transport in the intact and repacked soil columns were used to determine influence of macropore flow on Pb leaching. Typically, the saturated hydraulic conductivity, of intact soil columns (Table 4) was by far higher in the intact soil columns than repacked soil columns under the study sites. This guaranteed faster flow of chemical solutions (Pb in this case), and hence shorter transit time in the intact columns than the repacked columns as reported by several authors (e.g. Kung, 1990; Flury *et al.*, 1994; McGrath *et al.*, 2009; Melenya, 2014). van Tol *et al.* (2012) firmly stated that mass movement of solutes in macropores is dominantly controlled by gravity resulting in faster flow rates,

orders of magnitude higher than matrix flow. This accounted for the shortest transit time (Table 4) in both columns under close canopy cocoa followed by soils under open canopy cocoa and maize.

Relative concentrations of the effluent for all the intact columns fluctuated with time. The fluctuations, that produced peaks on the BTCs (Figure 5), were marked by higher concentrations at the 10<sup>th</sup> minute, and decreasing concentrations at the 20<sup>th</sup> and 30<sup>th</sup> minutes, however, these were followed by intermittent increases (peaks) in the effluent concentrations. Peak height(s) were more related to the degree of soil macroporosities in the order: close canopy cocoa > open canopy > maize. Macropore-matrix flow accounted for the shape of the BTCs when Pb solution was applied as a pulse as reported by Jury *et al.* (1991). In addition, the peaks on BTCs could be attributed to macropore flow effect (Larsbo *et al.*, 2014). Thus, soil macroporosity mainly determined the number and height of peaks until the breakthrough concentration was attained (Figure 5). The lower effluent concentrations along the BTCs could be related to the relatively slow matrix flow of solutes in the soil, which occurred concurrently with the macropore flow. This confirms the findings of Kung *et al.* (2000) and Jarvis (2007) that matrix flow and preferential flow occurred simultaneously in a given soil, but macropores transported solutes at higher water fluxes into the underlying layers of the soil and underground aquifers than the matrix pores. On the Contrary, the BTCs of the repacked columns were rather smooth with no clear peaks, largely due to the absence of macropores, and possibly the event of smooth flow due to the uniform flow of water and solutes in the soil matrix (Beven and German, 1982; Allaire *et al.*, 2009).

The observation of high initial Pb relative concentrations (Figure 5) in the intact soil columns in contrast to the repacked soil columns could be attributed to the ponding condition at the initial stages of the transport experiment. Thus, Pb solutions easily entered the macropores in the intact soil columns and later moved at higher velocities.

Meanwhile, flow of Pb solutions in the matrix of the repacked soil columns was reduced due to lower saturated hydraulic conductivities. Again the percolating Pb solutions had to displace the water already in the matrix pores, before bypassing it, and this, subsequently, decreased the flow rate of the Pb solutions and increased mixing and dilution of Pb concentration. As a result, Pb sorption at the upper soil layers increased and this accounted for the lower relative concentrations and non-significant differences in the breakthrough times of the repacked soil columns at the 10<sup>th</sup> to 40<sup>th</sup> minute.

Water and solute transport in the soil matrix have been reported as slow phenomena that allow long solute-matrix interactions such that there are non-significant differences in the initial stages of solute outflow concentrations (Garrido *et al.*, 2007; Melenya, 2014) as observed in this study. Matched with the effect of initial ponding conditions, it can be established that Pb sorption at the initial stages of the transport process, and matrix flux affect breakthrough times on the BTC. Again, it can be deduced from the flow rates of both intact and repacked soil columns that although the walls of the columns restricted lateral flow of the ponded water, soils without macropores or with low macroporosity may be apt to surface transport processes. Thus, if pollutants like Pb were present in the surface layers of these soils, they may be carried into surface water bodies by acid runoff and erosion, especially, when rainfall intensities and duration are high.

The intact soil columns recorded higher differences in relative concentrations from the BTCs (Figure 5) than the repacked columns from the close canopy cocoa, open canopy cocoa and maize fields, successively. This observation was due to the contrasting effect of macropores and matrix pores on Pb transport. Macropores reduced the matrix-lead interactions as a result of high flow rates, and later increased Pb effluent concentrations.

Thus, intact soil columns from soils under close canopy cocoa which had the highest macroporosity, had the highest effect on Pb fluxes followed by intact soil columns under open canopy cocoa and maize respectively. Since macropores were virtually absent in the repacked soil columns, this effect was not observed. Instead, lower saturated hydraulic conductivity of the repacked soil columns (Table 4), increased Pb sorption and later reduced Pb effluent concentrations. Kung *et al.* (2000), Borchert *et al.* (2010) and Klaus *et al.* (2013) posited that the effect of macropore flow on contaminant concentration with time was larger than matrix flux and this was also large in soils with higher macroporosities where both occurred concurrently.

The amount of Pb lost with respect to breakthrough concentrations and Pb flux (Table 4) depicted that much Pb leached in intact soil columns than the repacked soil columns within a shorter transit time. These observations were much noticeable in both intact and repacked soil columns from soils under close canopy cocoa than open canopy cocoa. However, soils under open canopy cocoa gave higher than soils under maize. Generally, these may be mainly due to differences in contact time for Pb sorption as affected by flow rates of Pb solutions, and sorption capacity. Sorption of Pb occurred simultaneously with the flow of Pb solutions suggesting relatively smaller contact time for Pb sorption in soils especially under close canopy cocoa. Hence sorption could be generally limited to faster

surface adsorption reactions depending on CEC. Once the CEC was exceeded, excess Pb in solution were carried along with water at a flow rate depending on saturated hydraulic conductivity. As a result, significantly higher Pb flux and breakthrough concentrations within shorter transit time, were observed in intact soil columns than repacked soil columns. Again it explained why the highest Pb flux and breakthrough concentrations were obtained for both soil columns under close canopy cocoa followed by open canopy cocoa and maize respectively.

As cited in literature, the Pb sorption behavior on transport applies to this also. Garrido *et al.* (2007) recounted that significant leaching of Pb in terms of Pb flux and breakthrough concentrations occurred in soils when flow rates were adjusted by higher orders of magnitude such that there was least contact time for matrix sorption in the soil columns. Thus it can be stipulated that Pb transport in soils under close canopy cocoa will increase Pb leaching than soils under open canopy cocoa and maize successively. In the main, there were positive correlations between soil physical and hydraulic properties (except bulk density), and Pb transport parameters of repacked and intact soil columns. It can be inferred from literature reviewed on effect of SOC on soil physical properties and effect of hydraulic properties on solute transport that physical transport of Pb in soils mainly depends on SOC content, soil total porosity and macroporosity, and saturated hydraulic conductivity. Therefore, irrespective of the benefits of SOC and soil worms, they may increase the rate of flow of highly sorbed contaminants into deeper layers of the soil profile.

Hence with all other factors of contaminant transport in soil held constant, highly sorbing Pb may bypass the soil matrix by mass flow into deeper soil layers and underground

aquifer through the contributive effect of SOC content, macroporosity, and soil physical and hydraulic properties.

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#### **5.4. Sorption of lead as affected by different soil depths**

Intact and repacked soil columns were used to obtain Pb sorption at different soil depths.

The concentration of Pb sorbed by soils under the three test sites generally decreased within the 30 cm depth of the soil columns. Several studies (e.g. Barriquelo *et al.*, 2003; Fodor and Szabo, 2004), have reported that due to organic matter accumulation in the upper soil layers, Pb sorption along the soil profile decreases significantly with soil depth, and this confirms the observations in this study.

With reference to Pb sorption according to the study sites, the highest amount of Pb was sorbed by the 0 – 10, 10 – 20 and 20 - 30 cm in both intact and repacked columns in soils from the maize field, and was followed by soils under close canopy cocoa and open canopy cocoa fields, successively. As stated earlier in literature (Sipos *et al.*, 2005; Olive, 2006), the properties of the soils from the close canopy cocoa field favoured sorption of Pb, but the opposite occurred in this study. Thus the differences in Pb sorption in the soils under the study sites cannot be mainly explained by reaction with soil colloids alone. Higher SOC content in soils under close canopy cocoa might have prevented the ability of the soils to sorb more Pb. The positive effect of SOC and macropore flow on Pb sorption as reported by Strawn and Sparks (2000) and Shougrakpam *et al.* (2010), applies to this phenomenon also. These contributed to relatively lower amount of Pb being sorbed in the intact soil columns in the order: maize > open canopy cocoa > close canopy cocoa.

Prolonged ponding on repacked soil columns and slower flow rates of Pb solutions relatively increased the contact time of Pb solution at the different soil layers (0-10, 10-20, and 20-30 cm). These contributed to high amount of Pb being sorbed in the repacked soil columns than the intact soil columns in the order: maize > open canopy cocoa > close canopy cocoa. Additionally, differences in contact time at the three soil layers mainly accounted for higher sorption of Pb by both soil columns under the test sites in the order: 0-10 cm > 10-20 cm > 20-30 cm. Matini *et al.* (2011), reported that the sorption capacity of soil colloids is significantly affected by the length of contact time. Thus the longer the length of contact time, the higher quantity of Pb being sorbed.

Sorption of Pb varies in different soils depending on several interconnected factors (Deiss *et al.*, 2002; Shahmohammadi-Kalalagh *et al.*, 2011). These differences in Pb sorption in soils justifies the need to carefully analyse organic fertilizers (including sewage sludge) and waste water for their Pb contents before using them in urban and peri-urban farming as sources of plant nutrients and irrigation water, respectively.

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## CHAPTER SIX

### 6.0 CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

From this study, Pb leaching in intact and repacked soil columns were significantly affected by SOC content, macroporosity, saturated hydraulic conductivity, total porosity, and bulk density.

Increasing the rates of Pb solutions applied on the surface of intact soil columns, significantly increased the concentrations of leachates under each study site.

Influence of macropore flow in intact soil columns on Pb transport was significantly higher than matrix flow in repacked soil columns under the study sites. In addition, the effect of macropore flow on Pb leaching in intact soil columns increased with increasing soil macroporosity.

Lead sorption decreased with soil depth and increasing soil macroporosity. Based on the findings, the hypotheses set for the study were accepted.

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## 6.2 Recommendations

From this study, the following recommendations are suggested:

1. Proper measures should be taken on the use of untreated sewage sludge, urban and industrial discharges that contain suspended and/or dissolved Pb and Pb-bearing compounds for agricultural purposes in order to safeguard soils, groundwater, and surface water bodies from contamination by Pb.
2. Further studies should be conducted on macropore characteristics such as continuity, connectivity, tortuosity, size distribution, and length, and their interactive effects on Pb transport.



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## APPENDICES

### Appendix 1: Determination of different lead concentrations (35, 70, and 105 mg/L) for the transport experiments

The chemical used for the study is lead nitrate  $\{Pb(NO_3)_2\}$ . It has molecular weight of 331.20 g. Molecular weight of lead is 207.20 g. Therefore, in every 100 mg lead nitrate, there is 62.56 mg lead.

35 mg Pb was obtained as follows:

65.56 mg Pb is contained in 100 mg  $Pb(NO_3)_2$

Therefore 35 mg Pb will be contained in  $\frac{35 \times 100}{65.56}$

$$= 53.39 \text{ mg Pb(NO}_3)_2$$

70 mg Pb was obtained as follows:

65.56 mg Pb is contained in 100 mg Pb(NO<sub>3</sub>)<sub>2</sub>

$$\text{Therefore 70 mg Pb will be contained in } \frac{70 \times 100}{65.56}$$

$$= 106.77 \text{ mg Pb(NO}_3)_2$$

105 mg Pb was obtained as follows:

65.56 mg Pb is contained in 100 mg Pb(NO<sub>3</sub>)<sub>2</sub>

$$\text{Therefore 105 mg Pb will be contained in } \frac{105 \times 100}{65.56}$$

$$= 160.16 \text{ mg Pb(NO}_3)_2$$

In order to obtain 35, 70, and 105 mg/L Pb, 53.39, 106.77, and 160.16 mg Pb(NO<sub>3</sub>)<sub>2</sub> were dissolved separately in 1 L deionized water at room temperature. They were then used for the transport experiments.

**Appendix 2a: Correlation matrices showing correlation coefficients between hydraulic and physical soil properties, and transport parameters of intact soil columns under the study sites**

							$\rho_b$	1 -
$K_s$	2	-	0.9189	-				
$f$	3	-1.0000	0.9189	-				
$C_b$	4	-0.9625	0.9505	0.9625	-			
$f_m$	5	-0.9137	0.9512	0.9137	0.9014	-		
$q_c$	6	-0.9012	0.9980	0.9012	0.9475	0.9381	-	

<i>t</i>	7	0.8360	-0.8795	-0.8360	-0.9020	-0.7572	-0.8835	-
		1	2	3	4	5	6	7

Two-sided test of correlations different from zero

$\rho_b$	1	-						
$K_s$	2	<0.001	-					
<i>f</i>	3	<0.001	<0.001	-				
$C_b$	4	<0.001	<0.001	<0.001	-			
$f_m$	5	<0.001	<0.001	<0.001	<0.001	-		
$q_c$	6	<0.001	<0.001	<0.001	<0.001	<0.001	-	
<i>t</i>	7	0.0050	0.0018	0.0050	<0.001	<0.001	<0.001	0.0181
			1	2	3	4	5	

$q_c$	6	-	
<i>t</i>	7	0.0016	-
		6	7

**Appendix 2b: Correlation matrices showing correlation coefficients between hydraulic and physical soil properties, and transport parameters of repacked soil columns under the study sites**

$\rho_b$	1	-			
$K_s$	2	-0.7512	-		
$C_b$	3	-0.8503	0.9700	-	
$q_c$	4	-0.6732	0.9858	0.9467	-
<i>t</i>	5	0.9290	-0.8444	-0.8987	-0.7643
		1	2	3	4

