

**ASSESSMENT OF VERTICAL TRANSPORT OF LEAD (Pb) FROM A FREE
DRAINAGE LYSIMETER IN CONTAMINATED SOILS IN SUDAN SAVANNA
OF NIGERIA**

BY

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JANUARY, 2014

DECLARATION

I hereby declare that the work in this thesis titled “**Assessment of Vertical Transport of Lead (Pb) From a Free Drainage Lysimeter in Contaminated Soils in Sudan Savanna of Nigeria**” was performed by me in the Department of Soil Science, under the supervision of Doctors Aisha Abdulkadir and Nafiu Abdu.

Information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this work has been presented for another degree or diploma at any institution.

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Date

CERTIFICATION

This thesis titled “**Assessment of Vertical Transport of Lead (Pb) From a Free Drainage Lysimeter in Contaminated Soils in Sudan Savanna of Nigeria**” by Jabir Haruna Abdulkareem meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literacy presentation.

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DEDICATION

This work is dedicated to my late parents Mallam Haruna Abdulkarim and Hajiya Asma'u Talatu Haruna through whom Allah brought me into this world. May your souls continue to rest in peace and may Aljannah Firdaus be your final resting home, Ameen.

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ABSTRACT

This study was conducted with the aim of determining the vertical movement of metal contaminants in a free drainage lysimeter at Dareta village, Anka Local Government Area of Zamfara State in northern Nigeria. A free drainage lysimeter was designed and constructed for collecting soil leachates from lead polluted soil. Lead movement in the soil was simulated using CHEMFLO-2000 computer simulation programme. Saturated hydraulic conductivity of soil samples were found to be slow (0.19 g cm^{-3}), moderately slow (1.61 g cm^{-3}), to moderate (4.64 g cm^{-3}), with mean values ranging from $0.19\text{-}4.64 \text{ cm sec}^{-1}$. Bulk density (ρ_b) of the soil surface (0-20 cm) of the study area were classified as moderate to high across the sampling coordinates. Mean values recorded were moderate to high with a range of $1.40\text{-}1.73 \text{ g cm}^{-3}$. The mean total pore spaces ranges from $37.73\text{-}47.30\%$ in the upper 0-20 cm depth. The vertical distribution of Pb with the highest concentration was 2025 mg kg^{-1} in Dareta North at the surface soil located near the gold ore processing site. Farms in Dareta South recorded lower values than Dareta North with values ranging between $1310\text{-}1586 \text{ mg kg}^{-1}$. Efficiency of leachates collection in the free drainage lysimeters installed in soil profiles across the sampling direction ranged from $40.03\text{-}50.65\%$ while discharge values obtained ranged from $8.01\text{-}10.13 \text{ li}$ per 3 days interval for a period of fourty days. The results of concentration of leachates collected with field drainage lysimeters compared with the laboratory soil columns shows the quantity collected from the former method were significantly higher than those from the laboratory soil columns. The contamination of soils was a result of processing of weathered lead-rich gold ores ($604\text{-}2025 \text{ mg kg}^{-1}$) and results from this research showed that the soils of the farmlands are highly contaminated with Pb. Leaching losses of Pb contaminants towards groundwater will increase with time as the drivers involved in solute transport in this study are identified as soil texture, porosity, concentration of contaminant and frequency of irrigation. Results from simulation using CHEMFLO-2000 modelling software indicate that Pb contaminants flux increases with increase in time. A flux density of $9.1 \times 10^{-5} \text{ cm hr}^{-1}$ was obtained at the initial stage of the simulation (0) and increased rapidly when the time of interest increased to $12.1 \times 10^{-5} \text{ cm hr}^{-1}$. While results for estimated values of Pb flux, distance of travel and breakthrough time using convective flux equations in Dareta village suggests that Pb travel through the soil down the groundwater at an increasing flux as this will require immediate measures to curtail this. As the break through time needed for Pb to travel at a distance of $3.46 \times 10^{-3} \text{ cm hr}^{-1}$ with a flux of 3.81×10^{-4} through the soil to the ground water (with at distance of 10 m from the ground) after ten years if all things being equal is estimated to be 289080 hr^{-1} .

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CHAPTER ONE

1.0 INTRODUCTION

Human activities greatly alter ecosystems worldwide at unprecedented rates leading to accelerated loss of biodiversity (Raven, 2002) and environmental pollution. Heavy metals are derived from both natural and anthropogenic sources (Foster and Charlesworth, 1996). Through natural process of pedogenesis, metals in minerals are released and translocated within the soil profile (Alloway, 1995). Concentration of heavy metals released into the soil system by natural pedogenic (or weathering) processes are largely related to the origin and nature of the parent material (Naidu *et al.*, 1997). Minerals like galena, cerussite, cassiterite and arsenopyrite can undergo dissolution through chemical weathering thereby releasing heavy metals such as lead. Trace elements occur as constituents of primary and secondary minerals through the process of inclusion, adsorption, and solid solution formation termed as coprecipitation (Sposito, 2008). Atmospheric deposition, as a result of acid rain and dew is another natural source of heavy metal pollution (Nriagu, 1990). Accessions from dust storms, volcanic eruptions and forest fires could also contribute significant amounts of heavy metals to the soil (Bolan and Duraisamy, 2003). The anthropogenic sources of heavy metals comprise all contributions made by mankind including mining and metallurgy, industrial processes that contribute to both atmospheric and land dispositions, municipal and industrial wastes, sewage, fertilizer and pesticides application (Naidu *et al.*, 1997; Abdu *et al.*, 2011). Mining and milling of metal ores coupled with industries have bequeathed many countries with the legacy of wide distribution of metal contaminants in soils (Bjuhr, 2007).

Lead (Pb) is a chemical element in the carbon group with symbol Pb (from Latin Plumbum) and atomic number 82. It is a soft and malleable metal which is regarded as a heavy metal but poor metal (due to low melting and boiling point). Metallic lead has a bluish-white colour after being freshly cut, but it soon tarnishes to a dull grayish colour when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid. It is a poisonous substance to animals including humans when in surface contact (non systemic) (Anon., 2013). Its toxicity can result in damaged or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs (CIS, 1999).

The chemical form of a metal contaminant influences its solubility, mobility and toxicity in groundwater system. Groundwater can be contaminated with Pb or other metals directly by infiltration of the leachates from land disposal of solid wastes, liquid sewage or sewage sludge, mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons, or from other spills and leaks from industrial metal processing facilities (such as steel plants, plating shops, amongst others.). Variety of reactions may occur influence the speciation and mobility of Pb such as acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange. Mobility of Pb and other solute movement in soils is strongly affected by regular flows in structured soils (Flury *et al.*, 1994; Quisenberry *et al.*, 1994; Shuh *et al.*, 1997); and preferential flow in soils with unstable wetting fronts (Starr *et al.*, 1978; 1986; Ghodrati and Jury, 1992; Ritsema *et al.*, 1993). Heterogeneity of soil properties further limits the capability to predict solute flow lines between soil surface and the soil leaching front (Roth *et al.*, 1991; Van Wesenbeeck and Kachanoski, 1991; Jury and Flühler, 1992; Snow *et al.*, 1994).

Lysimeters are widely used to study water flow and solute transport in soils (Bergström and Jarvis, 1993; Pütz *et al.*, 1998; Sangare *et al.*, 2012). The major advantage of lysimeters is the ability to control and measure the components of water as well as chemical balances and fluxes in soil. Water flow and solute transport in natural soils are significantly influenced by the occurrence of preferential flow and by the spatial variation of soil properties. Therefore, studies on undisturbed soil monoliths in lysimeters are expected to represent field conditions better than disturbed laboratory soil columns (Führ *et al.*, 1998). Lysimeter studies are therefore, considered to be an intermediate approach between field studies and small-scale laboratory experiments. Lysimeters have been of major importance in the development of our understanding of soil water and nutrient dynamics in ecosystems (Goss and Ehlers, 2009).

1.1 Background of the study

In March 2010 Medecins Sans Frontieres (MSF) a non-governmental organisation which means ‘Doctors Without Borders’ from France, discovered an epidemic of Pb poisoning in Zamfara State in northern Nigeria. Subsequent investigations by the Centers for Disease Control (CDC), the World Health Organization (WHO) and the Zamfara State Ministry of Health (ZMoH) confirmed that hundreds of children under the age of five years were either at risk of death or acute and long-term irreversible health risks due to very high levels of Pb. At least 10,000 people were estimated to be affected. The source of this outbreak was associated with artisanal gold ore processing that occurs in the villages. For several months grinding operations were conducted at numerous sites in villages while crushing, washing, and gold recovery were undertaken within the residential compounds. A particularly dangerous ore (galena or lead sulphite PbS) which is unstable and on prolonged exposure to the atmosphere oxidizes to minerals such as; cerussite (PbCO₃) and anglesite (PbSO₄). These ores which are of high

Pb content often exceeding 10% Pb were introduced into the stream in early 2010. In early April 2010, when death and illnesses became prevalent, the District Head of the affected area ordered these operations to be moved outside residential areas approximately about 0.5 kilometer from the villages and homes. Residual Pb-rich wastes and Pb contaminated soils remained in the compounds and areas where processing took place and in the re-located areas which are close to the farmlands. There still remains the risk of Pb movement to the food chain through the re-location and continued artisanal mining activities (UNICEF, 2011).

1.2 Problem statement

Pollutant movement towards the groundwater has become a severe problem globally in the last decades. In order to better understand the mechanisms of solute transport and to predict leachate masses and concentrations, appropriate in-situ monitoring techniques are required. Since every invasive soil water sampling system has an impact on the system behaviour, it is still an unsolved problem to get representative measurements of pollutant fluxes through a certain vertical section. This is even more problematic in heterogeneous soils with preferential flow paths that are rather common on the field scale (Flury *et al.*, 1994).

Lead in soil is relatively immobile and persistent whether added to the soil as halides, hydroxides, oxides, carbonates, or sulphates (USEPA, 1994). When released to soil, Pb is normally converted from soluble lead compounds to relatively insoluble sulfate or phosphate derivatives. It also forms complexes with organic matter and clay minerals which limits its mobility. The efficient fixation of Pb in soils limits the transfer of Pb to ground water systems. It has a slow mobility, so its effect might take years to be noticed and so far, few reports are available on the aspect of mobility of the metal. That is why the understanding of transport behaviour of Pb becomes crucial.

1.3 Justification

Understanding transport of solutes or contaminants in soil is important to many management problems in agriculture and environment. In general it is vital in developing procedures for maximizing the effective use of fertilizers, pesticides and other chemicals within root zone of crops while minimizing their movement into groundwater (Wilson *et al.*, 2000). Knowledge of these processes are important to understanding possible contamination of natural groundwater through solute leaching or redistribution within a vadose zone, availability of solutes for plant uptake, surface runoff, salt intrusion in coastal aquifers, seepage from storage or disposal systems and chemical residues (Lal and Shukla, 2004). Clean up or remediation technique to be adopted depends on the kinetics and mobility of the metal. And so far, the diagnosis presented by the different agencies (MSF, CDC, WHO, and UNICEF) did not include mobility based on reports and documents released. Mobility or movement might take years and this study intends to offer some understanding of Pb to provide long term solutions necessary for management and remediation of the polluted soils. Coupled with this, wastewater irrigation is gaining more ground in developing countries owing to the shortage of good quality irrigation water. This might contribute significantly to the movement of Pb and other contaminants therein contained into the groundwater reserve.

1.4 Research hypotheses

- i. Field measured vertical movement of contaminants with a free drainage lysimeters is the same with the laboratory measured.
- ii. Vertical transport is mainly dependent on nature of soil physico-chemical and hydraulic properties.

1.5 Objectives of the study

The main aim of the study is to determine vertical movement of Pb contaminants in a free drainage lysimeter. While the specific objectives are to:

1. Understand the process of Pb transport in a Pb contaminated soil of Sudan savanna, northern Nigeria.
2. Simulate the vertical leaching of Pb in the soil profile to the groundwater using CHEMFLO-2000 modelling software.
3. Compare between vertical movements of Pb in the laboratory using soil columns between field movements using a free drainage lysimeter.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy metals

The term 'heavy metal' in general includes elements that are metals and metalloids. They include both biologically essential [e.g cobalt (Co), copper (Cu), chromium (Ch), manganese (Mn) and zinc (Zn)] and non-essential [e.g Pb, cadmium (Cd), mercury (Hg)] and arsenic (As)] metals. The essential elements for plants and animal or human nutrition are required in low concentration, hence, they are known as trace elements or micro elements. The non-essential metals are phytotoxic to plants, animals and/or humans at high concentrations (Bolan and Durasaimy, 2003). Heavy metals are natural components of the environment and are classified as trace elements because they occur in concentrations less than 1% (frequently below 0.01% or 100 mg kg⁻¹) in rocks of the earth crust (Alloway, 1995) but are now an issue of concern because they are mined and exposed to the environment in elevated concentrations.

2.2 Lead as a pollutant

Human exposure to Pb can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the functioning of kidney, gastrointestinal tract, joints and reproductive system. (Lenntech, 2012) and death in critical cases (UNICEF, 2011).

Long term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's

disease, muscular dystrophy and multiple sclerosis (Ferner, 2001). Allergies are not uncommon and repeated long term contact with some metals or their compound forms may lead to carcinogenesis (CIS, 1999; Ferner, 2001).

Routes to Pb exposure include contaminated soil, air, water, food, and consumer products. Occupational exposure is a common cause of Pb poisoning in adults. One of the largest threats to children is Pb paint that exists in many homes, especially old homes. Thus children in old houses with chipping paint or Pb dust from moveable window frames coated with Pb paint are at greater risk. Prevention of Pb exposure can range from individual efforts (such as removing lead-containing items such as pipes from homes) to nationwide policies (such as laws that ban products manufactured with Pb, regulation of Pb levels in domestic water or soil, or provide clean-up and mitigation of contaminated soil, amongst others). Humans have been mining and using Pb-contaminated products for many decades with high risk of poisoning in the process (Anon., 2013). Although Pb poisoning is one of the oldest known environmental hazards, modern day understanding of small amounts of Pb necessary to cause harm was not realized until the latter half of the 20th century. Safe thresholds for Pb exposure are yet to be discovered, as such there is no known amount of Pb that is critical to harm the body (Anon. 2013).

2.3 Forms of Pb

Lead exists in both organic and inorganic forms. Inorganic Pb are those found in old paint, coal-fired power, ceramic manufacturing, ore processing, smelting of Pb ores, refining, the production and use of Pb alloys and compounds, recycling, combustion processes, industrial processes and direct disposal of Pb-containing substances. Elementary Pb does not dissolve in water under normal conditions (20⁰C and a pressure of 1 bar). It may however occur dissolved in water as PbCO₃ or Pb(CO₃)₂⁻². A well-

known example of a water soluble Pb compound is Pb sugar (lead (II) acetate) which derives its name from its sweet nature. Lead frequently binds to sulphur in sulphide form (S^{-2}), or to phosphorous in phosphate form (PO_4^{3-}). In these forms Pb is extremely insoluble and is present as immobile compounds in the environment. Lead compounds are generally soluble in soft, slightly acidic water (Lenntech, 2013). The organic forms of Pb exist mainly as sulphide in galena. Other Pb minerals include anglesite ($PbSO_4$), cerussite ($PbCO_3$), mimetite ($PbCl_2 \cdot 3Pb_3(AsO_4)_2$), and pyromorphite ($PbCl_2 \cdot 3Pb_3(PO_4)_2$) (Budavari, 1996).

2.4 Sources of Pb

Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil and dust from old paint containing Pb. In the general non-smoking, adult population, the major exposure pathway is from food and water. Food, air, water and dust/soil are the major potential exposure pathways for infants and young children. For infants up to 4 or 5 months of age, air, milk formulae and water are the significant sources (Anon., 2012).

Lead is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily in spite of declining prices. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. It is easily shaped, malleable and ductile. There are eight broad categories of use: batteries, petrol additives (no longer allowed in the European Union), rolled and extruded products, alloys, pigments and compounds, cable sheathing and ammunition (Anon., 2012).

Many contaminants including Pb are finding their way into the subsurface environment, either intentionally applied, for example in agricultural operations, or unintentionally released from leaking industrial and municipal waste disposal sites, or from other

sources (Šimůnek *et al.*, 2006). A broad range of fertilizers, pesticides and fumigants which contain minute quantities of heavy metals are now routinely applied to agricultural lands, thus, making agriculture one of the most important sources for non-point source contamination. The same is true for salts and toxic trace elements, which are often an unintended consequence of irrigation in arid and semi-arid regions. Agriculture also increasingly uses a variety of pharmaceuticals and hormones in animal production many of which, along with pathogenic microorganisms, are being released to the environment through animal waste. Similar problems arise with point-source contamination from industrial and municipal waste disposal sites, leaking underground storage tanks, chemical spills, nuclear waste repositories, and mine tailings, among other sources (Mallants *et al.*, 2011).

2.3 Movement of solute in soil

Many chemicals which are in soil solution and in soluble forms are referred to as solutes. The movement of these solutes through soil to groundwater or free water surfaces indicates process leading to the contamination of these resources. In many cases, serious human and health implications are associated with this form of pollution. The solutes contain nutrients and heavy metals from fertilizers, pesticides, salts, industrial and municipal wastes. In the case of nutrients, leaching losses represent a decline in soil fertility with economic consequences, and in the case of nitrate leaching, reduction of productivity due to soil acidification (Allinson *et al.*, 2000a, 2000b). In the case of pesticides and industrial wastes, small but toxic chemicals could be transported to groundwater reserve and remain there for hundreds and thousands of years (Ueoka *et al.*, 1999; Allinson *et al.*, 1999a, 1999b; Craymore *et al.*, 1999; Kelsall *et al.*, 1999). These chemicals or pollutants (as solutes) are often transported in the soil by

mass flow of water (convection), diffusion and/or dispersion in either the horizontal or vertical directions, or via stream flow in surface waters.

When a solute enters a soil matrix (which can be in a soil core, repacked soil column, or agricultural soil in a field) the initial sharp boundary between the resident and displacing solute starts diminishing mainly due to the twin processes of diffusion and dispersion. The transport of a solution through soil matrix consists of three main components: convection, diffusion, and dispersion, which are described below (Lal and Shukla, 2004).

2.3.1 Convection or mass transport

Convective or advective transport of a solution inside a soil matrix is known as the passive movement with flowing soil water. If the transport process has only convective transport without any diffusion, the water and solute move at the same average flow rate. Mathematically convective transport (J_m) can be expressed as:

$$J_m = q_s C \quad (2.1)$$

In which J_m is the flux density for convective or mass transport ($ML^{-2}T^{-1}$), q_s is the volumetric fluid flux density with dimensions of velocity (LT^{-1}), and C is the volume averaged solute concentration (ML^{-3}). The flux density of water can be calculated by the Darcy's equation for a steady state flow of water. The q_s is also analogous to θ , where v is the pore water velocity (LT^{-1}).

2.3.2 Diffusive transport

Diffusion is a spontaneous process resulting from random thermal motion of dissolved ions and molecules. In general, diffusion is an active process and diffusive transport tends to decrease existing concentration gradients and moves the process towards

homogeneity rather rapidly. Fick's law defines the diffusive transport and for one-dimensional steady state transport is given as:

$$JD = -D_m \frac{\partial C}{\partial x} \quad (2.2)$$

In which JD is solute flux density for diffusive transport of solute ($ML^{-2}T^{-1}$), θ is the volumetric moisture content (L^3L^{-3}). The diffusion coefficient in soils (D_m) is slightly less than the diffusion coefficient in pure water (D_0) mainly due to the tortuous flow paths in soils.

$$D_m = D_0 \theta \xi \quad (2.3)$$

where ξ is the dimensionless tortuosity factor ranging roughly from 0.3 to 0.7 for most soils, θ is the volumetric moisture content (L^3L^{-3}).

2.3.3 Dispersive transport

The soil matrix consists of pores of different shapes, sizes, and orientation. This heterogeneity of pore structure causes a large deviation of local pore water velocities inside each individual pore. If we consider a one-dimensional flow through a single capillary tube of constant radius R , according to Poiseuille's law, the flow rate through each pore varies proportionally to the fourth power of the radius R (Kutilek and Nielsen, 1994).

However, flow velocity (v) through the tube is a decreasing function of radial distance (r) from the center of tube. If average velocity is v' then $v=2v'(1-(r^2/R^2))$, when $r=R$, that is, at the wall of pore $v=0$, and at $r=0$, that is, at the center of pore $v=2v'$. It is, therefore, clear that microscopic scale variations of pore water velocity in the soil matrix are very important and large.

Dispersive transport occurs because of the velocity variations in soil matrix with respect to average pore water velocity. The velocity variations in a soil matrix is caused by

several factors such as zero velocity at the particle surface, which increases gradually and is maximum at the center of pore or at air water interface under unsaturated conditions (Fig 2.1a). Pore sizes also create velocity gradients with the velocity in larger pores greater than the velocity in smaller pores (Fig 2.1b). The other possible reason is the fluctuation of flow paths of an element of water with respect to the mean direction of flow (Fig 2.1c). Macroscopically, dispersion process is similar to the diffusion process, however, unlike diffusion, it occurs only during water movement. Field and laboratory experiments have shown that the dispersive transport can be described by an equation similar to diffusion as follows (Lal and Shukla, 2004):

$$J_h = -\theta D_h \frac{\partial C}{\partial x} \quad (2.4)$$

In which D_h is the mechanical dispersion coefficient (Bear, 1972) assumed to be a function of fluid velocity as follows and other terms as previously defined:

$$D_h = \lambda v^n \quad (2.5)$$

Where λ is the dispersivity and exponent “n” is an empirical constant generally assumed to be unity. The mixing or dispersion that occurs along the direction of flow path is called longitudinal dispersion and that in the direction normal to flow is known as transverse dispersion. Diffusion is an active process whereas dispersion is passive, in spite of this, most analysis on solute transport considers both processes to be additive because macroscopically both processes are similar. That is,

$$D = D_m + D_h \quad (2.6)$$

where D is the longitudinal hydrodynamic dispersion coefficient (Bear, 1972) or apparent dispersion coefficient (Nielsen *et al.*, 1972).

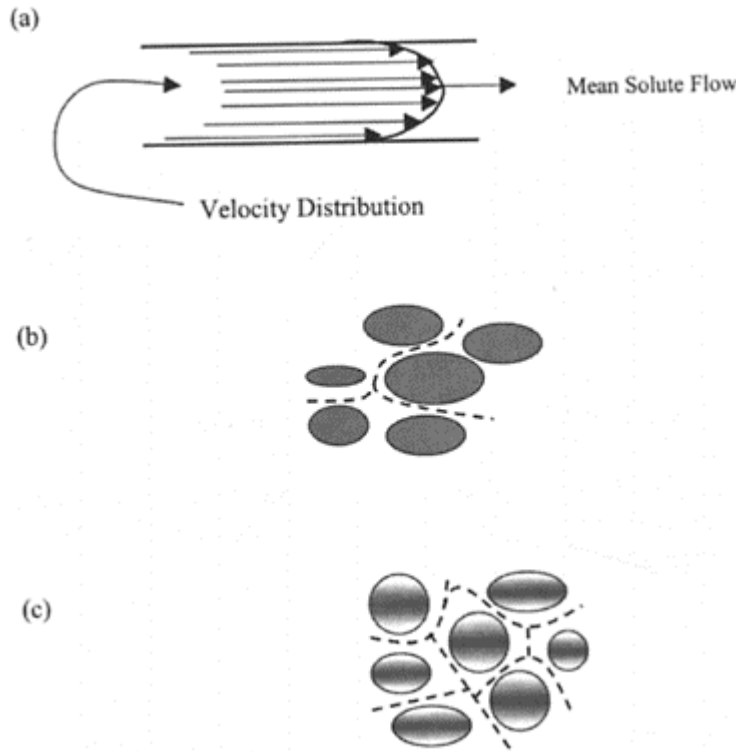


Figure 2.1: The physical mechanisms for hydrodynamic dispersion of solutes through soil matrix: (a) influence of velocity distribution within a soil pore; (b) influence of size of pore, and (c) influence of microscopic flow direction (Lal and Shukla, 2004).

By combining Eqs (2.1), (2.2), (2.4), and (2.6) leads to the following expression for solute flux, J_s

$$J_s = -\theta D \frac{\partial C}{\partial x} + qC \quad (2.7)$$

The equation of continuity states that (Lal and Shukla, 2004):

$$\frac{\partial J_s}{\partial x} = - \frac{\partial}{\partial t} (\theta C + \rho b S_s) \quad (2.8)$$

Where S_s is adsorbed concentration (MM^{-1}), ρ is the bulk density (ML^{-3}), and t is time.

Combining Eqs (2.7) and (2.8) gives the following solute transport equation:

$$\frac{\partial}{\partial t} (\theta C + \rho b S_s) = \frac{\partial}{\partial x} (\theta D \frac{\partial C}{\partial x} - qC) \quad (2.9)$$

Adsorption and exchange processes are usually nonlinear and also depend on the competing species in the soil system. Still, one of the most common approaches to describe the relationship between adsorbed and solution concentrations has been to

assume instantaneous adsorption and linearity between C and S of the form (forcing the constant or intercept to zero)

$$S_s = K_D C \quad (2.10)$$

Where K_D is the empirical distribution coefficient. Inserting Eq (2.10) into Eq (2.9) and dividing both sides with θ results in equation (2.11).

$$\frac{\partial}{\partial t} \left(C + \frac{\rho K_D C}{\theta} \right) = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} - \frac{q}{\theta} C \right) \quad (2.11)$$

Assuming that the soil profile is homogeneous and moisture content and flux density are constant in time and space, Eq (2.11) reduces to

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.12)$$

Where R is the retardation factor and is given by

$$R = 1 + \frac{\rho + K_D}{\theta} \quad (2.13)$$

K_D in Eq (2.10) can be obtained from the slope of sorbed concentration (MM^{-1}) versus solution concentration (ML^{-3}). A zero value of K_D in Eq (2.13) reduces R to 1, which indicates no interactions between solute and soil. A negative value of K_D makes R less than one, which indicates anion exclusion or immobile water, which does not contribute to convective transport. In case of anion exclusion, $(1-R)$ is known as anion exclusion volume. A positive K_D results in $R > 1$, which indicates sorption (Lal and Shukla, 2004).

2.4 Measurement of solute movement

Movements of soluble pollutants (solutes) and their concentrations can be determined by different methods. Measurement and modelling solute transport is complicated due to non-random spatial and temporal variations of physical, chemical and biological components of soils as well as lack of experimental research that examines transport mechanisms of chemicals through unsaturated field soils (Dagan, 1986; Jury and Flühler, 1992). Measurements range from field to laboratory procedures, while modelling involves the use of empirical equation to describe the flow or mathematical software to simulate the transport process in the soil. Some models used in determining transport parameters are the Convective-Dispersive equation (CDE) which is based on the assumption that solute front moves uniformly (Xue *et al.*, 1997; Mohanty *et al.*, 1998; Elliott *et al.*, 1998; Sarmah *et al.*, 2005). Other models with various degrees of complexity to simulate solute flow in the vadose zone have been tested, such models include, CHEMFLO-2000 (Nofziger and Jinquan, 2005), HYDRUS-1D (Šimůnek *et al.*, 1998), MACRO (Jarvis *et al.*, 1991); USDA's Root Zone Water Quality Model (RZWQM) (Ahuja *et al.*, 2000) and LEACHEM (Hutson and Wagenet, 1995). Conceptually, these models vary mainly in the amount of interaction of solutes with the soil matrix.

Laboratory experiments are based on repacked, sterile, homogenized soil cores that bear little resemblance to physical reality and have often been shown to underestimate the solute loss and risk of contamination to groundwater reserves (Stagnitti *et al.*, 1998). Multiple sample percolation systems are an excellent means to obtain accurate values of the solute and water flux in vadose zone experiments and have been shown to effectively show the impacts of soil heterogeneity on these fluxes (Stagnitti *et al.*, 1999).

Successful monitoring of solute transport and leaching through the soil requires accurate and appropriate methods in the field to capture soil solution and measure drainage water and estimate water fluxes within the vadose zone. The most common and currently available field methods for drainage water and flux monitoring and sampling employ various types of water samplers or lysimeters such as porous ceramic suction cups, zero tension pan lysimeters, gravity drainable soil columns, passive capillary fibre glass wick samplers (PCAPs), and weighing lysimeters and tile drainage samplers (Jabro *et al.*, 2008).

2.4.1 Lysimeters

Lysimeters or soil columns are containers or vessels containing disturbed or undisturbed soils. The optimal surface area and length of a lysimeter depend mainly on the scientific question, the filling procedure, the lower boundary, and the location of installation. The base area is strongly connected to the scale of observation, whereby small-scale heterogeneity will be averaged using large base areas. Lysimeters with crop stands should represent the natural crop inventory and the maximal root penetration depth should be taken into account. Lysimeters can be filled with either monolithic or disturbed soil or non-reactive materials such as sand. Disturbed lysimeters can be filled with the disturbed horizons of the natural soil or artificial material can be used instead. If disturbed soils or materials are used, the natural texture and the spatial heterogeneity will be changed, which will result in changes of the water and solute flow (Johnson *et al.*, 1995; Troxler *et al.*, 1998). The installation of the lysimeters can be in the field (Meissner *et al.*, 2000), at special lysimeter facilities, under controlled conditions in greenhouses, or in laboratories. In the case of installation under natural boundary conditions, the upper surface of the lysimeters should be equal to the top ground surface to minimize microclimatic changes. The space between the lysimeter vessel and the

surrounding soil should also be minimized to reduce artificial temperature gradients within the soil block. The lower boundary is often segmented to obtain information on the spatial heterogeneity of the water and solute fluxes (Schoen *et al.*, 1999). For acquisition of the surface run-off, the lysimeters can also be equipped with run-off /overflow tubes (van Weesenbeck *et al.*, 1998).

By the drainage behaviour of water from the system, two types of lysimeters can be distinguished: (i) Free drainage lysimeters, where water is allowed to drain freely through the soil under gravity, or (ii) suction controlled drainage system, where a defined suction is imposed at the lower boundary using suction cups, wick samplers, or porous plates.

In general, a free drainage lysimeter is easier to install and cheaper than the controlled suction system. A major concern of the free drainage lysimeter is that the lower boundary is exposed to atmospheric pressure, resulting in an evolution of a water-saturated zone at the bottom of the lysimeter before drainage (Abdou and Flury, 2004). This lower boundary imposes temporary anaerobic conditions which may influence degradation, solute transport, and capillary rise during evapotranspiration (Bergstrom, 1990; Giessler *et al.*, 1996). In comparison, suction lysimeters are more expensive and difficult to install, especially if they have large surface areas (Bergstrom, 1990). Another problem with suction controlled lysimeters is that water and solutes can interact with the material used for the suction devices. Also, the natural matric potential, water flow streamlines, and the composition of the leachates can be altered. The drainage patterns of both systems have been compared in several laboratory and numerical experiments, with the general finding that suction lysimeters drain more water continuously and in larger quantities (Colman, 1946; Dowdell and Webster, 1980; Vereecken and Dust, 1998; Abdou and Flury, 2004). A major concern of the lysimeter

concept is that it does not account for lateral water and solute fluxes, and that the vertical boundaries may cause fringe effects and preferential flow paths (Schoen *et al.*, 1999). Titus and Mahendrappa (1996) listed several techniques to minimize the fringe effect in lysimeters.

The general aim of lysimeter studies is the measurement of solute concentrations at the lower boundary (flux concentrations), in transport studies, and in calculations of mass balances for scientific questions and pesticide registration (EC, 1995). If the lysimeter is equipped for volatilization measurements a closed mass balance can be calculated even for volatile substances (Fuhr *et al.*, 1998; Meissner *et al.*, 2000; Wolters *et al.*, 2003). Additionally, information of the actual evapotranspiration can be drawn if the lysimeter is settled on a scale and if the percolate is logged at short time intervals (for example, using tipped buckets). Moreover, weighable lysimeters with ground water control are used to measure the soil water balance parameter (such as evapotranspiration, capillary rise and groundwater recharge for sites influenced by groundwater (Bethge-Steffens *et al.*, 2004).

Lysimeters installed into lysimeter facilities allow additional measurements using hydro geophysical methods (Vereecken *et al.*, 2006) such as Electrical Resistivity Tomography (ERT) (Binley *et al.*, 1996a, 1996b; Slater *et al.*, 2002) or Ground-penetrating Radar (GPR) (Schmalholz *et al.*, 2004) for the characterization of the water and solute flow. These techniques may provide additional high spatial and temporal information necessary to describe non uniform transport process within the soil profile.

2.4.2 Free drainage lysimeters

A free-drainage lysimeter is easy to install and is cheaper than the suction-controlled lysimeter. They collect gravitational water and require that the soil above the lysimeters be saturated during collection (Barbee and Brown, 1986). Generally, free drainage

lysimeters have low collection efficiencies ranging from 10 to 58%, as defined by the ratio of observed to expected percolation (Jemison and Fox, 1992; Zhu et al., 2002). To obtain samples, free drainage lysimeter require that the soil-pore water above the device attain a water potential greater than or equal to zero. Mostly soil water potentials are less than zero (unsaturated) resulting in flow away from the sampler due to local gradients in matrix potential (Jemison and Fox, 1992). The free drainage lysimeter system itself can be made of different materials such as steel, stainless steel, glass, ceramic, or plastic material depending on the scientific question and the target substance. The sampling surfaces of the system can exhibit several square meters for example, in waste disposal sealing, with standard dimensions being about 0.5m². In general, pan lysimeters are placed below the ground surface to capture drainage water. The installation is comparable to that of suction plates. They can also be used at shallow depths, for example, in organic or forest litter layers and hence called humus lysimeters (Marques *et al.*, 1996; Ranger *et al.*, 2001).

The installation of the free drainage lysimeter requires a filling with coarse gravel, sand or some other highly water conductive materials to guarantee easy interception of the drainage water and to divert it to the collection device. Placing a gravel drain in the soil subsurface generally creates a seepage flow boundary condition with a pressure head equal to the atmospheric pressure (Richards, 1950). Therefore, the soil gets saturated at the interface between the natural soil and the gravel filling. If the pan is filled with coarser material as the ambient soil, a tendency for water bypass is imposed as a response of the water potential gradients existing in the soil at the interface and the soil surrounding the system. The amount of bypass flow strongly depends on the water flux, the textural contrast between the filling material and the surrounding soil, and the gradients in water potential that exist in and around the pan lysimeter.

Due to the design of the sampler and the absence of capillary connection to the soil (fig 2.2 a, b, c, d), free drainage lysimeters operate reasonably well in soils with large macro-pores near saturation but are much less successful if the soil dries out (Zhu *et al.*, 2002). Initially, pan lysimeters were used primarily to analyze water quality and only occasionally to quantify drainage rates. More recently, zero-tension lysimeters have been used to estimate drainage rates over a wide range of soil conditions (Chiu and Shackelford, 2000; Zhu *et al.*, 2002; van der Velde *et al.*, 2003, 2004). Presence of water divergence cause collection efficiencies less than 10% to be noted for pan lysimeters (Jemison and Fox, 1992; Zhu *et al.*, 2002). Therefore, diversion around zero-tension lysimeters can be a significant problem. Flury *et al.*, (1999) also showed in numerical simulations that these seepage face conditions not only influence the water flow, but also the solute concentration in the sampled leachates. The prominent advantages of pan lysimeters are their low cost and ease of maintenance. Their shortcomings include; complex installation that causes considerable disturbance on experimental plots and the divergence of water flow around the system, which prevents quantitative estimates of flux concentrations. This complicates the interpretation of solute breakthrough and which may even lead to complete failure of the system. Humus lysimeters show less problems with saturation and bypass flow, due to the fact that humus has a more coarse and open-pored structure.

Humus lysimeters only have a nylon mesh at the top and are not filled with gravel or other mineral materials, because the water flowing out of the humus layer should not have contact with mineral surfaces which would cause flocculation and/or changes in solute chemistry (Guggenberger and Zech, 1993).

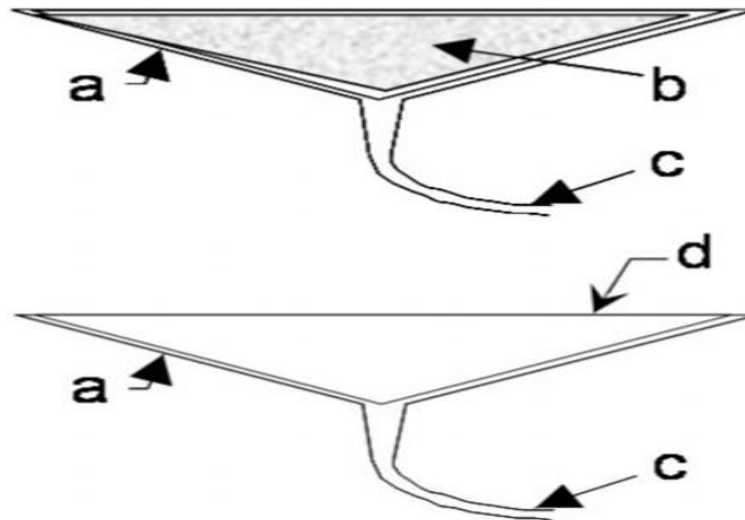


Figure 2.2: Schematical sketch of a pan lysimeter and a humus lysimeter with funnel (a), filter body (b) and tube connection (c) respectively nylon mesh (Source: Weihermüller *et al.*, 2007)

2.5 Modelling of solute transport

Reliable application of computer models to field-scale flow and transport problems demands a complimentary effort in quantifying a large number of model parameters. As increasingly more complicated flow and transport models are being developed, the accuracy of numerical simulation depends upon the accuracy with which various model parameters are estimated. Knowledge of the unsaturated soil hydraulic properties is especially important when numerical models are used to simulate variably saturated water flow and solute transport.

Such simulations are generally based on the numerical solutions of Richards' equation, which requires information about the soil water retention, $u(h)$, and unsaturated hydraulic conductivity, $K(h)$, functions involving the water content u , the saturated hydraulic conductivity K , and the soil-water pressure head h . Accurate measurement of these hydraulic properties is confounded by the extreme spatial heterogeneity of the subsurface environment. The hydraulic properties frequently also show significant variations in time because of cultivation or other agricultural activities, shrink-swell

phenomena of fine-textured soil, the effect of particle dispersion and soil crusting, and changes in the concentration and ionic composition of the soil solution (van Genuchten and Šimůnek, 1996). One of these models is described below.

2.5.1 CHEMFLO-2000 model

The movement of water and chemicals into and through soils has a large impact upon our environment and the entire ecosystem. Understanding these processes is of great importance in managing, utilizing, and protecting our natural resources. This software was written to enhance our understanding of the flow and transport processes. It was written primarily as an educational tool. As a result it is highly interactive and graphics oriented. This version (version 2005.10.13) of the software expands on that of Nofziger *et al.*, 1989 by providing a graphical user interface and other enhancements. The software enables users to define water and chemical movement systems. The software then solves mathematical models of these systems and displays the results graphically (Nofziger and Jinquan, 2005).

Water and chemical movement in soils are dynamic processes, changing dramatically over time and space. Soil properties, chemical properties, and water and chemical application rates interact in complex ways within the soil system to determine the direction and rate of movement of these materials. Researchers have worked many years to understand the physical and chemical mechanisms responsible for the movement of these materials. They have developed mathematical models describing these processes and compared the predictions of these models with field and laboratory measurements. The resulting mathematical models form a basis for predicting the behavior of water and chemicals in soils.

2.5.2 Mathematical models governing CHEMFLO-2000 model

2.5.3 Partial differential equation for water movement:

The partial differential equation used to describe one-dimensional water movement was published by Richards (1931) and can be written as;

$$\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} \left[K(h) \left(\frac{\partial h}{\partial x} - \sin(A) \right) \right] \text{ or}$$
$$C(h) \frac{\partial h}{\partial x} - \frac{\partial}{\partial x} \left[K(h) \left(\frac{\partial h}{\partial x} - \sin(A) \right) \right]$$

(2.14)

where $\theta = \theta(h)$ is the volumetric water content, $h = h(x, t)$ is the matric potential, x is the

position coordinate parallel to the direction of flow; t is the time; $\sin(A)$ is the sine of the angle A

between the direction of flow and the vertical direction; $K(h)$ is the hydraulic conductivity of the

soil at matric potential h ; and $C(h)$ is the specific water capacity. That is;

$$C(h) = \frac{d\theta}{dh}$$

(2.15)

An angle of 90 degrees corresponds to vertical flow with x increasing in the downward direction

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study location

The study was conducted at Dareta village, Anka Local Government Area of Zamfara State, northern Nigeria. Dareta village is a place where major outbreaks of Pb poisoning has been occurring since 2010, which is related to mining processes of Pb rich ore for the extraction of gold (WHO, 2010; UNICEF, 2011). Dareta is located on latitude 12°06'30"N and longitude 5°56'00"E, and has an area of 2,746 km² and a population of 142,280 according to the 2006 population and housing census (NPC, 2006). Farming is one of the major activities of the inhabitants of Dareta under rain-fed and irrigation conditions. The irrigated crops are mostly vegetables such as spinach, lettuce, cabbage and onions while rain-fed crops produced are cowpea, millet, sorghum, ground nut. The climate is warm with mean daily temperature rising up to 30 °C between March and May. Rainy season starts in late May to September while the cold season known as Harmattan last from December to February. The onset of the rains, on the average, is between mid-July lasting for about three months up to the end of October with an annual average of about 579 mm (Anon., 2012).

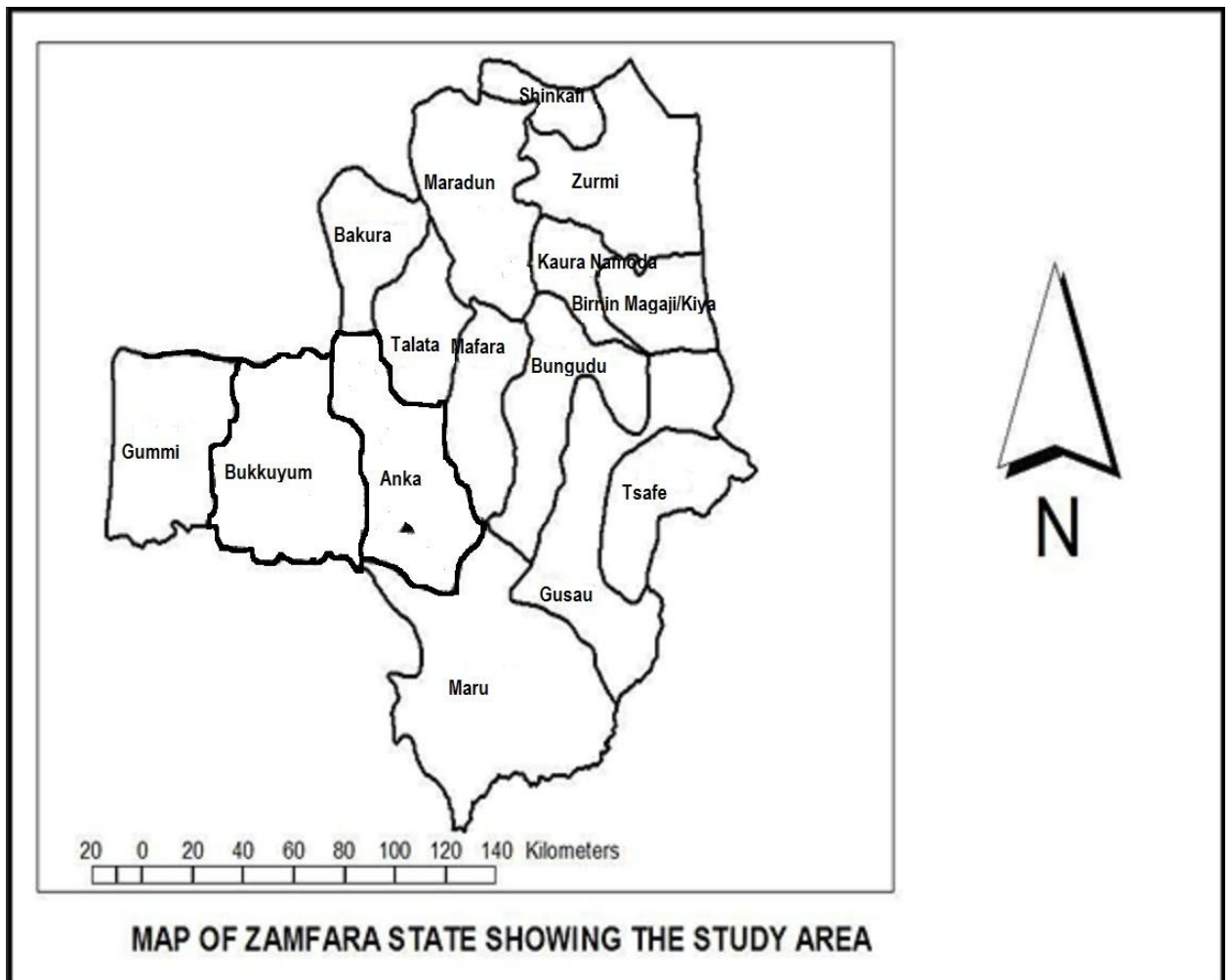


Figure 3.1: Map of Zamfara, showing the location of Daretta Village, where soils for the study were obtained

3.2 Soil sampling, handling and preparation

Eight soil profile pits were dug to a depth and width of both 1 m in eight different farmlands. The living perimeter of the village was secured and profile digging proceeded along the four coordinates (North, South, East and West) starting from the first farmland after the last house, on a grid at distances 50 and 100 m (fig 3.2). Two replicates of both disturbed and undisturbed core samples were taken from each of the profile pits at depths of 0-20 cm, 20-40 cm and 40-60 cm and 60-100 cm. Also 10-15 samples were taken to come up with a composite and three replicates

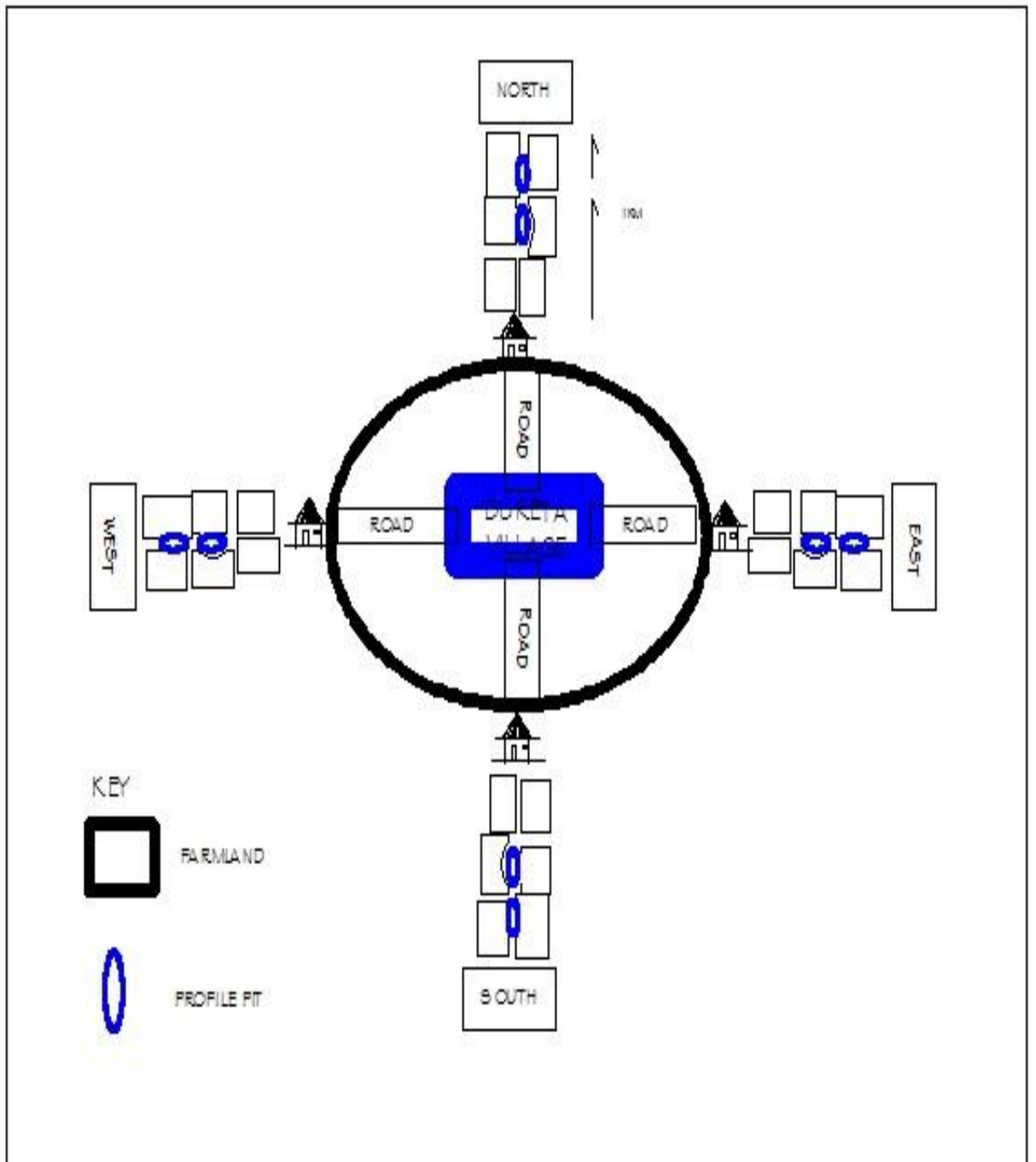


Figure 3.2: Field layout of the sampling points in the study location with respect to the last house in Daretta village

of core samples were also taken randomly at each farm where the profile pit was sunk. This gave a total of twenty six core samples and twelve disturbed samples per sampling direction. The disturbed soil samples collected were bulked, air-dried and sieved through 2 mm sieve. The less than 2 mm sample were stored properly for physical and chemical analysis.

3.3 Free drainage lysimeters used in this study

The original design used for collecting soil leachates in soil amendment experiment by Li *et al.* (2002) and Wang *et al.* (2005) was modified in this study. A modification to this design was constructed to provide efficient collection surface and stronger connections with lysimeter collection plate. The design includes the following materials: 10-litre capacity bucket 30 cm in height and diameter, bucket lid, 4-litre collection bucket 14 cm in height and diameter, fittings for flexible tubing, 2 cm flexible tubing, collection plate of 35 cm in diameter and mesh filter, acid-washed sand (Plates 3.1, 3.2 and 3.3). The flexible tube provides access to the inside of the lysimeter once it is installed. The collection plate was attached to the bucket lid. A hole was then drilled through the collection plate and lid to allow the collected water to be channeled into the lower collection bucket (Plate 3.1). A mesh filter is glued over the drilled hole to prevent debris (soil, rocks, and so on) from blocking and passing through the buckets. Leachates collection from the lysimeter was done by downward movement of the leachates under the influence of gravity from the lysimeter to a smaller collecting bucket. The lysimeters were inserted into the enclosures of the soil profile. Firm contact between the profile surface and the contact surface of the collection plate was maintained with the acid-washed sand (Belford, 1979; Cameron *et al.*, 1990; Moyer *et al.*, 1996).

Two soil profile pits were sunk up to a depth of 1 m in two different farms at each of the four sampling directions in the village (North, East, West and South). A window hole

about the size of the lysimeter (30 cm) was dug at one side of each profile where the lysimeter was installed at a depth of 25 cm so that the top of the lysimeter will be below the soil surface as shown in plate 3.1. The flexible tube was left protruding from the ground. Leachates were collected from the lysimeter from the lower bucket by gravity movement (Migliaccio *et al.*, 2009) (Plate 3.2). Leaching of solutes was monitored at different time intervals starting from 0 time (t) and subsequently, leachates were collected at time (t) intervals of 3 days, up to a period of 40 days during the dry season. This was achieved by ponding the sampling point with 20 litres of water to a sunken bed at a depth of 10 cm and these was repeated severally once the water at the points dried up. The leachates collected were properly transferred into 100mls bottle, labelled and taken to the laboratory where they were refrigerated before further analysis.

The main advantages of this type of lysimeter are that; it is easy to assemble, requires minimum maintenance once installed and the total cost is relatively low. Some of its short comings are that; installing the lysimeters involves destroying the soil which is not good for the physical properties and that it must be checked on a regular schedule and leachates collected when full (depending on irrigation frequency and intensity and nature of the soil as this can be quite often).



Plate 3.1: Free drainage Lysimeter used in this study



Plate 3.2: Scientist installing free drainage lysimeter in the field



Plate 3.3: Free drainage lysimeter installation in the field

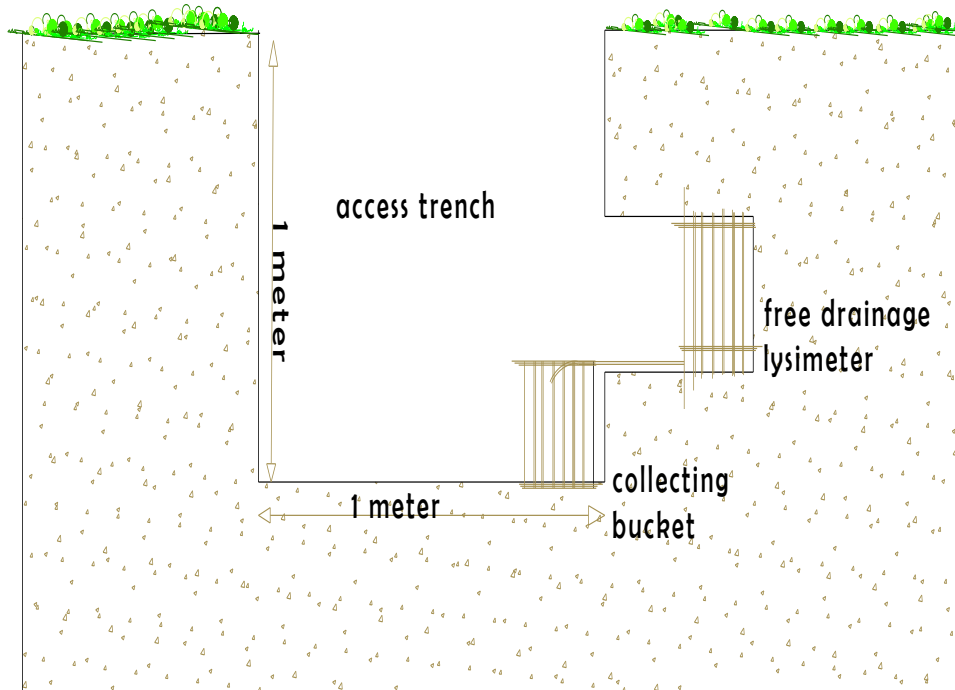


Figure 3.3: Sampling set up modified for this study

3.4 Laboratory measurement of vertical movements of solutes

Eight columns packed with soil were collected using a high pressure PVC pipe (10 cm diameter and 100 cm high) and taken to the laboratory to determine the vertical movement of metal contaminants. The pipe has an opening at the top that serves as the feeder but attached to a collection cup at the lower/other end. The cup is separated from the tube by a mesh/muslin cloth to avoid migration of soils to the collection cup. The soil columns were wetted with distilled water to saturation level and thereafter 1 litre of tap water were added to eight columns. Monitoring of leaching and leachates collection of all the soil columns at different time intervals was done as earlier stated. The leachates collected were measured and transferred to 50 ml plastic containers, carefully measured and were immediately stored in the refrigerator before further analysis.

3.5 Measurement of physical properties

3.5.1 Soil texture

The particle size analysis was determined by the standard hydrometer method (Gee and Bauder, 1986) which involves the dispersion of soil particles with sodium hexametaphosphate (Calgon). Fifty gram of sieved soil was weighed into polythene bottle, 100 mls of calgon solution was added into the bottle and the mixture was placed on a mechanical shaker and agitated for 15 minutes. The soil suspension was transferred into one-liter capacity cylinder and diluted up to the 1 litre mark with water. The suspension was stirred using a plunger before the hydrometer was inserted. The hydrometer reading after 40 seconds were recorded for determining silt and clay contents. Readings after 2 hours were also recorded and used to determine the proportion of clay fraction alone. The temperature and hydrometer reading for the blank were taken and calculations were made for the particle size fraction using Eq 3.1 and the textural classes of the soils were determined using the United States Department of Agriculture (USDA, 1962) textural triangle.

$$\% \text{ Sand} = \frac{\text{Corrected 2 hours reading} - \text{Blank} \times 100}{\text{weight of soil}} \quad (3.1)$$

$$\% \text{ Silt} = \frac{\text{Corrected 40 Seconds reading} - \text{Blank} \times 100}{\text{weight of soil}} - \% \text{ Clay} \quad (3.1a)$$

$$\% \text{ Sand} = 100 - (\text{Sand} + \text{Clay}) \quad (3.1b)$$

3.5.2 Bulk density (ρ_b)

Bulk density was determined by gravimetric method as described by Blake and Hartge, (1986a). The undisturbed cores obtained from the field were taken to the laboratory where the moist weights were immediately taken before placing in the oven. The oven

dried weight was taken at 105°C after 24 hours. The oven dry weights obtained were used in the calculation of dry bulk density, that is, mass of dry soil per unit bulk volume of soil.

$$\rho_b = M_s/V_s \quad (3.2)$$

where:

ρ_b = bulk density

M_s = mass of oven dry soil, g

V_s = volume of soil, equivalent to volume of core ring, cm³

3.5.3 Total porosity (f)

The total porosity (f) was calculated from the values of bulk density of the soil and particle density using the expression.

$$f = \left(1 - \frac{\rho_b}{\rho_d}\right) \times 100 \quad (3.3)$$

In ρ_d = particle density, and other terms as previously defined.

Total porosity is also regarded as the moisture content at saturation.

3.5.4 Effective porosity (P_e)

Effective porosity (P_e) is the soil porosity that contributes most to the flow of water when the soil is saturated (Ahuja *et al.*, 1984). Effective porosity was determined as the difference in soil water content at 33 KPa matric potential (percentage volume) and moisture content at saturation otherwise known as total porosity (Ahuja *et al.*, 1984; Mbagwu 1995; Suleiman and Ritchie, 2001).

$$p_e = f - \theta_c \quad (3.4)$$

Where:

pe = effective porosity, (cm^3/cm^3)

θ_c = moisture content at field capacity i.e 33 kpa, (cm^3/cm^3), and other

terms as previously defined.

Free drainage of the saturated soil was allowed to occur, after which the soils were carefully transferred to the pressure plate apparatus and were set at 33 kpa pressure potential and the moisture content was determined (Vomicil, 1965; Wuddivira *et al.*, 2001). Extraction with pressure plate apparatus at saturation could not be achieved because some drainage must have occurred before placing the soil sample in the apparatus, thus total porosity was used in calculating effective porosity (Vomicil, 1965; Wuddivira *et al.*, 2001).

3.5.5 Saturated hydraulic conductivity (Ks)

The saturated hydraulic conductivity was determined with the undisturbed soil cores by the constant head permeameter method (Klute and Dirksen, 1986) using the ICW laboratory permeameter (Eijikelkamp Agrisearch N0. 09.02.). The core rings containing the soil were saturated over night but this was done by first covering the blunt end of the ring with a muslin sheath (nylon and cloth) which was held in place by means of rubber band to prevent soil loss. The core ring was then secured to a plastic container after which it was held in place by a special mesh and clamp to fit the core. This was then inserted into the permeameter after a constant head has been established. A small tube initially filled with water was used as a junction between the inside of the plastic holder and water in the permeameter, which aids water flow into the burette. A chosen volume of water collected in the burette was taken at the time of flow via stop watch. The heights of water both inside the ring holder and outside were measured by means of the meter bridge as the hydraulic head difference.

Darcy's law of inflow of water in soils was applied for computing K_s after measuring the volume of flow through the soil column, V , in time t , of known area, A and with hydraulic head difference, ΔH from Eq 3.5:

$$K_s = \frac{VL}{At\Delta H} \quad (3.5)$$

In which L is the length of soil column (cm) and other terms as previously defined. K_s is an important input variable in modelling Pb transport in the CHEMFLO-2000 model.

3.6 Measurement of soil chemical properties

3.6.1 Soil reaction (pH)

Soil pH was measured at 1:2.5 soil to solution ratio with water and 0.01M calcium chloride (CaCl_2) using a glass electrode. The suspension was vigorously stirred within a period of 15-20 minutes and was allowed to stand undisturbed. The pH electrode was immersed into the soil suspension and pH value was read for all the samples in both water and CaCl_2 .

3.6.2 Cation exchange capacity

Cation Exchange Capacity (CEC) was determined by 1N ammonium acetate (NH_4OAc) saturation method. (Anderson and Ingram, 1993). Ten (10) grams of soil samples was weighed and saturated with 30 ml ammonium acetate (NH_4OAc) solution. One normal NH_4OAc was used to wash out the excess ammonia (NH_3) that might have lodged in the non-exchange site of the soils. Acidified 1N sodium chloride (NaCl) was then used to displace or leach out the NH_3 on the exchange site up to the 250 ml mark of the conical flask. The amount of NH_3 displaced was then determined by distilling the leachate to volatilize the NH_3 and was trapped by boric acid. This was titrated with 0.1N hydrochloric acid (HCl) and the titre value was used for calculating the cation exchange

capacity of the soils. (Anderson and Ingram, 1993).

$$CEC = \frac{(Titre-Blank) \times NA \times 100}{weight\ of\ soil} \quad (3.6)$$

In which *NA* is the normality of acid and other terms as previously defined.

3.6.3 Exchangeable bases

Exchangeable bases (sodium, Na⁺; potassium, K⁺; calcium, Ca²⁺ and magnesium (Mg²⁺) were determined after saturating and leaching the soil with 1N NH₄OAc solution. Ca²⁺ and Mg²⁺ were obtained from titration using ethylene diamine tetra-acetic acid (EDTA) method as described by Devis and Freitas (1970) and read using Fast Sequential Atomic Absorption Spectrophotometer (AAS: Model VARIAN AA240FS). Na⁺ and K⁺ were determined using flame photometry (Rich, 1965).

3.6.4 Organic carbon

Organic carbon (OC) was determined by dichromate oxidation method (Nelson and Sommers, 1982). One gram of soil was weighed into a 250 ml conical flask and 5 ml of 1N potassium dichromate (K₂Cr₂O₇) solution was added and the flask was swirled. Ten (10) millilitres of concentrated sulphuric acid (H₂SO₄) was added into the flask and allowed to stand for 30 minutes, before it was titrated with 0.4N ferrous ammonium sulphate (NH₄)₂.Fe(SO₄)₂. The organic carbon was determined using the expression below;

$$\% OC = \frac{(Blank-Titre) \times NF \times 100 \times 1.33}{weight\ of\ soil} \quad (3.7)$$

In which *NF* is the normality of ferrous sulphate and other terms as previously defined.

3.6.5 Total metal concentration

Total concentration of metals in the soil and leachates was determined by Fast Sequential Atomic Absorbtion Spectrophotometer (AAS: Model VARIAN AA240FS) following aqua regia digestion as described by Lim and Jackson (1986). 0.2 g of finely ground soil sample was added into a 30 ml platinum crucible. This was followed by wetting the soil with few drops of water prior to the addition of 5 ml of hydrofluoric (HF) acid and 0.5 ml perchloric acid (HClO₄). The soil-acid mixture was then heated on a hot plate until white fumes of HClO₄ acid appears. The crucible was cooled after which 5 ml of HF acid was added. It was then placed on a sand bath and covered with a platinum lid and heated to a temperature of about 200 to 250 °C in order to evaporate the contents to dryness. The samples were allowed to cool and 2 ml of distilled water and a few drops of HClO₄ acid were added. The crucible was replaced in the sand bath and then the samples were allowed to evaporate to dryness after which they were removed from the bath to cool again. Five millilitres of 6N hydrochloric (HCl) and about 5 ml of distilled water were added prior to heating the crucible. Heating continued until solution heats gently. When the sample dissolved, it was filtered into 25 ml volumetric flask and made to mark with distilled water.

For the leachates twenty milliliters (20) from both the field and laboratory were measured into a glass beaker and digested with a 5:1 mixture of nitric (HNO₃) and HCl at 80 °C. The beaker was swirled gently and digested on a digestion block until brown fumes appeared which subsequently turned white indicating full digestion. The digested leachate samples were set aside to cool and filtered through Whatman No. 42 filter paper and diluted to 50 ml with distilled water in clean plastic containers prior to analysis. Concentration of Pb in the soils extract and leachates were determined in AAS.

3.7 Water and Pb simulation using CHEMFLO-2000

CHEMFLO-2000 computer simulation programme was used to simulate the movement of adsorbed Pb in the soil when irrigation water was applied at an initial depth of ponding of 5 cm. Lead is present in the soil before irrigation. Where will it be after seventy two hours (3 days), 8,760 hours (1 year), 43,800 hours (5 years) and 87,600 (10 years) of irrigation?

The following steps were used to carry out the simulation.

1. The “Soil System” button was selected.
 - a. The “Default Soil” was selected from the pull-down list
 - b. A finite soil was selected.
 - c. A length of 100 cm was specified for the soil.
 - d. The angle of inclination was set to be 90^0 .
 - e. Conductivity functions were set using the default, van Genuchten parameters (1980) were selected; K_s (cm/hr) = 2.0, α (1/cm) = 0.015, $n = 1.875$ (α and n van Genuchten constants).
 - f. Water characteristic function were set, van Genuchten parameters were selected; θ_s (v/v) = 0.43, θ_r (v/v), α (1/cm) = 0.015, $n = 1.875$ (θ_s , and θ_r van Genuchten constants).
 - g. Organic carbon was set at 0.019 and ρ_b as 1.57.
2. The “Initial Conditions” button was selected.
 - a. A uniform matric potential of -500 cm was selected.
 - b. Uniform total concentration of 0 was selected.
3. The “Boundary Conditions” button was selected.
 - a. The “initial depth of ponding” as the water boundary condition at $x = 0$ was selected.
 - b. Initial depth of ponding was selected as 5 cm.
 - c. The “Free Drainage” as the water boundary condition at $x = 100$ button was selected.

- d. The “Specified Concentration of Inflowing Solution” at $x = 0$ was selected.
 - e. The “Convective Flow” as the chemical boundary condition at $x = 100$ was selected.
4. The “Transport Properties” button was selected.
 - a. Two centimetre was selected for Dispersivity.
 - b. Zero was selected for all other properties
 5. The “Graphs” button was pressed.
 - a. The graphs of flux density vs. time and flux density vs. distance were selected.
 - b. Seventy two hours was selected as the initial time of interest.
 - c. Hundred centimetres were chosen as the position of interest.
 - d. Calculate button was then pressed.
 - e. The various graphs of water and chemical were observed. The depth at which the chemical penetrate into the soil was observed. Also the leading edge of the chemical was observed.
 - e. The “Retain Line” button was pressed to save the current lines on the screen
 - f. The time was changed to 8,760 hours (1 year) and the “Calculate” button was pressed with every change in time. The distributions of different parameters at these four times were observed to gain understanding of how time influences the movement throughout the soil profile.
 6. The “Boundary Condition” button was selected.
 - a. A concentration of 0 was specified for the water entering the soil at $x = 0$.
 - b. In the “Simulations Options” box at the upper right, “Continue simulation with new boundary condition” was selected.
 7. The “Graphs” button was selected.
 - a. The time of interest was set at 43,800 hours (5 years) and 87,600 (10 years),
 - b. The “Calculate” was selected.

c. The water content and chemical distributions were observed.

An overview of the CHEMFLO-2000 model user interface used in this study is given in Plate 3.4-3.6.

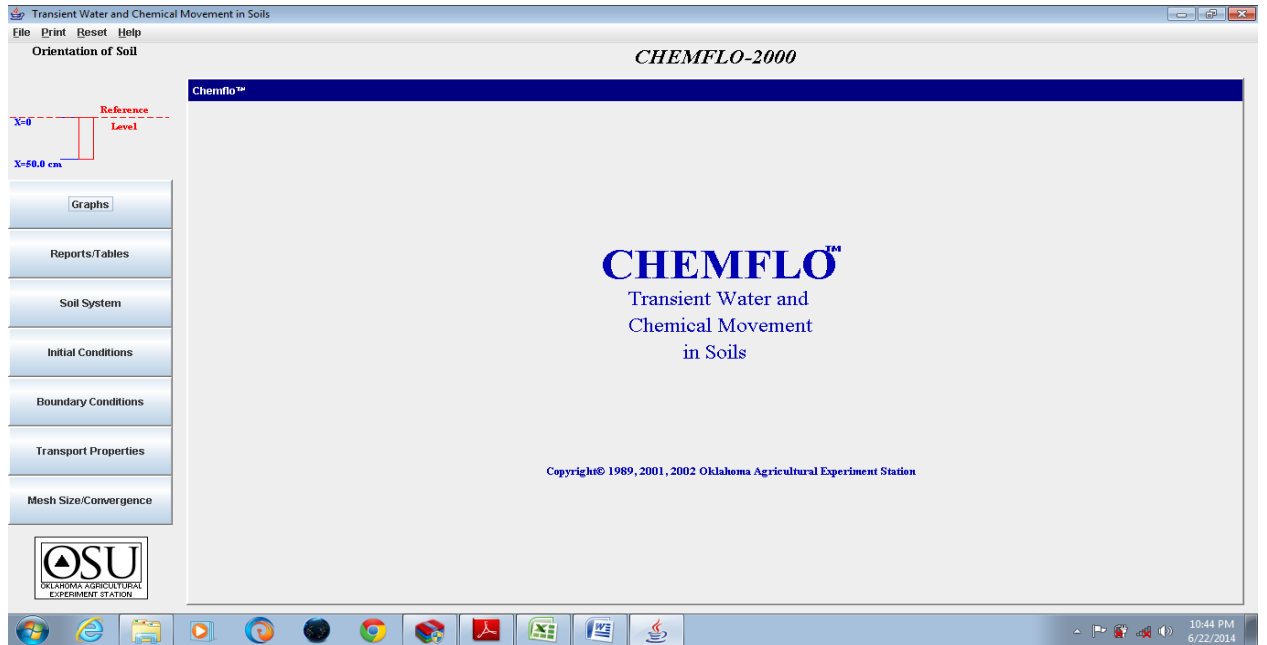


Plate 3.4: The user interface of the CHEMFLO-2000 model upon booting.

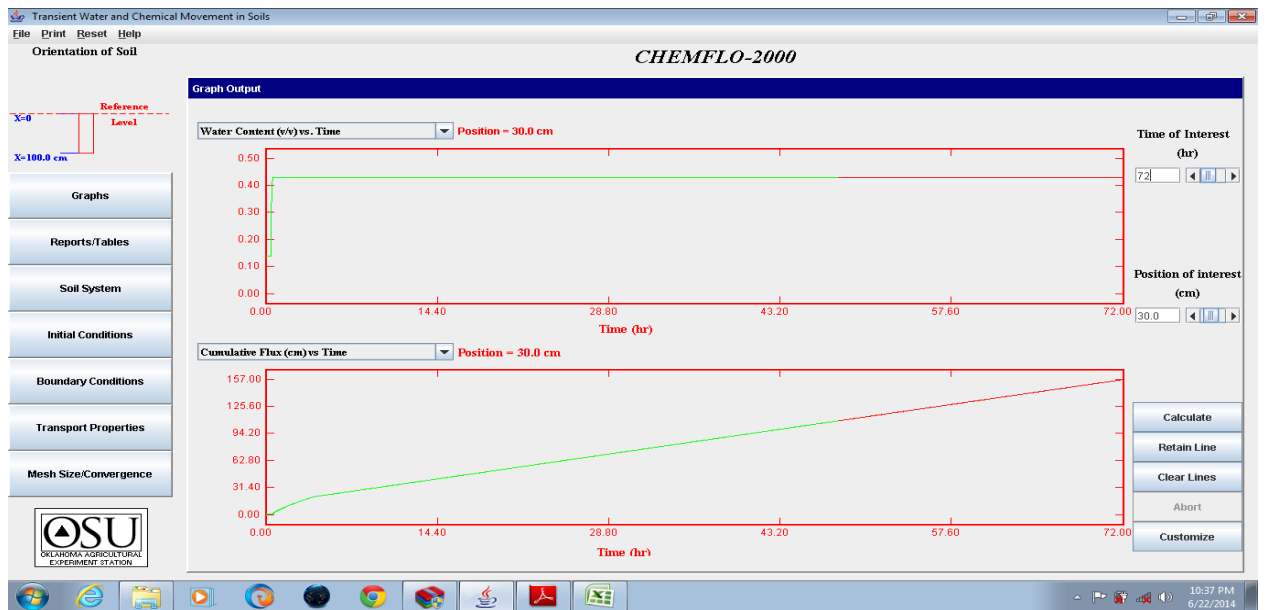


Plate 3.5: Graphic view of the CHEMFLO-2000 model

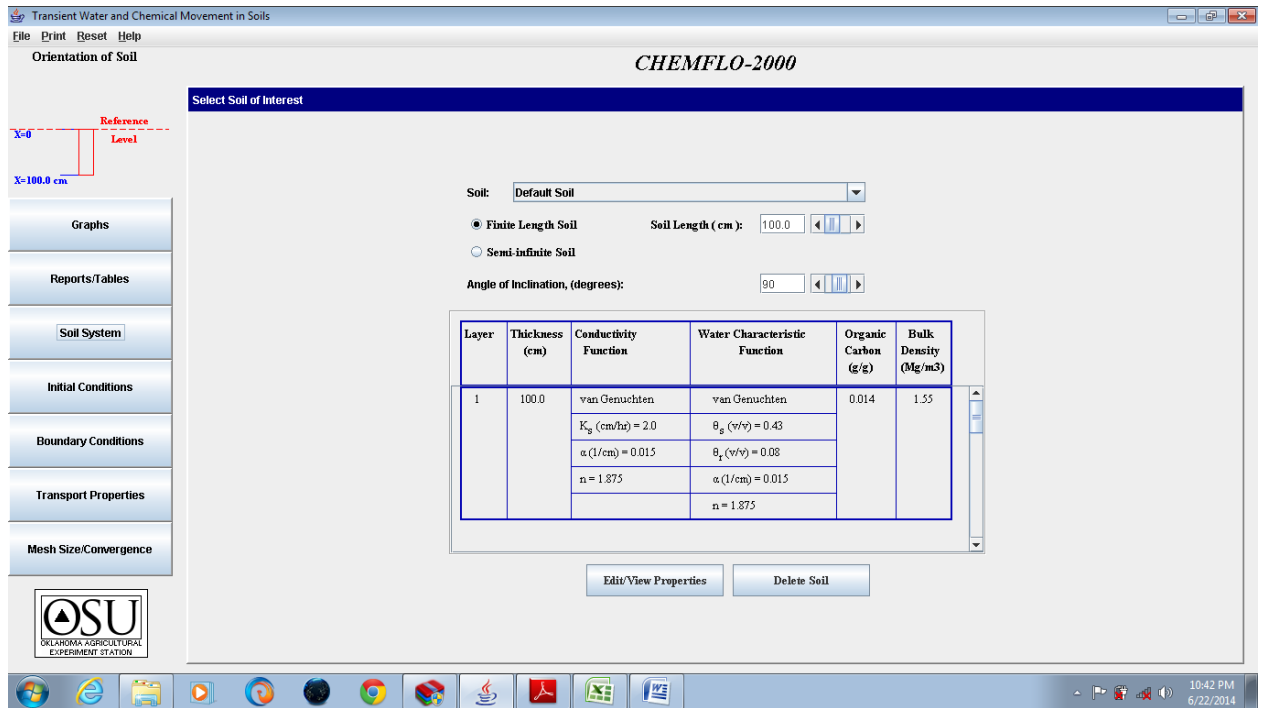


Plate 3.6: An interface of the model calibration with soil characteristics in the CHEMFLO-2000 model

3.8 Model sensitivity

In order to test the sensitivity of CHEMFLO-2000 model output to changes in input parameters such as particle size, K_s and organic carbon, we adopted an elasticity measure. The elasticity measure was used to detect the relative effect of small changes in the input variables on the output of Pb flux (Pannell, 1997; Leffelaar, 2008; Abdulkadir, 2012).

$$E_{s,p} \approx \frac{(S_{p=max} - S_{p=min}) / S_{p=product}}{(P_{max} - P_{min}) / P_{default}} \quad (3.8)$$

When in

P_{max} = maximum value of parameter P over the range of its change

P_{min} = minimum value of parameter P over the range of its change

P_{max} =default value of parameter P

$S_{p=max}$, $S_{p=min}$, $S_{p=default}$, are the resulting output values (state variable) S , calculated at maximum, minimum and default values of P , respectively.

Sensitivities of the different output variables were calculated for each input parameter using the central difference methods expressed by the Eq 3.8 above. These values are taken with respect to $\pm 2\%$ deviations (from the default values) to better approximate these sensitivities. The degree of sensitivity is described in Appendix VIII.

3.9 Water flux determination of soils columns using Darcy's equation in Daretta village

The Darcy's equation (1856) was used to determine water flux of soil columns in Daretta village. The equation is expressed as follows;

$$Q = v/t \quad (3.9)$$

$$q = Ks \frac{\Delta Hh}{L} \quad (3.10)$$

$$q = Q/A \quad (3.11)$$

If we consider the soils column used in Daretta village where 1 litre of water is added in 3 days. The column was 100 cm high and has an inner diameter (d) of 10 cm. In order to determine the flow per unit cross sectional area per unit time (q_s), we first determine the volumetric flow rate across the column Q ;

Where;

$$V = 1 \text{ litre} = 1000 \text{ cm}^3$$

$$t = 3 \text{ days} = 72 \text{ hours}$$

$$Q = 1000/72$$
$$= 13.87 \text{ cm}^3 \text{ hr}^{-1}$$

To determine cross sectional area (A);

$$A = \pi r^2 h$$

$$d = 10 \text{ cm radius } (r) \text{ will be } d/2 = 5 \text{ cm}$$

Where $\pi = 3.142$

$$h = 100 \text{ cm}$$

$$A = 3.142 \times 5^2 \times 100$$

$$= 7855 \text{ cm}^2$$

$$q_s = 13.87/7855$$

$$1.77 \times 10^{-3} \text{ cm hr}^{-1}$$

3.10 Estimation of Pb flux, distance of travel and break through time through calculations from convective flux equations

Because of the inability of the CHEMFLO-2000 simulation software to simulate flux at higher time of interest, the convective transport equation was used to estimate solute flux density of soil columns for 72 hours (3 days), 8,760 hours (1 year), 43,800 hours (5 years), 87,600 (10 years), 175200 hours (20 years) and 438000 hours (50 years) in

Dareta village that is to predict the flux of solute and make projections of the time it will reach some distant points in the village from the polluted sites.

$$I_m = q_s C \quad (3.12)$$

In which C is the mass per unit volume of solution (concentration of Pb contaminant) and other terms as previously defined.

In;

$$C = 12.43 \text{ mg l}^{-1}$$

$$q_s = ?$$

To determine flux we use;

$$q_s = Q/A$$

But $Q = v/t$

Where $v = 20 \text{ litre} = 20000 \text{ cm}^3$

$$t = 3 \text{ days} = 72 \text{ hours}$$

$$Q = 20000/72$$

$$= 277.78 \text{ cm}^3 \text{ hr}^{-1}$$

To determine cross sectional area (A)

$$A = l \times b$$

$$l = 30 \text{ cm (length of ponding surface)}$$

$$b = 10 \text{ cm (breadth of ponding surface)}$$

$$A = 30 \times 10$$

$$= 300 \text{ cm}^2$$

$$q_s = 277.78 / 300$$

$$9.26 \times 10^{-1} \text{ cm hr}^{-1}$$

Therefore;

$$J_m = 9.26 \times 10^{-1} \times 12.43$$

$$= 11.51 \text{ mg cm hr}^{-1}$$

The distance of travel per unit term of solute is given by;

$$V = q_s / \theta \tag{3.13}$$

In which is moisture content and other terms as previously defined.

Where;

$$q_s = 9.26 \times 10^{-1} \text{ cm hr}^{-1}$$

$$\theta = 0.22$$

$$V = 9.26 \times 10^{-1} / 0.22$$

$$= 4.21 \text{ cm hr}^{-1}$$

To estimate the distance of travel of Pb pollutant from the soil to the water table through the water table we use;

$$t_r = \frac{l\theta}{q_s} \tag{3.14}$$

In which l is the depth of water table in Dareta village which was determined to be = 1000 cm and other terms as previously defined.

$$t_r = \frac{1000 \times 0.22}{9.26 \times 10^{-1}}$$

$$= 237.6 \text{ hr}^{-1}$$

3.11 Statistical analyses

The data obtained on metal concentration and the measured soil properties were subjected to simple descriptive statistics. T-test was used to compare the metal concentration of the sampled farms, metal concentration obtained from free drainage lysimeters and soil columns, as well as efficiency of free drainage lysimeters soil columns. Correlation analysis was done to between K_s , particle size and organic carbon in order to determine the driving force behind K_s . All statistical analyses were conducted using Excel 2007 and SAS software (version 9.2; 2008).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Chemical properties of soils in Dareta village

Results of the soil chemical properties are presented in Table 4.1. Generally, pH of the surface soil (0-20 cm) of Dareta village is slightly acidic to slightly alkaline in water and moderately acidic to slightly acidic in CaCl₂, with mean values of 6.87 and 7.45 for Dareta North and South respectively and 7.40 and 7.34 for East and West respectively. Soil pH values in the profile at lower depths (20-40 cm, 40-60 cm, 60-80 cm and 80-100 cm) were found to be neutral to slightly alkaline in water and moderately acidic to neutral in CaCl₂ in Dareta North and South (Table 4.2 and 4.3). Mean pH of 7.76 (pH in water) and 5.95 (pH in CaCl₂) was observed for farm I and II in Dareta North and 7.46 (pH in water) and 6.04 (pH in CaCl₂) for Dareta South. Similar trend was observed in Dareta East and West where the pH in water was between neutral to slightly alkaline and strongly acidic to slightly acidic in CaCl₂ with means of 7.57 (pH in water) and 5.96 (pH in CaCl₂) for Dareta East 7.57 and 5.91 (pH in CaCl₂) for farm I and II in Dareta West. High Pb concentration in the study area is favoured by high pH values across the sampling directions as reported by Alloway (1995), who found that; in heavily polluted soils, high Pb concentration is greater in soils with higher pH.

Cation exchange capacity values for the surface (0-20 cm) soils in Dareta village range from 8.60-9.70 cmol₍₊₎kg⁻¹ and classified by the Soil Survey Staff (1993) as medium fertility as shown in Table 4.1. Mean values of CEC at lower soil depths (0-100 cm) of the northern and

Table 4.1: Chemical properties of surface soil (0-20cm) in the different cardinal directions in Dareta village

Surface soil 0-20 cm								
Sampling Direction	pH (water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
Dareta North I	6.80	5.60	9.00	3.00	0.26	0.42	4.19	3.33
Dareta North II	6.90	5.80	9.10	3.60	0.27	0.67	4.45	3.07
Means	6.87	5.7	9.05	3.30	0.27	0.55	4.32	3.20
Dareta South I	8.10	6.30	9.70	1.40	0.16	0.35	4.91	3.28
Dareta South II	6.80	5.70	9.60	5.00	0.17	0.38	4.20	3.34
Means	7.45	6.00	9.65	3.20	0.17	0.37	4.56	3.31
Dareta East I	7.00	5.90	9.00	11.00	1.00	0.45	4.44	2.65
Dareta East II	7.80	5.90	8.90	5.80	0.82	0.40	4.64	3.32
Means	7.40	5.90	8.95	8.40	0.91	0.43	4.54	2.99
Dareta West I	7.10	5.90	9.70	7.60	0.22	0.34	4.54	3.91
Dareta West II	8.50	6.30	8.60	0.60	0.13	0.38	4.62	2.01
Means	7.34	5.93	9.15	4.10	0.18	0.36	4.28	2.96

I = farm I, II = farm II

Southern part of the study area were $12.58 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $15.00 \text{ cmol}_{(+)}\text{kg}^{-1}$ respectively (Table 4.2). In the eastern and western part of Dareta village, CEC values ranged from $4.50\text{-}16.30 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $5.30\text{-}21.70 \text{ cmol}_{(+)}\text{kg}^{-1}$ respectively as shown in Table 4.3. Mean CEC of $11.52 \text{ cmol}_{(+)}\text{kg}^{-1}$ were obtained for Dareta East and $14.51 \text{ cmol}_{(+)}\text{kg}^{-1}$ for Dareta West. This classifies the soils as low to highly fertile by Soil Survey Staff (1993). The moderately high CEC values obtained might be attributed to high percentage of clay values (180 g kg^{-1} and 200 g kg^{-1}) obtained in the Dareta North and South. Owing to the low OC content of the studied soil in Dareta North and South, this finding did not corroborate that which states that CEC of savanna soils are influenced more by organic carbon than the clay content (Jones and Wild, 1975; Wuddivira, 1998). The results for the OC at the surface soil (0-20 cm) are presented in Table 4.1. The results ranged from $0.6\text{-}11.00 \text{ g kg}^{-1}$. Mean soil organic carbon contents obtained are 3.30 g kg^{-1} in Dareta North, 3.20 g kg^{-1} in Dareta South, 8.40 g kg^{-1} in Dareta East and 4.10 g kg^{-1} in Dareta West. At lower soil depths (0-100 cm), similar results were obtained which ranged from $0.2\text{-}7.8 \text{ g kg}^{-1}$ in the Dareta North, and $1.6\text{-}7.0 \text{ g kg}^{-1}$ in Dareta South (Table 4.3).

Mean values of 3.3 g kg^{-1} and 4.6 g kg^{-1} were obtained in Dareta West (Table 4.2) which classifies the soils as having low organic carbon across the sampling direction and which also substantiated that CEC obtained may be attributed to clay content rather than organic carbon. These values are consistent with the findings of Wuddivira (1998) for savanna soils and due to poor organic matter status of most savanna soils due to rapid decomposition of organic materials (Jones and Wild, 1975).

Exchangeable Na at the surface soils across all the sampling directions recorded mean values of $0.35 \text{ cmol}_{(+)}\text{kg}^{-1}$, $0.41 \text{ cmol}_{(+)}\text{kg}^{-1}$, $0.24 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $0.46 \text{ cmol}_{(+)}\text{kg}^{-1}$ for Dareta North, South,

Table 4.2: Mean of profile soil chemical properties in different sampling directions of Dareta village (0-100 cm)

Sampling Direction	pH (water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
Dareta North I	7.58	5.86	14.00	4.70	0.40	0.45	9.42	2.85
Dareta North II	7.94	6.04	11.16	3.46	0.30	0.37	6.68	3.63
Mean	7.76	5.95	12.58	4.08	0.35	0.41	8.05	2.24
Dareta South I	7.6	6.14	12.08	5.04	0.26	0.35	7.99	2.98
Dareta South II	7.32	5.94	17.92	2.16	0.56	0.40	9.59	4.13
Mean	7.46	6.04	15.00	3.60	0.41	0.38	10.29	3.05
Dareta East I	7.58	5.96	12.74	3.72	0.27	0.30	7.70	2.63
Dareta East II	7.56	5.96	14.30	2.94	0.20	0.30	10.75	2.89
Mean	7.57	5.96	13.52	3.33	0.24	0.30	9.23	2.76
Dareta West I	7.72	5.82	15.90	4.54	0.35	0.30	11.26	3.81
Dareta West II	7.42	6.00	13.12	4.72	0.57	0.46	7.96	4.84
Mean	7.57	5.91	14.51	4.60	0.46	0.38	10.61	4.32

Mean represents values from five samples taken for each soil property, I = farm I, II = farm

East and West sampling directions respectively (Table 4.1). These values indicate moderate to high Na levels at the surface soil as classified by Soil Survey Staff (1993). Higher Na contents were obtained at lower soil depths across the sampling direction than upper depths, with values as high as $0.87 \text{ cmol}_{(+)}\text{kg}^{-1}$ at 60-80 cm and $0.52 \text{ cmol}_{(+)}\text{kg}^{-1}$ at 80-100 cm of Daret North I. High levels of exchangeable Na in the study area were $0.65 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $0.98 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the surface soils of Daret North I and II, as well as $0.70 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $0.91 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the surface soils of Daret West I and II. Exchangeable Na content of the surface soil were generally lower or similar than the underlying subsoil (Table 4.2 and 4.3) with the exception of the Daret South where higher contents were obtained in the subsoil than on the surface soil and could be an indication that Na is usually held with a much lower energy on soil colloids than either K or the divalent Ca and Mg ions and is, therefore, easily lost through leaching (Tisdale and Nelson, 1975). The main problem with high sodium concentration in soil is on its effect on soil structural stability which makes it weak and easily dispersed and the surface are prone to surface capping (Malgwi, 2001). Although the structural stability index was not measured in this study, high exchangeable Na content in the subsoil might have reduced the rate at which water infiltrates into the soil during lysimeters studies. High lysimeter efficiency (50.65%) was obtained in Daret East where the lowest mean Na ($0.24 \text{ cmol}_{(+)}\text{kg}^{-1}$) was recorded. While low efficiency value was recorded with high mean Na concentration, 40.03% and $0.41 \text{ cmol}_{(+)}\text{kg}^{-1}$, respectively in Daret South with the exception of Daret West where high mean Na of $0.46 \text{ cmol}_{(+)}\text{kg}^{-1}$ recorded higher efficiency lysimeter value of 50.10%, this might be due to the higher mean organic carbon content than the other sampling directions.

Table 4.3: Chemical properties of soil profiles (0-100 cm) sampled in each of the different cardinal directions of Dareta village Dareta North I

Depth (cm)	pH (Water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
0-20	7.10	5.70	12.50	1.40	0.26	0.36	8.42	1.85
20-40	8.80	6.50	9.10	1.20	0.26	0.36	7.57	1.40
40-60	7.70	5.70	9.70	4.40	0.43	0.43	7.22	1.09
60-80	6.9	5.50	19.40	8.30	0.87	0.77	11.98	4.20
80-100	7.40	5.90	19.30	8.20	0.17	0.35	11.90	5.69
Dareta North II								
0-20	8.50	6.00	8.70	7.80	0.35	0.29	4.76	3.97
20-40	8.60	5.80	11.60	4.60	0.26	0.37	7.07	3.01
40-60	7.40	5.90	7.30	2.80	0.17	0.36	3.89	2.33
60-80	7.40	6.70	12.20	0.20	0.22	0.46	7.47	3.95
80-100	7.80	5.80	16.00	1.90	0.52	0.35	10.21	4.87
Means	7.76	5.95	12.58	4.08	0.35	0.41	8.05	2.24

Table 4.3: Continued

Dareta South I								
Depth (cm)	pH (Water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
0-20	8.20	6.30	16.10	7.00	0.65	0.42	8.75	4.94
20-40	7.00	6.00	10.20	5.80	0.17	0.23	7.77	1.98
40-60	7.30	5.80	9.40	5.20	0.09	0.30	7.51	1.55
60-80	7.90	6.30	13.70	4.00	0.25	0.45	8.38	3.79
80-100	7.60	6.30	11.00	3.20	0.13	0.34	7.51	2.65
Dareta South II								
0-20	6.80	5.60	23.90	2.60	0.98	0.35	12.78	7.44
20-40	8.00	5.50	17.50	2.40	0.43	0.47	9.01	3.21
40-60	7.40	6.30	14.70	2.20	0.78	0.43	7.65	2.14
60-80	6.40	6.20	19.90	2.00	0.39	0.40	11.47	4.97
80-100	8.00	6.10	13.60	1.60	0.21	0.36	7.05	2.88
Means	7.46	6.04	15.00	3.60	0.41	0.38	10.29	3.05

Table 4.3: Continued

Dareta East I

Depth (cm)	pH (Water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
0-20	7.60	5.90	8.20	6.40	0.26	0.30	6.92	1.45
20-40	7.20	5.80	11.40	5.80	0.22	0.44	10.9	4.37
40-60	7.30	5.60	9.50	4.60	0.25	0.32	7.82	2.43
60-80	7.30	6.20	4.50	1.00	0.24	0.28	3.84	2.02
80-100	8.50	6.30	10.10	0.80	0.39	0.18	9.01	2.90
Dareta East II								
0-20	7.80	6.00	18.20	4.10	0.17	0.36	15.76	2.29
20-40	7.50	6.00	9.00	3.20	0.23	0.28	6.98	1.45
40-60	7.10	6.40	12.50	3.00	0.10	0.26	7.23	3.81
60-80	7.50	5.50	16.30	2.20	0.23	0.23	11.50	3.94
80-100	7.90	5.90	15.50	2.20	0.26	0.37	12.29	2.96
Means	7.57	5.96	11.52	3.33	0.24	0.30	9.23	2.76

Table 4.3: Continued

Dareta West I								
Depth (cm)	pH (Water)	pH (CaCl₂)	CEC (cmol₍₊₎kg⁻¹)	OC (g kg⁻¹)	Na (cmol₍₊₎kg⁻¹)	K (cmol₍₊₎kg⁻¹)	Ca (cmol₍₊₎kg⁻¹)	Mg (cmol₍₊₎kg⁻¹)
0-20	7.50	5.60	17.00	6.60	0.70	0.20	10.45	5.23
20-40	7.50	5.60	19.30	5.40	0.30	0.29	13.86	4.07
40-60	8.30	6.10	21.70	5.10	0.20	0.31	16.98	4.12
60-80	7.80	5.80	11.70	3.00	0.13	0.33	8.77	1.74
80-100	7.50	6.00	9.80	2.60	0.44	0.35	6.25	3.89
Dareta West II								
0-20	7.40	5.80	12.20	7.20	0.91	0.34	9.25	2.56
20-40	7.40	6.10	19.20	5.40	0.17	0.38	11.22	8.87
40-60	7.40	6.10	11.50	5.40	0.69	0.32	8.24	3.82
60-80	6.80	5.90	17.40	3.20	0.65	0.77	10.00	5.97
80-100	8.10	6.10	5.30	2.40	0.43	0.51	1.09	2.98
Means	7.57	5.91	14.51	4.60	0.46	0.38	10.61	4.32

Exchangeable K is ranked next to Na on the exchange site. It ranged from 0.34-0.55 $\text{cmol}_{(+)}\text{kg}^{-1}$ in the 0-20 cm depth indicating high K content as shown in Table 4.2 (Soil Survey Staff, 1993). Potassium was also found to be high in the Daret North and Daret South across all soil depths as shown in Table 4.2. Mean values of 0.41 $\text{cmol}_{(+)}\text{kg}^{-1}$ and 0.38 $\text{cmol}_{(+)}\text{kg}^{-1}$ were recorded for the for Daret North and Daret South respectively. In Daret East and Daret West, the trend varied where values obtained indicated medium to high exchangeable K contents. Values ranged from 0.18-0.44 $\text{cmol}_{(+)}\text{kg}^{-1}$ in the Daret East to 0.20-0.77 $\text{cmol}_{(+)}\text{kg}^{-1}$ in the Daret West. No clear distribution with respect to K content was observed. This may be attributed to more intense weathering, release of labile K from organic residues, application of K fertilizers and upward translocation of K from lower depth along with the capillary use of ground water (Sai Kumar *et al.*, 2013). Potassium had little or no influence on Pb transport in the soil.

Exchangeable cations in the soils are presented in Table 4.1-4.3. Calcium is the dominant exchangeable base across the soils in all the sampling directions of Daret, with mean values of 4.32 $\text{cmol}_{(+)}\text{kg}^{-1}$, 4.56 $\text{cmol}_{(+)}\text{kg}^{-1}$, 4.54 $\text{cmol}_{(+)}\text{kg}^{-1}$ and 4.28 $\text{cmol}_{(+)}\text{kg}^{-1}$ for the surface soil (0-20 cm) in North, South, East and West sampling directions, respectively. These placed the Ca contents as high according to the Soil Survey Staff (1993). At lower soil depths (0-100 cm), mean values of 8.05 $\text{cmol}_{(+)}\text{kg}^{-1}$ in the Daret North and 10.29 $\text{cmol}_{(+)}\text{kg}^{-1}$ in the Daret South were obtained. Similar patterns of high Ca contents were also obtained in both eastern and western parts of the study area. The content of exchangeable Ca in the soils appeared to be directly related to leaching intensity, as affected by the amount of effective precipitation received (Shobayo, 2010), thus, Ca was lower at the surface than the underlying subsoil. The predominance of Ca over cations may be related to high Ca content of harmattan dust

material added annually and/or to parent materials high in Ca (Malgwi, 2001). This dominance of Ca over other exchangeable bases is in consonance with results of several other researchers (Mosugu, 1989; Zarafi, 1993; Abdullahi, 1997; Maniyunda, 1999; Yaro *et al.*, 2002). Soils containing high calcium content are known to alter porosity and structure and are therefore considered a factor that influences water flow towards ground water.

Exchangeable Mg ranked next to Ca on the exchange site. Magnesium values are generally in the high range as shown in Table 4.1-4.3 even though soils were rated to have low to medium concentration. At the surface soil, mean values of $3.20 \text{ cmol}_{(+)}\text{kg}^{-1}$, $3.31 \text{ cmol}_{(+)}\text{kg}^{-1}$, $2.99 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $2.96 \text{ cmol}_{(+)}\text{kg}^{-1}$ were obtained for Dareta North, South, East and West, respectively. Down the profile (100 cm) a mean value of $2.24 \text{ cmol}_{(+)}\text{kg}^{-1}$ was observed in Dareta North. While in Dareta South, a mean value of $3.05 \text{ cmol}_{(+)}\text{kg}^{-1}$ was obtained. Increase in Mg content with depth in soil may be attributed to the leaching of Mg from the surface to the subsoil as this does not influence infiltration during lysimeters studies.

4.2 Physical properties of soils in Dareta village

4.2.1 Particle size distribution

The particle size distributions of the experimental area are presented in Table 4.4. Soils at the 0-20 cm depth were predominantly sandy loam and loam, according to the USDA classification system. This coincides with reports by Jones and Wild (1975), Ogunwole and Ogunleye (2005) and that of Abdulkareem *et al.* (2012) that cultivated soils of the savannah region of West Africa are predominantly loamy sand, sandy loam to loam in nature depending upon the location.

Table 4.4: Particle size distribution of surface soil (0-20cm) in the different cardinal directions of Dareta village

Sampling Direction	Clay (g kg⁻¹)	Silt (g kg⁻¹)	Sand (g kg⁻¹)	Textural Class
Dareta North I	100.00	380.00	520.00	Sandy Loam
Dareta North II	120.00	360.00	520.00	Sandy Loam
Mean	110.00	370.00	520.00	Sandy Loam
Dareta South I	120.00	320.00	560.00	Sandy Loam
Dareta South II	80.00	260.00	660.00	Sandy Loam
Mean	100.00	290.00	610.00	Sandy Loam
Dareta East I	120.00	420.00	460.00	Loam
Dareta East II	200.00	360.00	440.00	Loam
Mean	110.00	390.00	450.00	Loam
Dareta West I	80.00	220.00	700.00	Sandy Loam
Dareta West II	80.00	260.00	660.00	Sandy Loam
Mean	80.00	240.00	680.00	Sandy Loam

I = farm 1, II = farm II.

Mean values of 110.00 g kg⁻¹ (clay), 370.00 g kg⁻¹ (silt) and 520.00 g kg⁻¹ (sand) were observed in Daret North, while the mean sand content in Daret South was found to be 610.00 g kg⁻¹ and that of silt and clay were 290.00 g kg⁻¹ and 100 g kg⁻¹, respectively. Sand fractions (680.00 g kg⁻¹) were higher in Daret West than values obtained in other sampling directions while the clay fractions were found to be lower in Daret West than with other sampling directions. Mean value of clay in Daret East was 110.00 g kg⁻¹, while that of silt was 390.00 g kg⁻¹ higher than in Daret West with a value of 240.00 g kg⁻¹ silt fraction.

Clay loam soils predominates in Daret South with the exception of soils in the 0-20 cm where the soils texture were found to be sandy loam, as shown in Appendix I. Mean values for this sampling direction across the profile were found to be 321.00 g kg⁻¹ for clay, 253.00 g kg⁻¹ for silt and 426.00 g kg⁻¹ for sand as shown in Table 4.5. Soils of both eastern and western parts of Daret were both predominantly clay loam at lower depths with the exception of 0-20 cm depth where the soils were found to be sandy loam (Table 4.5). Mean values of 326.00 g kg⁻¹ clay, 274.40 g kg⁻¹ silt and 389.00 g kg⁻¹ for sand were recorded in the Daret East. While in Daret West, the mean values of soil fractions were 306.00 g kg⁻¹ clay, 302.00 g kg⁻¹ silt and 392.00 g kg⁻¹ sand. Along the soil depths, clay content increases with depth though not consistent; thus affirming clay illuviation into lower soil layers in the study area (Ogunwole *et al.*, 2001). The coarse textured soils obtained in this study were observed to increase Pb transport through water flow though some soils across the sampling directions were observed to have moderate bulk density and low total porosity. This might have resulted from continuous cultivation that led to decrease in soil organic matter which might in turn, reduce Pb transport. Miriti *et al.* (2013) and Cogo *et al.* (1983) reported that high bulk density

Table 4.5: Mean particle size distribution of soil profile (0-100 cm) in the different cardinal directions of Dareta village

Sampling Direction	Clay (g kg⁻¹)	Silt (g kg⁻¹)	Sand (g kg⁻¹)	Textural Class
Dareta North	308.00	286.00	406.00	Clay Loam
Dareta South	321.00	253.00	426.00	Clay Loam
Dareta East	326.00	274.40	389.60	Clay Loam
Dareta West	306.00	302.00	392.00	Clay Loam

Mean values is for two farms across sampling direction.

induced soil compaction causing low porosity, reduced infiltration, increased penetration resistance and limited root growth.

4.2.2 Effect of saturated hydraulic conductivity (Ks) on Pb transport

Laboratory measured saturated hydraulic conductivities of the study area are presented in Table 4.6 and 4.7. The Ks of the surface (0-20 cm) soil recorded a mean of 3.96 cm sec⁻¹ and 1.02 cm sec⁻¹ for farm I and farm II respectively, in Daret North while a mean of 2.50 cm sec⁻¹ and 3.79 cm sec⁻¹ was obtained for Daret South I and II respectively. This categorize the soils in farms I and II of Daret North according to Ghildyal and Tripatti (1987) as having moderately rapid Ks.

Both farms in Daret village have soils that are moderately rapid according to Ghildyal and Tripatti, (1987) classification. Mean Ks values of 1.06 cm sec⁻¹ for farm I and 4.64 cm sec⁻¹ for farm II in Daret East makes the soils to be moderate and moderately rapid in conducting water

(Ghildyal and Tripatti, 1987). A mean of 1.68 cm sec⁻¹ was obtained in Daret West I while that of Daret West II is 1.39 cm sec⁻¹. The variable nature of tropical soils (Lal, 1979) coupled with the fact that laboratory Ks measurements are on undisturbed soil core samples may be possible reasons for the wide variations of Ks (Abdulkadir, 2006). Ks is related to saturated flow where there is complete filling up of the pore spaces with water (along with dissolved chemicals) moving through the soil profile (Abdulkadir, 2006). Water movements during drainage and in ground water system are obvious cases of saturated flow (Wuddivira, 1998) where only solid and liquid states of matter exist and this will in turn influence metal transport, such as Pb towards ground water. The first experimental study on the movement of water in the soil was done by Henry Darcy in 1856, using soil columns of saturated sand (Darcy, 1856). In 1907, Buckingham described the water flow in unsaturated porous media modifying the equation obtained

Table 4.6: Average physical properties of surface soils (0-20 cm) from two farms in the different sampling directions of Dareta Village

Sampling Direction	Ks (cm sec⁻¹)	Bulk Density (g cm⁻³)	Total Porosity (%)	EP (%)
DN I	3.96	1.61	39.25	16.38
DN II	1.02	1.40	47.30	18.06
DS I	2.50	1.54	41.89	23.45
DS II	3.79	1.73	34.59	14.22
DE I	1.06	1.49	43.77	11.77
DE II	4.64	1.56	41.01	19.28
DW I	1.68	1.65	37.73	17.80
DW II	1.39	1.60	39.75	15.05

Mean represents values from three samples taken for each soil property, DN = Dareta North, DS = Dareta South, DE = Dareta East, DW = Dareta West, I = farm 1, II = farm II, Ks = saturated hydraulic conductivity; EP = effective porosity.

Table 4.7: Average physical properties of soil profiles (0-100 cm) sampled in each of the different cardinal directions of Dareta village

Soil depth (cm)	Ks (cm sec⁻¹)	Bulk Density (g cm⁻³)	Total Porosity (%)	EP (%)
Dareta North I				
0-20	1.98	1.29	51.33	22.53
20-40	2.60	1.40	47.17	34.83
40-60	4.41	1.51	43.21	22.61
60-80	4.35	1.62	39.06	25.06
80-100	4.64	1.64	38.12	14.37
Dareta North II				
0-20	0.67	1.21	54.53	36.08
20-40	0.73	1.54	41.89	21.74
40-60	0.98	1.28	51.89	34.64
60-80	1.37	1.27	52.08	20.88
80-100	1.61	1.64	38.12	14.37
Dareta South I				
0-20	3.88	1.20	54.91	27.76
20-40	2.19	1.24	53.40	27.80
40-60	2.07	1.33	49.81	24.96
60-80	0.39	1.34	49.44	33.12
80-100	0.19	1.51	43.11	30.60
Dareta South II				
0-20	2.01	1.28	51.70	26.01
20-40	1.58	1.26	52.65	36.00
40-60	1.31	1.40	47.17	13.60
60-80	1.18	1.44	45.85	26.67
80-100	0.82	1.63	38.49	22.89

Mean represents values from two samples taken for each soil property, Ks = saturated hydraulic conductivity, EP effective porosity, I = farm I, II = farm II.

Table 4.7: Continued

Depth	Ks (cm sec⁻¹)	Bulk Density (g cm⁻³)	Total Porosity (%)	EP (%)
Dareta East I				
0-20	3.71	1.21	54.53	25.04
20-40	2.72	1.24	53.21	25.92
40-60	2.28	1.42	46.68	27.00
60-80	1.28	1.52	42.84	39.48
80-100	0.98	1.60	39.81	11.61
Dareta East II				
0-20	2.59	1.57	48.12	13.82
20-40	1.95	1.59	40.95	24.05
40-60	1.57	1.95	46.04	27.24
60-80	1.57	1.57	40.34	23.78
80-100	1.49	1.49	38.87	14.57
Dareta West I				
0-20	2.08	1.33	50.00	28.49
20-40	1.52	1.36	48.68	19.38
40-60	1.37	1.37	48.30	27.70
60-80	0.38	1.43	46.04	28.80
80-100	0.42	1.58	40.57	17.62
Dareta West II				
0-20	4.35	1.18	55.48	28.84
20-40	2.42	1.22	53.96	29.67
40-60	1.68	1.28	51.89	37.83
60-80	1.34	1.36	48.67	28.68
80-100	1.01	1.44	50.00	21.00

Mean represents values from two samples taken for each soil property, Ks = saturated hydraulic conductivity, EP = effective porosity, I = farm I, II = farm II.

by Darcy (Nimmo and Landa, 2005). In 1931, Richards combined the equations of Darcy and Buckingham with the equation of continuity to establish an overall relationship, which is yet used (Richards, 1931). Klute (1972) describes several methods for estimating the K_s and diffusivity for unsaturated soils insitu and in laboratory (Klute, 1972), including the instantaneous profile method (Sisson *et al.*, 1980). Down the profile in Daret North I, the highest mean was observed at 80-100 cm depth (4.64 cm sec^{-1}), followed by 40-60 cm (4.41 cm sec^{-1}) and 60-80 cm (4.35 cm sec^{-1}) having moderately slow to moderate conductivity as shown in Table 4.6. Mean value of K_s in Daret North II range from 0.67 sec^{-1} in the 0-20 cm depth to 1.61 cm sec^{-1} in the 80-100 cm depth. Saturated hydraulic conductivity values in Daret South I as shown in Table 4.6 were found to be having some variations with the 0-20 cm depth having the highest mean of 3.88 cm sec^{-1} and the 80-100 cm depth having lowest the lowest mean of 0.39 cm sec^{-1} (Table 4.6). In Daret South I there was little variation as mean values ranged from 0.19 - 3.88 cm sec^{-1} , while it ranges from 0.82 - 2.01 cm sec^{-1} in Daret South II. This classifies the soils in this cardinal point from slow to moderately rapid. K_s values in the eastern part of Daret village are classified as moderately slow to moderate. Previous studies show that high bulk density and low total porosity have a negative influence on K_s and infiltration rates (Miriti *et al.*, 2013; Bhattacharyya *et al.*, 2006, Gicheru *et al.*, 2004). The availability of more water conducting pore sizes (sand fraction) in this experimental area (Table 4.5, 4.6 and Appendix II) may be viewed to be responsible for the K_s value observed (Brady and Weil, 1999). Saturated hydraulic conductivity values in the western part followed the same trend with other cardinal points where K_s decrease with increase in soil depth. This might be due to increase in bulk density with depth as observed by Ohu *et al.*, 1989 and due to densification of soil as observed by Igbal *et al.* (2005). Another possible reason might be also increased in

clay content with depth. Clay particle may clog water conducting pores and decrease the saturated hydraulic conductivity (Okai, 1995). Dareta East I and II gave the same trend of K_s values, as the highest means were observed at 0-20 cm depth (3.71 cm sec^{-1} for Dareta East I and 2.59 cm sec^{-1} for Dareta East II) and the lowest means at 80-100 cm depth (0.98 cm sec^{-1} for Dareta East I and 1.49 cm sec^{-1} for Dareta East II). Mean values ranges from $0.42\text{-}2.08 \text{ cm sec}^{-1}$ in Dareta West I at all depths. Similar trend was also observed in Dareta West II where 0-20 cm depth has the highest mean (4.35 cm sec^{-1}) and the lowest mean was observed at 80-100 cm depth (1.01 cm sec^{-1}).

Pearson correlation coefficients for soils in the 0-20 cm depth indicated that K_s positively correlated with sand and organic carbon as shown Appendix VI. This indicates that sand and organic carbon are the drivers for K_s . Long term cultivation of same piece of land with continue addition of organic manure may lead to surface crusting and degradation of soil structural stability which in turn reduce soil macropores (Ogunwole and Ogunleye, 2005). As this might be the possible reason for the observed positive correlation between K_s and organic carbon. In the 0-100 cm different drivers for K_s were obtained as K_s was found to be clay and silt (Appendix VII). The positive correlation between K_s and clay content might be as a result of increase in clay content with depth, where clay particles will clog conducting pores and decrease K_s (Okai, 1995).

4.2.3 Effect of bulk density (ρ_b) on Pb transport

The mean bulk density (ρ_b) of the soil surface (0-20 cm) for Dareta North I was 1.61 g cm^{-3} while in Dareta North II, it was found to be lower with a mean of 1.40 g cm^{-3} (Table 4.6). Both Dareta North I and II are classified as having low ρ_b according to the Soil Survey Staff (1993). Similar finding was observed in the surface soils of other

cardinal directions in Dareta Village with mean values that range from 1.49-1.73 g cm⁻³. This classifies the bulk density of the study area as moderate (Soil Survey Staff, 1993). High mean values were observed in Dareta South II (1.73 g cm⁻³), Dareta West I and II (1.65 and 1.60 g cm⁻³). Low ρ_b values may be associated with incorporation of crop residues and application of farm yard manure in the study area by the villagers (Bhattacharyya *et al.*, 2006) while the high ρ_b may be attributed to large proportion of sand fraction and trampling caused by livestock activities. Sand can easily be deformed; the particles roll into a compact state and lay in close contact because of lack/ low content of bridging materials like organic matter across the sampling direction, and result in high bulk density of soils (Ogban *et al.*, 1999).

Bulk density increased with depth in the northern part of the study area as shown in (Table 4.7). With mean values ranging from and 1.21-1.64 g cm⁻³ for Dareta North I and Dareta North II. The low level of (ρ_b) of the topsoil is a reflection of the enhanced soil cohesiveness (Heard *et al.*, 1988). Similar trend was observed in the other sampling directions of Dareta village where ρ_b was observed to increase with depth. Higher mean values were observed at the 80-100 cm in all farms across sampling directions than all other depths. A probable reason for this might be associated to the presence of more clay either due to illuviation or compacted layer formed as a result of the used of trampling by animals in the sub soils (Ogunwole and Ogunleye, 2004). Lower ρ_b with high Ks values will imply more water flow as oppose to high bulk with lower Ks. Higher ρ_b will lead to surface crusting and compaction that will decrease porosity and inhibit water entry into the soil, possibly increasing surface runoff and erosion (Al-Ghazal, 2002). Crusting is a soil surface characteristic that provides information on soil strength or penetration resistance. Higher crust strength caused by high bulk density values has been reported to reduce soil water storage due to the reduction of crust

conductance and infiltration rates (Miriti *et al.*, 2013; Gicheru *et al.*, 2004; Shivonje *et al.*, 2005). Several scientists had documented high bulk density is a strong indicator of low soil porosity and high compaction (Arshad *et al.*, 1996; Liebbig and Doran, 1999).

4.2.4 Effect of total porosity (f) on Pb transport

The total porosities (f) in soils of Dareta village are presented in Table 4.6 and were obtained from assumed particle density (ρ_d) of 2.65 g cm^{-3} . The mean total pore spaces ranges from 37.73-47.30% in the upper 0-20 cm depth. While irregular pattern of f was observed across sampling directions, most values were observed to reduce with depth. Mean values (Table 4.7) across the sampling directions ranges from 38.11-54.13% in Dareta North, 38.49-54.91% in Dareta South, 38.87-54.53% in Dareta East. While in Dareta West, mean values range from 40.57-55.48% for the two sampling directions. The low f values recorded might have influence Pb transport through reduction of water flow in soils of the study area.

4.2.5 Effect of effective porosity (P_e) on Pb transport

Soil effective porosity (P_e) values for Dareta village are presented in Table 4.6. There was no regular pattern for changes in P_e though K_s were observed to decrease with depth while ρ_b increased with depth. At the surface soil P_e values differ across sampling directions. With the highest mean values obtained from Dareta South I (23.45%) followed by Dareta East II with mean value of 19.28%. Lowest mean values recorded are 14.22% and 15.05% for Dareta South II and Dareta West II respectively. This indicates that, the soils of the study area are dominated by macropores because of the rapid decline in soil moisture as the water held tends away from field capacity (Mbagwu, 1995). Effective porosity (P_e) is the soil porosity that contributes most to the

flow of water when the soil is saturated (Ahuja *et al.*, 1984), and thus, soils with low P_e are more likely to reduce water flow than soils with high effective porosity. The P_e values obtained compared favourably with those of Anosike (1999) and Kowal and Knabe (1972) who obtained similar values for similar savannah soils.

4.3 Total soil Pb concentration in Daretta village

The total Pb concentration of surface soil samples is presented in Table 4.8. The international threshold value for Pb in soils is 300 mg kg⁻¹ for both EU and USA, while its 150 mg kg⁻¹ for Canada and 70 mg kg⁻¹ for UK. A significant difference ($p < 0.05$) was observed between Daretta North and Daretta South from statistical T test, with mean values of 1812.17 mg kg⁻¹ and 1456.83 mg kg⁻¹, respectively. The reason for these differences might be due to intensive activities such as grinding, washing and other processing activities of gold ore that were predominantly carried out in the northern and southern part of Daretta. A highly significant difference ($p < 0.01$) was also observed when Daretta North (1812.17 mg kg⁻¹) was compared with Daretta East (791.58 mg kg⁻¹) and Daretta West (867.75 mg kg⁻¹). Lead contamination in the study area was attributed to Pb deposited from the processing of the contaminated gold ore (BI, 2011) as shown in Figure 4.1 and 4.2. Both Daretta East and Daretta West experience has similar concentrations of Pb in their soils probably due to less processing activities of the Pb ore, although these observations indicate extreme levels of concentration for Pb in arable soils considering the international threshold (Table 4.9) of 300 mg kg⁻¹ by EU and USA standards (Abdu, 2010). Thus, indicating Pb contamination and a possible health risk. Reasons for the observed high concentrations in these cardinal directions might be due to the activities of moving winds (aeolians) that carries smaller particles along with it, and that the Pb in the study area, were part of the parent materials which are often considered as the initial sources of heavy metals. However, total

Table 4.8: Average total soil lead (Pb) concentration in surface soils in the different cardinal directions of Dareta village

Sampling Direction		Pb (mg kg⁻¹)	Standard Deviation	SEM	Significance
North	n = 12	1812.17	106.48	±30.73	*
South	n = 12	1456.83	124.70	±35.60	
North	n = 12	1812.17	106.48	±30.74	**
East	n = 12	791.58	188.97	±54.55	
North	n = 12	1812.17	106.48	±30.74	**
West	n = 12	867.75	141.08	±40.73	
South	n = 12	1456.83	124.70	±35.60	**
East	n = 12	791.58	188.97	±54.55	
South	n = 12	1456.83	124.70	±35.60	**
West	n = 12	867.75	141.08	±40.73	
East	n = 12	791.58	188.97	±54.55	NS
West	n = 12	867.75	141.08	±40.73	

SEM standard error mean; * Significant at 5% level of probability; ** Significant at 1% level of probability; NS = not significant using Student T-test

Table 4.9: International threshold values for heavy metals concentration (mg kg⁻¹) in soils

Heavy metal	Regulatory System			
	EU	USA	Canada	UK
Cd	3.0	3.0	19.5	1.4
Zn	300	200-300	1400	200
Cr	180	400	1500	6.4
Cu	140	80-200	170	63
Pb	300	300	150	70
Ni	75	50-110	210	50

Source: Abdu, 2010.

concentrations of Pb and its forms are modified by pedogenic processes (Herawati *et al.*, 2000). When Dareta South and Dareta West were compared, a highly significant difference ($p < 0.01$) was observed.

4.4 Vertical distribution of Pb in Dareta village

The vertical distribution of Pb in Dareta village is presented in Figures 4.1 and 4.2 for farm I and farm II, respectively, across the sampling directions. In farm II of Dareta North, the Pb concentration ranges from 1627-2025 mg kg⁻¹ with the highest concentration (2025 mg kg⁻¹) observed at the surface soil in located near the gold ore processing site. Farms in Dareta South recorded lower values than Dareta North with values ranging from 1310-1586 mg kg⁻¹. Lower concentrations at lower depths were observed in surface soils of Dareta East and Dareta West. Lead concentrations as low as of 604 mg kg⁻¹ and 625 mg kg⁻¹ were observed in farms I and II of Dareta East respectively, and 740 mg kg⁻¹ and 876 mg kg⁻¹ for farms I and II in Dareta West respectively. High concentrations of Pb down the soil profile suggest geological sources of Pb across the sampling directions. The trend for high concentration of Pb in the upper depths than the lower depths may be as a result of superficial enrichment through human activities such as mining. It could also reflect metals affinity for organic matter (Agbenin, 2002). Lead fixation by organic matter has been shown to be more important than fixation by hydrous oxides (Li and Shuman, 1996), and the surface horizons of most soils contain higher organic matter relative to the successive lower horizons. High concentrations of Pb observed at lower depth suggested that Pb was translocated via facilitated transport with the colloidal clay particles during illuviation, hence deposition of clay was accompanied by that of Pb as clay increased with increase in depth. Similar observations were made by Mohammed and Abdu (2013) on Pb distribution in the same soils of Dareta It could also be as a result of capillary rise of Pb polluted ground water.

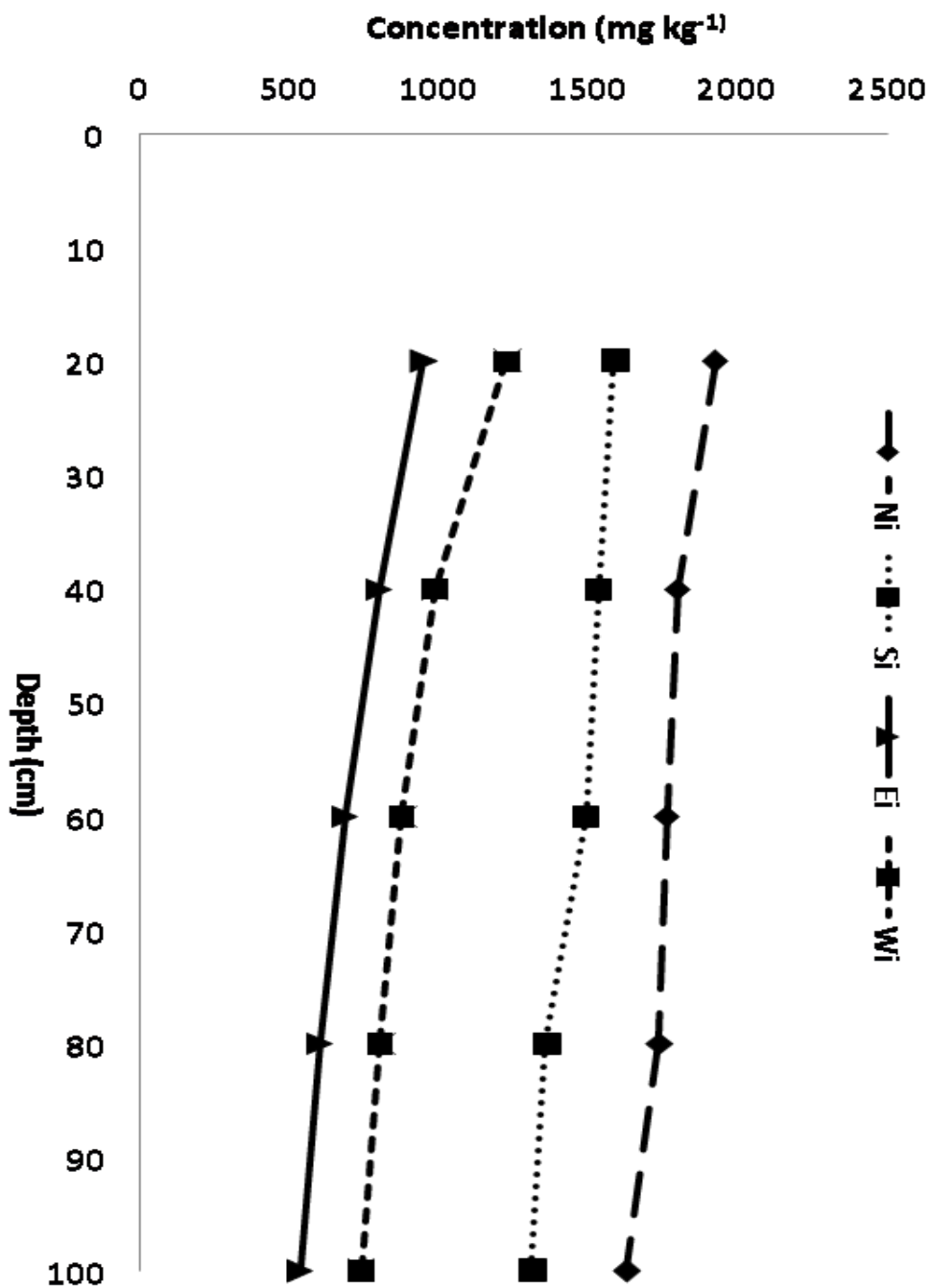


Figure 4.1: Vertical distribution of Pb in soils of farm I in the different cardinal directions of Dareta village. (Ni=Dareta North farm I; Si =Dareta South farm I; Ei =Dareta East i; Wi=Dareta West I)

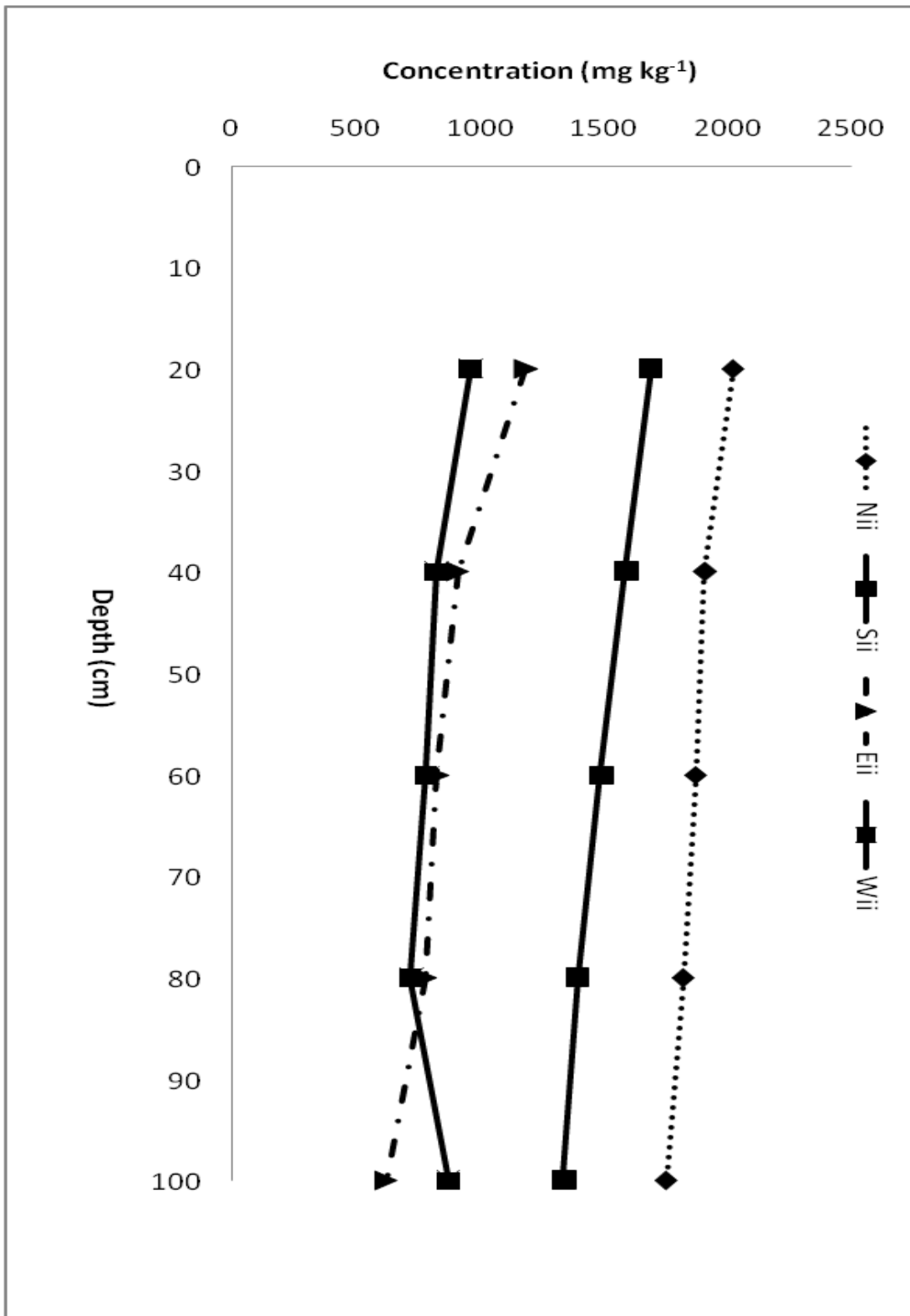


Figure 4.2: Vertical distribution of Pb in soils of farm II in the different cardinal directions of Dareta village (Nii=Dareta North farm II; Sii=Dareta South farm II; Eii=Dareta East II; Wii=Dareta West II)

The source of pollution of the ground water is most likely from the washing of metal ores in streams and household wells as observed in this study. Where the water saturating this horizon is polluted, it could result in accumulation of metals at this zone relative to other zones; hence contamination from a receding ground water table may occur with time.

4.5 Pb concentration in well water used for irrigation during lysimeter studies

The Pb concentration of the wells used for irrigation during lysimeter studies is shown in fig 4.3. A total of four wells were used randomly used for irrigating the sites where the lysimeters were installed. Mean values of the Pb concentration for three samples each per well does not pose immediate risk of Pb contamination as their concentrations are not above the threshold limit set by the United States Environmental Protection Agency (USEPA, 2004). Mean values obtained are in the range of 5-10 mg l⁻¹.

4.6 Total Pb concentration of leachates collected from free drainage lysimeters

The results of the total Pb concentration in leachates collected from free drainage lysimeters are presented in Table 4.10. Leachates collected from the village showed no immediate risk of Pb contamination. The concentrations are not above the threshold limit set by USEPA (2004) as they are in the range of 5-10 mg l⁻¹. The results of typical Pb uptake from water in the affected village was estimated at 10-75 µg day⁻¹, which alone will result in blood vessels exceeding 10 µg day⁻¹ (Abdu and Yusuf, 2012; BI, 2011). Of the sixteen lysimeters installed, five initially functioned properly while the other fifteen worked after being recharged (Omoti *et al.*, 1983). Their mal-function is said to be as a result of the activities of rodents in the soil where the lysimeters were installed. The lysimeters were inserted into the enclosures of the soil profile. Firm contact between the profile surface and the contact surface of the collection plate was

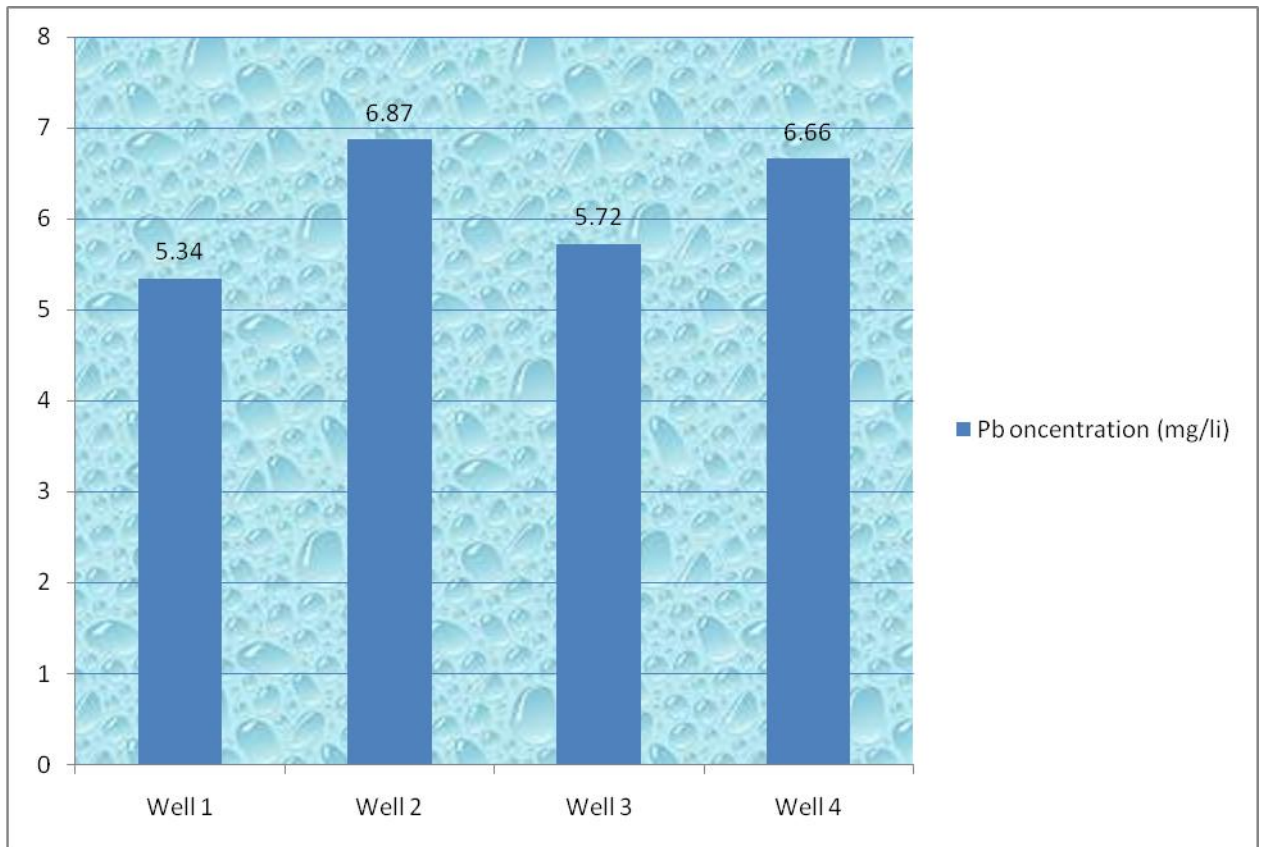


Figure 4.3: Lead (Pb) concentration in the Wells of Dareta village. Values represent averages of three samples per well.

Table 4.10: Mean of total lead (Pb) concentration in leachates collected from free drainage lysimeters in Daretta village

Sampling Direction	Pb (mg l⁻¹)	SEM	Significance
North	8.35	±0.75	NS
South	8.02	±0.70	
North	8.35	±0.75	NS
East	7.17	±0.65	
North	8.35	±0.75	NS
West	7.47	±0.65	
South	8.02	±0.70	NS
East	7.17	±0.65	
South	8.02	±0.70	NS
West	7.47	±0.65	
East	7.17	±0.65	NS
West	7.47	±0.65	

SEM = standard error mean NS = not significant

maintained with the acid-washed sand (Belford, 1979; Cameron *et al.*, 1990; Moyer *et al.*, 1996).

A window hole about the size of the lysimeter (20 cm) was dug at one side of each profile where the lysimeter was installed at a depth of 25 cm so that the top of the lysimeter will be below the soil surface. The flexible tube was left protruding from the ground. Leachates were collected from the lysimeter from the lower bucket by gravity movement (Migliaccio *et al.*, 2009). No significant difference was observed when compared using Students' T-test between concentrations of leachates in all the lysimeters, although the concentration of Pb in the well water used for irrigation was similar in all the sampling directions (Fig 4.3). Lead concentrations in leachates collected from all the sampling directions were found to be lower than threshold values. Previous studies have shown that water flow and solute transport processes are influenced by soil type (Vanderborght *et al.*, 1997, 2001), flow rate (Vanderborght *et al.*, 1997; Forrer *et al.*, 1999; Wildenschild *et al.*, 2001), flow regime (Bowman and Rice, 1986; Jaynes *et al.*, 1988), irrigation method (Ghodrati and Jury, 1990; Troiano *et al.*, 1993; Flury *et al.*, 1994), surface flow depth (Abbasi *et al.*, 2003), preferential flow (Flury *et al.*, 1994), soil heterogeneity (Roth *et al.*, 1991; Jacques, 2000), initial conditions (White *et al.*, 1986; Steenhuis and Muck, 1988), and/or boundary conditions (Russo *et al.*, 1994a, 1994b).

4.7 Leachates collection efficiency of free drainage lysimeters and soil columns in Dareta village

The results of the efficiency of free drainage lysimeters in leachates collection is shown in Table 4.11. The amount of leachates collected is expressed as percentage of the total irrigation water applied. Even with evaporation losses and soil moisture storage, about 8-10 litres of leachates were collected. Twenty litres of water were ponded to a sunken

Table 4.11: Efficiency of leachates collection of the free drainage lysimeters installed in soil profiles in different cardinal directions of Daretta village

Sampling point	Volume of water added (l) at 3 days interval for 40 days	Average volume of leachates collected (l) at 3 days interval for 40 days	Efficiency (%)
North			
Lysimeters 1	20.00	10.33	45.85
2	20.00	9.98	45.05
3	20.00	9.49	44.70
4	20.00	10.28	44.90
Mean	20.00	10.02	45.13
South			
Lysimeters 1	20.00	8.58	42.90
2	20.00	8.33	41.65
3	20.00	7.59	37.95
4	20.00	7.52	37.60
Mean	20.00	8.01	40.03
East			
Lysimeter 1	20.00	9.85	49.25
2	20.00	10.07	50.35
3	20.00	10.38	51.90
4	20.00	10.22	51.10
Mean	20.00	10.13	50.65
West			
Lysimeter 1	20.00	9.17	51.65
2	20.00	9.01	49.90
3	20.00	8.94	47.45
4	20.00	8.98	51.40
Mean	20.00	9.03	50.10

Lysimeters installed at 30 cm depth in a 100 cm profile via a window hole of 20 cm.

bed of about 10 cm dug to improve the leachates collection efficiency, as this experiment was performed during the dry season when the soils are extremely dry. The surface was shallowly dug to increase the ponding area to ensure that soils around the area beneath which the lysimeters was placed, gets saturated enough to allow water to infiltrate into the soil and get to the lysimeter. The four lysimeters installed in Daret North recorded a mean discharge capacity of 45.13% while the Daret South lysimeters recorded a mean of 40.03%. Discharge values within the range 9.17-10.38 litres were observed for the Daret East and Daret West. Mean values for the latter two sampling directions were found to be similar both around 50%. Higher percentage efficiency values were observed in Daret East and Daret West, more than in the north and south, which may be attributed to higher K_s , P_e and sand fractions observed in the former sampling directions than in the latter points. Even though all the soils were initially ponded to saturation before the onset of the trials, factors such as preferential flow (due to presence of roots), evaporation and percolation losses and the activities of soil fauna (rodents in particular) might have played a role in influencing the results. Also the pore size is also a determining factor that might influence leachates collected. The sandy loam and loam dominated soils in the study area are characterised by many macropores giving rise to low effective porosity because of the loose arrangement of larger particles with one another. The findings in this experiment are in agreement with that Jemison and Fox (1992) and Zhu et al. (2002) who obtained an efficiency ratio of 10-58% as defined by the ratio of observed to expected percolation. A wide range of leachates collection efficiencies (Table 4.12) has been reported in the literature. For example, the leachates collection efficiency of the wick-pan lysimeters ranged from 98-108% (Boll *et al.*, 1991), 66 -80% (Brandi-Dohrn *et al.*, 1996), 125% with a coefficient of variation of 36% (Louie *et al.*, 2000), 47-206% (Zhu *et al.*, 2002), and 0 to negligible (Steenhuis *et*

Table 4.12: Different lysimeters types and their leachates collection efficiencies

Method	Collection Efficiencies (%)	Source
Wick-pan lysimeters	98-108	Boll <i>et al.</i> , 1991
Wick-pan lysimeters	68-80	Brandi-Dohrn <i>et al.</i> , 1996
Wick-pan lysimeters	125	Louie <i>et al.</i> , 2000
Wick-pan lysimeters	47-206	Zhu <i>et al.</i> , 2002
Wick-pan lysimeters	0-negligible	Steenhuis <i>et al.</i> , 1998
Zero-tension pans	10-58	Jemison and Fox, 1992; Zhu <i>et al.</i> , 2002

Source: Barzegar *et al.* (2004)

al., 1998). Leachates collection efficiency of the zero- tension pans ranged from 10-58% (Jemison and Fox, 1992; Zhu *et al.*, 2002) as this is similar to what is obtained in this study (40-50%).

Water in soil columns was applied at a flux of 1.77×10^{-1} cm hr⁻¹ and the efficiency of soil columns is given in Table 4.13. The amount of leachates collected is expressed as percentage of the total irrigation water applied. The mean efficiency for soil columns was found to be 31% for Daret North, 26% for Daret South, 36% for Daret and 37% for Daret West. Higher percentage efficiency values were observed in Daret East and Daret West more than the north and south as earlier mentioned in this section.

4.8 Field drainage lysimeters and laboratory soil columns leached with water

The concentration of leachates collected with field drainage lysimeters were compared with the laboratory soil columns, the result shows that the quantity collected from the former method were significantly higher than those from the laboratory soil columns (Table 4.14). Even though eight columns used were packed with soil and wetted with distilled water to saturation level and there after one litre of tap water was applied. This is justified by Stagnitti *et al.* (1998) who states shown to that; laboratory experiments are based on repacked, sterile cores that bears little resemblance with the physical reality and have often been shown to underestimate the solute loss and risk of contamination to groundwater reserves (Stagnitti *et al.*, 1998). While the use of soil columns in the laboratory represents a highly restricted set of conditions (Ermakov *et al.*, 2007), free drainage lysimeters mostly collect gravitational water, and consequently collect more water. This is particularly true in coarse textured soils (such as those obtained from the study area) where the dominant water flow is matrix-related water flow (Jemison and Fox, 1992; Steenhuis *et al.*, 1995). Another possible observation is

Table 4.13: Efficiency of leachates collection from soil columns packed with soils collected from different cardinal directions in Dareta village

Sampling Point	Volume of water added (l) at 3 days interval for 40 days	Average volume of leachates collected (l) at 3 days interval for 40 days	Efficiency (%)
North Columns			
1	1.00	0.33	33.00
2	1.00	0.28	28.00
Mean	1.00	0.31	31.00
South Column			
1	1.00	0.28	28.00
2	1.00	0.23	23.00
Mean	1.00	0.26	26.00
East Column			
1	1.00	0.35	35.00
2	1.00	0.37	37.00
Mean	1.00	0.36	36.00
West Column			
1	1.00	0.37	37.00
2	1.00	0.36	36.00
Mean	1.00	0.37	37.00

1 m soil columns

Table 4.14: Comparison of Pb concentration collected from field drainage lysimeters and laboratory soil columns leached with water in Dareta village

Method	Means (mg l⁻¹)		SD	SEM	Significance
Field	7.75	n = 208	4.95	0.34	**
Laboratory	2.13	n = 208	1.73	0.12	

SD = standard deviation; SEM = standard error mean ** = Significant level at 1% probability level using Student T-test n = number of leachates collected from both field and laboratory.

the preferential flow in the field drainage lysimeters than in the laboratory soil columns which has been shown to greatly increase the mobility and velocity of solute movement to the groundwater (Steenhuis *et al.*, 1995). In this study sites which were dominated by sandy soils, preferential flow may have caused instability at the wetting front or by sloping soil textural interfaces. The reasons mentioned above are responsible for highly significant difference in quantities of leachates even though same soil were used for both experiments. The volume and efficiency of free drainage lysimeter and soil columns is shown in Table 4.15. A highly significant difference was observed when the volumes of water applied to free drainage lysimeter and that of soil columns. This is as results of the water applied during lysimeter studies are in the ratio of 1:10 to that used during column experiment. A highly significant level of probability was obtained at 1% when the efficiencies of two experiments (Lysimeter and column) were compared. Mean efficiency value of 46.48% and SEM value of ± 1.18 for lysimeter studies while that of column experiment recorded an efficiency of 14.18% and SEM of ± 5.31 . This may due to the reasons given by Stagnitti *et al.* (1998) as earlier mentioned in this section. Lysimeters that involves multiple sample percolation systems has proven to be excellent means of obtaining accurate values of the solute and water flux in vadose zone experiments and have been shown to effectively indicate the impacts of soil heterogeneity on these fluxes (Stagnitti *et al.*, 1999).

4.9 Simulation using CHEMFLO-2000

When the chemical movement was calculated based on CHEMFLO calibration with data collected from this study, the graph for flux density vs time was obtained (Figure 4.4a). Flux density was uniform ($9.1 \times 10^{-5} \text{ cm hr}^{-1}$) at the initial stage of the simulation (0) and increased rapidly when the time of interest was approached (72 hours) to $12.1 \times 10^{-5} \text{ cm hr}^{-1}$ as shown in green colour in the Figure 4.4b. The flux density of 12.1×10^{-5}

Table 4.15: Volume and efficiency of field drainage lysimeters and laboratory soil columns leached with water in Daretta village

Method	Mean volum e (li)	Mean efficieinc y (%)	SEM (volume)	SEM (efficiency)	Significanc e (volume)	Significanc e (efficiency)
Lysimeter s (n = 16)	9.30	46.48	±0.24	±1.18	**	**
Columns (n = 8)	0.32	14.18	±0.02	±5.31		

SEM =standard error mean; NS = Not significant ** Significant level at 1% probability level using Student T-test

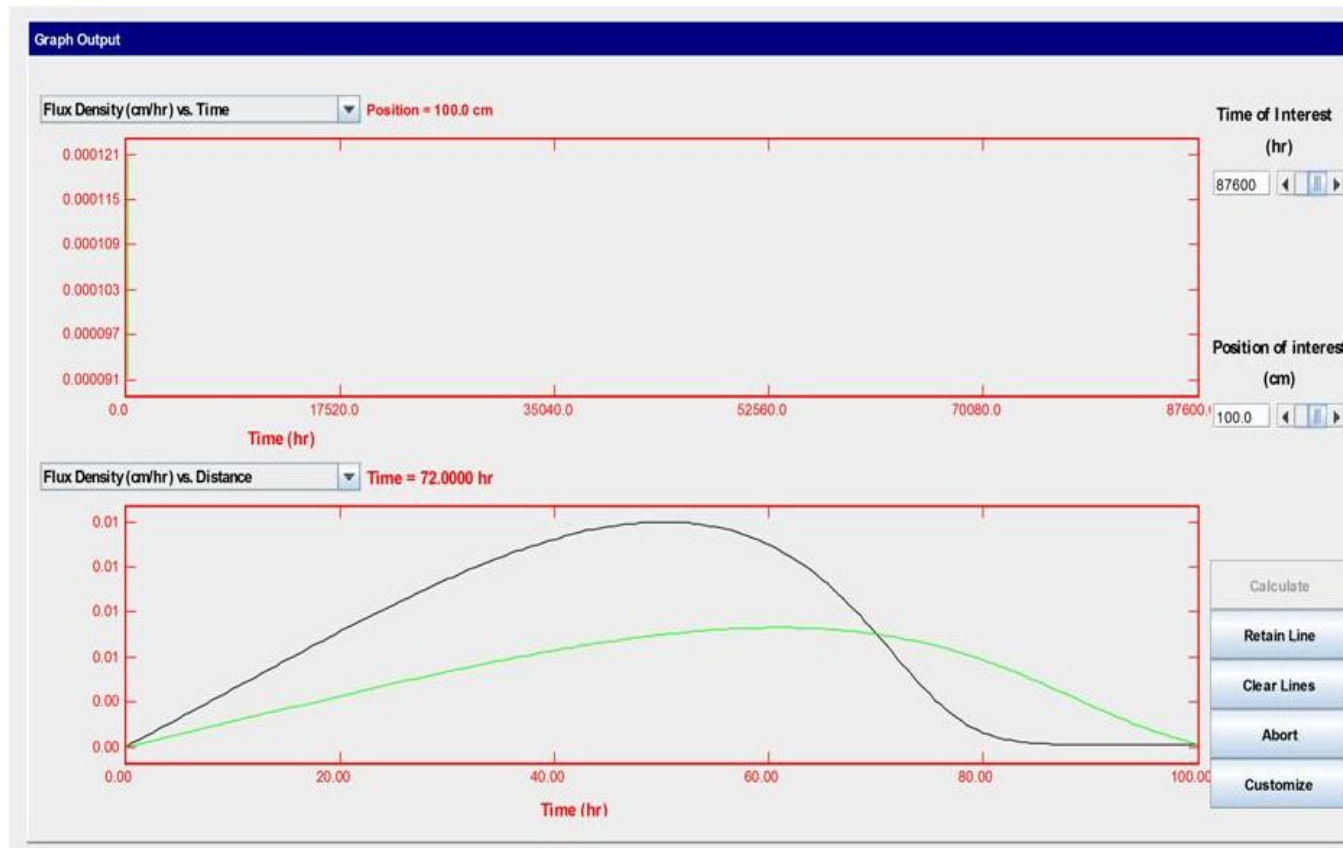


Figure 4.4: (a) Flux density vs. Time (b) Flux density vs. Time

cm hr⁻¹ is maintained even when the time of simulation is increased to 8,760 hours (1 year). The graph of flux density vs distance is shown in Figure 4.4b, Flux was observed to increase with increase in time. It started from 0 distance at the initial stage of the simulation and reaches maximum at a distance of 60 cm when t = 72 hours as shown in green colour in the graph. When t is increased to 8,760 hours, there is an increase in the flux density with the highest value observed at a distance of 50 cm as shown in black in the graph. This indicates that more Pb contaminants are expected to migrate from the soil over time as flux density is observed to increase over time and over certain distance.

4.10 Sensitivity of model parameters

Result from CHEMFLO-2000 model sensitivity analysis using input parameters such as particle size, K_s and organic carbon were based on the sensitivity classes given in Appendix VIII. The model was found to be very sensitive for particle size and K_s at $\pm 2\%$ to soil particle size and K_s . While it was rather sensitive to changes in organic carbon with an elasticity value of 0.35 (Appendix VIII). Based on this result obtained, it is recommended that careful use and measurement of these parameters be ensured during model calibration in order to obtain valid results from the model.

4.11 Estimated values of Pb flux, distance of travel and break through time using convective flux equations in Dareta village

The results for estimated values of Pb flux, distance of travel and break through time using convective flux equations in Dareta North, South, East and West are presented in Table 4.16-4.19. Volumetric flow rate (Q), Pb flux (q_s), convective flux (J_m) and distance of travel (V) all decrease with increase in time. Even though the same values of

Table 4.16: Estimated solute flux, distance of travel and break through time from convective equations in Dareta North

D	hr	Q (cm³ hr⁻¹)	q_s (cmhr⁻¹)	J_m (cm hr⁻¹)	V (cm hr⁻¹)	t_r (hr⁻¹)
3	72	2.77×10^2	9.26×10^{-1}	1.15×10^1	0.42×10^1	237.6
30	720	2.77×10^1	9.26×10^{-2}	0.11×10^1	4.21×10^{-1}	2376
365	8760	0.22×10^1	7.61×10^{-3}	9.46×10^{-2}	3.46×10^{-2}	28908
1825	43800	4.57×10^{-1}	1.52×10^{-3}	1.89×10^{-2}	6.92×10^{-3}	144540
3650	87600	2.28×10^{-1}	7.61×10^{-4}	9.46×10^{-3}	3.46×10^{-3}	289080
7300	175200	1.14×10^{-1}	3.81×10^{-4}	4.73×10^{-3}	1.73×10^{-3}	578160
14600	438000	4.57×10^{-2}	1.52×10^{-4}	1.89×10^{-3}	6.92×10^{-4}	1445400

D = days, hr = hour = Q = volumetric flow rate across the lysimeter, q_s = flow per unit cross sectional area per unit time, J_m=convective flow (mass flow), V = distance of travel, t_r = break through time.

Table 4.17: Estimated solute flux, distance of travel and break through time from convective equations in Dareta South

D	hr	Q (cm³ hr⁻¹)	q_s (cmhr⁻¹)	J_m (cm hr⁻¹)	V (cm hr⁻¹)	t_r (hr⁻¹)
3	72	2.77×10^2	9.26×10^{-1}	1.17×10^1	0.44×10^1	226.8
30	720	2.77×10^1	9.26×10^{-2}	0.11×10^1	4.75×10^{-1}	2106.0
365	8760	0.22×10^1	7.61×10^{-3}	9.18×10^{-2}	3.86×10^{-2}	25885.8
1825	43800	4.57×10^{-1}	1.52×10^{-3}	1.72×10^{-2}	7.61×10^{-3}	131400
3650	87600	2.28×10^{-1}	7.61×10^{-4}	7.83×10^{-3}	4.09×10^{-3}	244404
7300	175200	1.14×10^{-1}	3.81×10^{-4}	3.88×10^{-3}	2.15×10^{-3}	465156
14600	438000	4.57×10^{-2}	1.52×10^{-4}	1.39×10^{-3}	7.69×10^{-4}	1300860

D = days, hr = hour = Q = volumetric flow rate across the lysimeter, q_s = flow per unit cross sectional area per unit time, J_m = convective flow (mass flow), V = distance of travel, t_r = break through time.

Table 4.18: Estimated solute flux, distance of travel and break through time from convective equations in Daretu East

D	hr	Q (cm³ hr⁻¹)	q_s (cmhr⁻¹)	J_m (cm hr⁻¹)	V (cm hr⁻¹)	t_r (hr⁻¹)
3	72	2.77×10^2	9.26×10^{-1}	1.06×10^1	0.43×10^1	233.3
30	720	2.77×10^1	9.26×10^{-2}	0.10×10^1	4.70×10^{-1}	2127.6
365	8760	0.22×10^1	7.61×10^{-3}	8.05×10^{-2}	4.07×10^{-2}	24571.8
1825	43800	4.57×10^{-1}	1.52×10^{-3}	3.72×10^{-2}	7.61×10^{-3}	131400
3650	87600	2.28×10^{-1}	7.61×10^{-4}	7.43×10^{-3}	4.32×10^{-3}	231264
7300	175200	1.14×10^{-1}	3.81×10^{-4}	3.78×10^{-3}	2.15×10^{-3}	465156
14600	438000	4.57×10^{-2}	1.52×10^{-4}	1.32×10^{-3}	8.10×10^{-4}	1235160

D = days, hr = hour = Q = volumetric flow rate across the lysimeter, q_s = flow per unit cross sectional area per unit time, J_m = convective flow (mass flow), V = distance of travel, t_r = break through time.

Table 4.19: Estimated solute flux, distance of travel and break through time from convective equations in Dareta West

D	hr	Q (cm³ hr⁻¹)	q_s (cmhr⁻¹)	J_m (cm hr⁻¹)	V (cm hr⁻¹)	t_r (hr⁻¹)
3	72	2.77×10^2	9.26×10^{-1}	1.10×10^1	0.46×10^1	216.0
30	720	2.77×10^1	9.26×10^{-2}	0.19×10^1	4.68×10^{-1}	2138.4
365	8760	0.22×10^1	7.61×10^{-3}	8.11×10^{-2}	4.05×10^{-2}	24703.2
1825	43800	4.57×10^{-1}	1.52×10^{-3}	1.57×10^{-2}	7.15×10^{-3}	139941
3650	87600	2.28×10^{-1}	7.61×10^{-4}	8.42×10^{-3}	3.88×10^{-3}	257544
7300	175200	1.14×10^{-1}	3.81×10^{-4}	3.56×10^{-3}	2.47×10^{-3}	404712
14600	438000	4.57×10^{-2}	1.52×10^{-4}	1.41×10^{-3}	9.22×10^{-4}	1084050

D = days, hr = hour = Q = volumetric flow rate across the lysimeter, q_s = flow per unit cross sectional area per unit time, J_m = convective flow (mass flow), V = distance of travel, t_r = break through time.

Q and q_s were used in estimating the t_r for all the sampling directions. This is because values such as volume of V , t , A , L used in estimating Q and q_s across the sampling direction were the same as previously mentioned in chapter three. Highest J_m values obtained was after three days of estimation with Daret North having a J_m 1.15×10^1 cm hr^{-1} while Daret South recorded 1.17×10^1 cm hr^{-1} . Distance of travel (V) decrease with increase in time across the sampling directions. This decrease which is not rapid may cause all the soil layers in that location to be contaminated with before reaching the groundwater. Daret East and West recorded lowest V values of 8.10×10^{-4} cm hr^{-1} and 9.22×10^{-4} cm hr^{-1} respectively when an estimated time of 14,600 days (40 days) was used. Break through time (t_r) values estimated unlike other values increases with increase in t across the sampling directions because of decrease in volumetric flow rate (Q) and flux (q_s). Its estimated as the amount of time it will take the Pb contaminant to reach ground water. Higher t_r values are required for lesser Q and q_s values. Break through values ranged from 237.6-1445400 hr^{-1} in Daret North while it was found to range from 216-1084050 hr^{-1} in Daret West. Chemicals in the soil undergo two fates based on their duration whether on a short-term or a long-term disposition to another chemical or storage (Gulliver, 2007). The time scale of the calculations is important in determining how we deal with the problem or how we set up our solution. If Pb contaminant is in groundwater, the media are soil and water. The short-term fate will be that the Pb will be primarily adsorbed to the soil. Soil organic matter and high surface area clays tend to be the strongest absorbents of some contaminants although they are little for Pb contaminants while oxide coatings on soil particles strongly adsorb others (Brady and Weil, 2008). The long-term fate is that it will desorb and the Pb-laden water may be consumed when sourced from natural ground-water sources such as wells, streams, rivers, bore holes (Gulliver, 2007).

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 SUMMARY

The study was conducted with the aim of determining the vertical movement of metal contaminants in a free drainage lysimeter at Daretta village, Anka Local Government Area of Zamfara State in northern Nigeria. Daretta village is a place where major outbreaks of Pb poisoning has been occurring since 2010, which is related to mining processes of Pb-rich ore for the extraction of gold. Free drainage lysimeters were used for collecting soil leachates in a Pb-contaminated soil. Monitoring of leaching and leachates collection of all the soil columns at different time intervals was done. The results of concentration of leachates collected with free drainage lysimeters were related with laboratory values in a soil column experiment. Lead movement in the soil was simulated using CHEMFLO-2000 computer simulation programme.

The result obtained showed that soils at the 0-20 cm depth were predominantly sandy loam and loam. Sandy, sandy loam and loam soils however, dominate the four sampling directions down the profile. The K_s of sampling location was found to be slow, moderately slow, moderate, to moderately rapid with mean values ranging 0.19-4.64 cm sec^{-1} . Bulk density (ρ_b) of the soil surface (0-20 cm) of the study area were classified as low across the sampling coordinates. Mean values recorded were 1.40-1.73 g cm^{-3} . The mean total pore space ranges from 37.73-47.30% in the upper 0-20 cm depth. Down the profile mean values ranged from 14.37-36.08% in Daretta North, 13.60-36.00% in Daretta South, 11.61-39.48% and 17.62-37.83% in Daretta West.

The vertical distribution of Pb with the highest concentration was 2025 mg kg^{-1} in Daretta North at the surface soil located near the gold ore processing site. Farms in

Dareta South recorded lower values than Dareta North with values ranging from 1310-1586 mg kg⁻¹. Lower Pb concentrations of 604 mg kg⁻¹ and 625 mg kg⁻¹ were observed in Dareta East respectively, and 740 mg kg⁻¹ and 876 mg kg⁻¹ in Dareta West respectively.

Mean values of the Pb concentration for three samples of well water ranged from 5.34-6.87 mg li⁻¹. No significant difference was observed when the total Pb concentration of leachates collected from free drainage lysimeter were compared using Students' T-test between concentrations of leachates in all the lysimeters.

Efficiency of leachates collection of the free drainage lysimeters installed in soil profiles across the sampling direction ranged from 40.03-50.65% while discharge values obtained ranged from 8.01-10.13 li. The mean efficiency for soil columns was found to be 31% for Dareta North, 26% for Dareta South, 36% for Dareta and 37% for Dareta West.

When the results of concentration of leachates collected with free drainage lysimeters were related with the laboratory soil columns, the quantity collected from the former method were significantly higher than those from the laboratory soil columns. No significant difference was observed between the volumes of water applied to free drainage lysimeter and that of soil columns.

Results of concentration of leachates collected with field drainage lysimeters were compared with that from laboratory soil columns and shows that quantity collected from field drainage method were significantly higher than those from the laboratory soil columns. No significant difference was observed when the volumes of water applied to free drainage lysimeter and that of soil columns.

Soil pH in Dareta village is slightly acidic to strongly alkaline in water and moderately acidic to slightly acidic in CaCl₂. Down the profile the values are found to be neutral to slightly alkaline in water and moderately acidic to neutral in CaCl₂ in Dareta North and South. Cation exchange capacity values for the surface (0-20 cm) soils in Dareta village are classified by the Soil Survey Staff (1993) as low to medium fertility. Same trend was observed down the profile where CEC values were classified as low to moderate across the four sampling directions. Mean soil OC contents obtained signify low OC at the surface soil. At lower soil depths (0-100 cm), similar results were obtained which classifies the soils as having low OC across the sampling direction. Values of the exchangeable bases obtained at the surface soil and lower depths down the profile indicate high values of the cations in the study area.

The results of chemical movement based on CHEMFLO calibration collected from this study based on the graph for flux density vs time shows that flux density was uniform ($9.1 \times 10^{-5} \text{ cm hr}^{-1}$) at the initial stage of the simulation (0) and increased rapidly when the time of interest was approached (72 hours) to $12.1 \times 10^{-5} \text{ cm hr}^{-1}$ flux density of $12.1 \times 10^{-5} \text{ cm hr}^{-1}$ is maintained even when the time of simulation is increased to 8,760 hours (1 year). In the graph of flux density vs distance, flux was observed to increase with increase in time. It started from 0 distance at the initial stage of the simulation and reaches maximum at a distance of 60 cm when $t = 72$ hours as shown in green colour in the graph. When t is increased to 8,760 hours, there is an increase in the flux density with the highest value observed at a distance of 50 cm as shown in black in the graph.

The results for estimated values of Pb flux (q_s), distance of travel and break through time using convective flux equations in Dareta village shows that q_s values were the same across the estimated times chosen in all sampling directions because a constant value of Q and t were used all through during the estimation. Highest q_s value of

$9.62 \times 10^{-3} \text{ cm hr}^{-1}$ was obtained at the initial time of estimation (72 hours) while the lowest q_s value estimated is found to be 1.58×10^{-7} when the highest time (438000 hours) was used in the estimation. Break through values ranged from 17822.57- $1.08 \times 10^8 \text{ hr}^{-1}$ in Daret North, while it ranges from 11275.5-68592631 hr^{-1} in Daret South. Chemicals in the soil undergo two fates based on their duration whether on a short-term or a long-term disposition to another chemical or storage (Gulliver, 2007). The time scale of the calculations is important in determining how we deal with the problem or how we set up our solution. If Pb contaminant is in groundwater, the media are soil and water. The short-term fate will be that the Pb will be primarily adsorbed to the soil. Soil organic matter and high surface area clays tend to be the strongest adsorbents of some contaminants although they are little for Pb contaminants while oxide coatings on soil particles strongly adsorb others (Brady and Weil, 2008). The long-term fate is that it will desorb and the Pb-laden water may be consumed when sourced from natural ground-water sources such as wells, streams, rivers, bore holes (Gulliver,2007).

5.2 CONCLUSION

The following conclusions were drawn from this research:

1. The contamination of soils and farmlands is a result of processing of weathered Pb-rich gold ores and results from this research showed that the soils of the farmlands are highly contaminated with Pb.
2. Leaching losses of Pb contaminants towards groundwater will likely increase with time (from 3-14600 days) as estimated in this study.
3. The hypothesis that field measured vertical movement of contaminants with a free drainage lysimeters is the same with the laboratory measured was

found not to be true and therefore the alternate hypothesis is taken. While the hypothesis that vertical transport is dependent on soil on soil physico-chemical and hydraulic properties was found to be correct and therefore the null hypothesis is accepted.

4. The results for estimated values of Pb flux, distance of travel and break through time using convective flux equations in Dareta village suggests that the rate at which Pb travel through the soil down the groundwater and that that immediate measures have to be taken to curtail this.
5. The lysimeter design presented provides an alternative method for collecting agrochemical leachates. These devices can be used to compare best management practices, identify and quantify potential pollutant sources, and gain a better understanding of the infiltration properties of a particular soil type.

5.3 RECOMMENDATIONS

1. Although acute Pb poisoning of young children has been the most immediate and severe consequence, older children, adult workers, pregnant women and their unborn fetus, and breastfeeding infants are also at risk. Therefore it is recommended that strict legislation be made to restrict artisanal gold mining in order to limit heavy metal discharges especially around human habitations.
2. Further work should aim at evaluating the free drainage lysimeter in the field at different seasons of the year and under different crop management systems to determine its efficiency. This will help in adequate monitoring of solutes and contaminants movement in the vadose zone with a greater accuracy obtained with other existing methods.

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APPENDICES

Appendix I: Particle size distribution of surface soil (0-100 cm) in the different cardinal directions of Dareta village

Depth (cm)	Dareta North I			Textural Class
	Clay (g kg ⁻¹)	Silt (g kg ⁻¹)	Sand (g kg ⁻¹)	
0-20	120	320	560	Sandy Loam
20-40	360	260	380	Clay Loam
40-60	380	280	340	Clay Loam
60-80	400	240	360	Clay Loam
80-100	340	260	400	Clay Loam
		Dareta North II		
0-20	160	340	500	Loam
20-40	320	280	400	Clay Loam
40-60	360	300	340	Clay Loam
60-80	320	280	400	Clay Loam
80-100	320	300	380	Clay Loam
Means	308.00	286.00	400.00	Clay Loam

Appendix I: Continued

Dareta South I				
Depth (cm)	Clay (g kg⁻¹)	Silt (g kg⁻¹)	Sand (g kg⁻¹)	Textural Class
0-20	100	100	800	Loamy Sand
20-40	370	260	370	Clay Loam
40-60	320	240	440	Clay Loam
60-80	400	240	360	Clay Loam
80-100	320	240	440	Clay Loam
Dareta South II				
0-20	240	440	320	Loam
20-40	360	260	380	Clay Loam
40-60	360	250	390	Clay Loam
60-80	400	260	340	Clay Loam
80-100	340	240	420	Clay Loam
Means	321.00	253.00	426.00	Clay Loam

Appendix I: Continued

Dareta East I				
Depth (cm)	Clay (g kg⁻¹)	Silt (g kg⁻¹)	Sand (g kg⁻¹)	Textural Class
0-20	140	304	520	Sandy Loam
20-40	380	260	360	Clay Loam
40-60	360	300	340	Clay Loam
60-80	400	240	360	Clay Loam
80-100	370	280	350	Clay Loam
Dareta East II				
0-20	180	220	600	Sandy Loam
20-40	400	260	340	Clay Loam
40-60	320	300	380	Clay Loam
60-80	380	280	340	Clay Loam
80-100	300	400	300	Clay loam
Means	323.00	274.40	389.00	Clay Loam

Appendix I: Continued

Dareta West I				
Depth (cm)	Clay (g kg⁻¹)	Silt (g kg⁻¹)	Sand (g kg⁻¹)	Textural Class
0-20	80	320	600	Sandy Loam
20-40	380	240	380	Clay Loam
40-60	340	280	380	Clay Loam
60-80	360	310	330	Clay Loam
80-100	280	460	260	Clay Loam
Dareta West II				
0-20	120	280	600	Sandy Loam
20-40	400	250	350	Clay Loam
40-60	360	260	380	Clay Loam
60-80	380	300	320	Clay Loam
80-100	360	320	320	Clay Loam
Means	306.00	302.00	392.00	Clay Loam

Appendix II: Physical properties of surface soils (0-20 cm) from two farms in the different sampling directions of Dareta village

Sampling Direction	Ks (cm sec⁻¹)	Bulk Density (g cm⁻³)	Total Porosity (%)	EP (%)
NF I 1	3.80	1.73	34.72	11.62
2	3.97	1.61	39.25	18.55
3	4.11	1.49	43.77	18.97
Means	3.96	1.61	39.25	16.38
NF II 1	1.09	1.22	53.96	23.76
2	1.12	1.46	44.91	14.41
3	0.86	1.51	43.02	16.02
Means	1.02	1.40	47.30	18.06
SF I 1	2.46	1.68	36.60	23.80
2	2.55	1.62	38.88	25.17
3	2.50	1.32	50.19	21.39
Means	2.50	1.54	41.89	23.45
SF II 1	3.88	1.74	34.34	11.14
2	3.63	1.78	32.83	12.13
3	3.87	1.68	36.60	19.40
Means	3.79	1.73	34.59	14.22
EF I 1	0.89	1.30	50.94	15.44
2	1.08	1.72	35.09	5.39
3	1.21	1.45	45.28	14.48
Means	1.06	1.49	43.77	11.77
EF II 1	4.46	1.61	39.25	24.65
2	5.06	1.63	38.50	18.70
3	4.39	1.45	45.28	14.48
Means	4.64	1.56	41.01	19.28
WF I 1	1.68	1.64	38.11	16.81
2	1.66	1.63	38.49	12.99
3	1.69	1.68	36.60	23.60
Means	1.68	1.65	37.73	17.80
WF II 1	1.28	1.66	37.36	19.76
2	1.36	1.48	44.15	13.95
3	1.52	1.65	37.74	11.44
Means	1.39	1.60	39.75	15.05

N = north, S = south, E = east, W = west, Ks = saturated hydraulic conductivity, EP effective porosity, I = farm I, II = farm II.

Appendix III: Hydraulic conductivity for saturated soils

Class	Hydraulic Conductivity cm hr ⁻¹
Very slow	< 0.125
Slow	0.125 - 0.5
Moderately slow	0.5 - 2.0
Moderate	2.0 - 6.25
Moderately rapid	6.25 - 12.5
Rapid	12.5 - 25.0
Very rapid	> 25.0

Source: Ghildyal and Tripatti, 1987.

Appendix IV: Chemflo-2000 graph line data print preview

GRAPH LINE COLOR: GREEN

Time of interest: 72.0000 hr

Position of interest: 100.0 cm

Soil: Name: Default Soil

Extent: 100.0 cm

Orientation: Angle of Inclination is 90.0 degrees

Properties:	Layer	Thickness	Conductivity	Water Characteristic	Organic	Bulk
	(cm)	Function	Function	Carbon	Density	
			(g/g)	(Mg/m3)		
1	100.0	van Genuchten	van Genuchten	0.019	1.57	Ks (cm/hr) = 2.0 θ_s (v/v) = 0.43
		α (1/cm) = 0.015	θ_r (v/v) = 0.08	$n = 1.875$		α (1/cm) = 0.015
			$n = 1.875$			

Initial Conditions:

Initial Condition for Water Movement:

Uniform Matric Potential 500.0 cm Corresponding Water Content 0.13941 (m3/m3)

Initial Condition for Chemical Movement: Uniform Total Concentration 0.0 (g/m3 Bulk Soil)

Boundary Conditions:

Location	Time(hr)	Component	Boundary Condition	
X = 0 cm	0.0000 to 72.0000	Water	Falling Head:	Initial Ponding Depth = 5.0 cm
X = 0 cm	0.0000 to 72.0000	Chemical	Inflow Solution Conc. = 0.0000 g/m3	
X = 100.0 cm	0.0000 to 72.0000	Water	Free Drainage	
X = 100.0 cm	0.0000 to 72.0000	Chemical	Convective Flow Only	

Transport properties:

Parameter	Value	Diffusion Coefficient	0.0 cm2/hr
Dispersivity	2.0 cm	Partition coefficient	0.0 m3/Mg
First-order degradation rate const. in liquid	0.0	1/hr	
First-order degradation rate const. on solids	0.0	1/hr	
Zero-order production rate	0.0	g/m3/hr	

Mesh Size/Convergence:

Mesh size in time: 0.0050 hr
 Mesh size in length: 0.5 cm
 Convergence criteria: 1.0E4
 Maximum Absolute Error: 0.125 cm
 Maximum Relative Error: 5.0%
 Critical Cumulative Flux: 2.5 cm

GRAPH LINE COLOR: GREEN

Time of interest: 72.0000 hr

Position of interest: 100.0 cm

Soil: Name: Default Soil Extent: 100.0 cm Orientation: Angle of Inclination is 90.0 degrees

Properties:	Layer	Thickness	Conductivity	Water Characteristic	Organic	Bulk
	(cm)	Function	Function	Carbon	Density	
			(g/g)	(Mg/m3)		
(Mg/m3)	1	100.0	van Genuchten	van Genuchten	0.019	1.57
			K_s (cm/hr) = 2.0	θ_s (v/v) = 0.43	α (1/cm) = 0.015	θ_r (v/v) = 0.08
			$n = 1.875$	α (1/cm) = 0.015		$n = 1.875$

Initial Conditions:

Initial Condition for Water Movement:

Uniform Matric Potential 500.0 cm Corresponding Water Content 0.13941 (m3/m3)

Initial Condition for Chemical Movement: Uniform Total Concentration 0.0 (g/m3 Bulk Soil)

Boundary Conditions:

Location	Time (hr)	Component	Boundary Condition	X = 0 cm	0.0000 to 72.0000	Water	Falling Head:
							Initial Ponding Depth = 5.0 cm
				X = 0 cm	0.0000 to 72.0000	Chemical	
				X = 100.0 cm	0.0000 to 72.0000	Water	Free Drainage
				X = 100.0 cm	0.0000 to 72.0000	Chemical	Convective Flow Only

Transport properties:

Parameter	Value	Diffusion Coefficient	0.0 cm2/hr
Dispersivity	2.0 cm	Partition coefficient	0.0 m3/Mg
First-order degradation rate const. in liquid	0.0	1/hr	
First-order degradation rate const. on solids	0.0	1/hr	
Zero-order production rate	0.0	g/m3/hr	

Mesh Size/Convergence:

Mesh size in time: 0.0050 hr
Mesh size in length: 0.5 cm
Convergence criteria: 1.0E4
Maximum Absolute Error: 0.125 cm
Maximum Relative Error: 5.0%
Critical Cumulative Flux: 2.5 cm

Appendix V: Rating for soil data interpretation

1. Soil Reaction

Extremely acid	< 4.5
Very strongly acid	4.5 - 5.0
Strongly acid	5.1 - 5.5
Moderately acid	5.6 - 6.0
Slightly acid	6.1 - 6.5
Neutral	6.6 - 7.3
Slightly alkaline	7.4 - 7.8
Moderately alkaline	7.9 - 8.4
Strongly alkaline	8.5 - 9.0
Very strongly alkaline	> 9.0

2. Exchangeable bases ($\text{cmol}_{(+)}\text{kg}^{-1}$)	Ca	Mg	K	Na
	0 - 2	0 - 0.3	0 - 0.15	0 - 0.1
	2 - 5	0.3 - 1.0	0.15 - 0.30	0.1 -
0.3				
	> 5	> 1.0	> 0.30	>
0.30				

3. Cation exchange capacity ($\text{cmol}_{(+)}\text{kg}^{-1}$)

Low	< 6
Medium	6 - 12
High	>12

4. Bulk density (g cm^{-3})

Moderate	< 1.60
High	> 1.60

Source: Soil Survey Manual, U. S. Department of Agriculture, 1993.

Appendix VI: Pearson correlation matrix for selected soil physico-chemical properties in 0-20 cm depth in Daretta village

	K _s	Clay	Silt	Sand	OC
K _s	1.00				
Clay	-0.27	1.00			
Silt	-0.29	-0.11	1.00		
Sand	0.39	-0.82	-0.47	1.00	
OC	0.58	-0.32	-0.24	0.41	1.00

Appendix VII: Pearson correlation matrix for selected soil physico-chemical properties in 0-100 cm depth in Dareta village

	K _s	Clay	Silt	Sand	OC
K _s	1.00				
Clay	0.42	1.00			
Silt	0.06	0.56	1.00		
Sand	-0.21	-0.81	-0.94	1.00	
OC	-0.36	-0.29	-0.71	0.41	1.00

Appendix VIII: Sensitivity classes used to describe the degree of model sensitivity to changes in input variables or model parameters

Sensitivity class	Degree of sensitivity
0.1-0.1	Hardly
0.1-0.5	Rather
0.5-1.0	Quite
1.0-2.0	Very
>2.0	Extremely

Source: Leffelaar, 2008; Abdulkadir, 2012