DISTRIBUTION OF HEAVY METALS IN COCOA FARM SOILS IN THE WESTERN REGION OF GHANA

BY

JUSTICE EDUSEI ACKAH

(10193655)

A THESIS SUBMITTED TO THE UNIVERSITY OF GHANA, LEGON IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF MPHIL CHEMISTRY DEGREE

OCTOBER 2012

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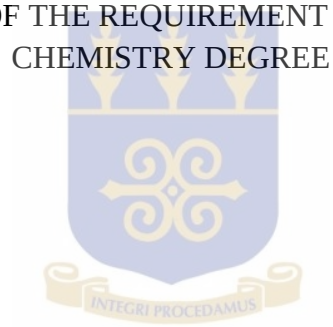

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF GHANA

OCTOBER 2012

DECLARATION

It is hereby declared that this thesis is the outcome of research undertaken by Justice Edusei Ackah towards the award of MPhil Chemistry degree in the Department of Chemistry, University of Ghana, and has neither in part nor in whole been presented for another degree elsewhere.

…..…… Date……..……

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Professor Derick Carboo

(Principal Supervisor)

…..…….. Date…….……

Dr. Eric K. Nartey

(Co-supervisor)

DEDICATION

To the Almighty God, and to the

Ben Ackah family, Sefwi Bekwai.

……. JE Ackah

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ABSTRACT

Western Region is the largest cocoa producer in Ghana. Cocoa farmlands have over the past decades received heavy doses of agrochemical application to boost cocoa production. These agrochemicals, however, may contain heavy metals and it is therefore likely that the metals may have accumulated in the soils. Evaluating the total concentrations and understanding the distribution characteristics of heavy metals in cocoa growing soils can aid environmental managers and even help regulate the rate of agrochemical application. A study was therefore, carried out on some selected soils of major cocoa growing areas in Western Region of Ghana to determine the levels of cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) in the soils and also to determine some of the soil factors that control the distribution of the heavy metals in the soil. Eight soils (two Haplic Luvisols, three Ferric Acrisols, one Haplic Ferrasol and two Dystric Fluvisols) and their accompanying pristine soils as control were taken from adjacent natural forests sampled at depths of 0 – 10 cm, 10 – 30 cm, 30 – 50 cm, 50 – 80 cm and 80 – 100 cm. These soils were analysed for their particle size distribution, pH, organic carbon, cation exchange capacity, exchangeable bases, and total and bio-available Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The study indicated that the ΔpH which is $pH_{KCl} - pH_{H2O}$ were all negative indicating that the soils generally had net negative charges on their colloidal surface. For all soils, clay content and pH increased with depth indicating co-migration of the two soil parameters whilst total organic carbon content decreased with depth. Cation exchange capacity, however, did not show any clear pattern with depth in the soils. The average abundance of heavy metals determined in these soils decreased as follows: Fe > Mn > Cr > Zn > Cu > Cd > Pb > Ni. The soils had low metal contents, less than or within the range of concentration for non-polluted soils and for European norms. However, total concentrations of Cd, Cu, Cr and Pb in the surface soils (0 – 10 cm) exceeded the thresholds for atmospheric fallout concentrations in

top soil to 20 cm depth indicative of anthropogenic contamination. The lowest heavy metal contents were observed in the Haplic Luvisols while the highest metal loadings were in the Haplic Ferrasols and the Dystric Fluvisols. Depth function plots, ANOVA and correlation analyses indicated that clay influenced the distribution of Cr, Cu, Fe, Ni and Zn in the soils. Clay and total organic carbon controlled Cd distribution while pH and clay were associated with the distribution of Mn. Thus, clay had the most pronounce effect on the distribution of the metals in the soils. Accumulation-depletion ratios, enrichment factors and principal component analysis indicated that the distribution of Cd, Cu, Mn and Pb in the soils highlighted an anthropogenic pollution, most probably, from agrochemical inputs and/or from atmospheric deposition. Iron and Ni distributions were associated with lithogenic origin whereas Zn and Cr distribution were related to both anthropogenic and lithogenic contributions.

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CHAPTER ONE

1.0 GENERAL INTRODUCTION

1.1 BACKGROUND

The natural occurrence of heavy metals is mostly from weathering of parent rocks and pedogenesis, and the anthropogenic inputs are associated with industrialization and agricultural activities such as fertilizer application and long-term application of wastewater in agricultural land (Baize and Sterckeman, 2001; Koch and Rotard, 2001; McLaughlin *et al.*, 2000).

In Ghana, agriculture is the main industrial activity and cocoa is the major cash crop grown. Ghana is the world's second largest producer of cocoa beans and cocoa has, for many years, been the backbone of the country's economy. Governments, therefore, never relent in the pursuit and implementation of measures to boost cocoa production (Osei, 2007; Dorman *et al.*, 2004; Ahenkorah *et al.*, 1982). The high output of cocoa beans in recent times in Ghana is due largely to the application of a wide variety of agrochemicals such as pesticides, herbicides and fertilizers which over the recent decades have been recommended (Appiah *et al.*, 1997) and massively patronized by cocoa farmers (Vigneri, 2007). However, high application rates of fertilizers and fungicides have been shown to result in heavy metal accumulation in surface horizons making farmlands susceptible to heavy metal contamination (Faβbender and Bornemisza, 1987).

These heavy metals often occur as cations which strongly interact with the soil matrix and may consequently become mobile as a result of changing environmental conditions (Facchinelli *et al.*, 2001). Heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn accumulate in the soil and do not only circulate in the soil ecosystem but also enter crops

grown in contaminated soils thereby gradually ending up in the food chain (Ghrefat and Yusuf, 2006). Though some can be beneficial, heavy metals are the most dangerous contaminants for the environment and human beings especially when their levels exceed specific thresholds mainly due to the fact that they are non-degradable (Dyer, 2007; Bradl, 2005): Cadmium toxicity, for example, has side effects such as kidney dysfunction; Copper toxicity has been reported to cause liver cirrhosis (Graham and Cordano, 1976); Toxicity of zinc may lead to anaemia and lethargy (Fairweather-Tait, 1988); and lead toxicity manifestations include cancers, typically involving the skin, lung and bladder (Groten and VanBladeren, 1994; Gazza, 1990).

The accumulation of heavy metals in agricultural soils is thus of increasing concern due to the food safety issues and potential health risks as well as their detrimental effects on soil ecosystems (McLaughlin *et al.*, 1999). These concerns have attracted the attention of many countries who import agricultural products. Ghana's cocoa beans thus need scrutiny as well as the soils in which they are cultivated. Evaluating the total concentrations and understanding the distribution characteristics of heavy metals in cocoa growing soils can aid environmental managers and even help regulate the rate of agrochemical application.

Though the total metal concentrations may indicate the overall level of metals in soils, they provide no information regarding potential mobility and/or bioavailability of a particular element (Powell *et al.*, 2005; Vijver *et al.*, 2004). Heavy metals in soil can exist in various fractions showing varying availability. These include: (i) simple or complex ions in soil solution; (ii) exchangeable ions; (iii) ions linked to organic substances; (iv) ions occluded or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals; and (v) ions in the crystalline lattice of primary minerals (Soon and Bates, 1982). Not all these forms are equally important from an ecological point of view. The (iii), (iv) and (v) fractions are

very stable and hence unlikely to be released under weathering conditions whereas the soluble and exchangeable fractions are quite mobile (Kabata-Pendias, 1993). The mobile fraction may be taken up by plants or leached into the groundwater (Allen *et al.*, 1995; Brummer *et al.*, 1986; MahatTey *et al.*, 1975). Accurate measurements of both the total and bio-available (mobile or exchangeable) concentrations of heavy metals are thus required to create a distinction between the concentrations that are in the soil and the proportion that may get to plants or enter the food chain.

The physicochemical properties of soil also affect the distribution of heavy metals in soils. Clay content and type, soil pH, organic matter and cation exchange capacity are the predominant parameters controlling the accumulation and the availability of heavy metals in soil (Nyamangara and Mzezewa, 1999). For example, low pH of soil tends to increase the rate of desorption of heavy metals from soil particle surfaces into solutions that remain in the capillaries of the soil making them available for uptake by plants or leached into underground water. Each heavy metal undergoes differing reactions in the soil depending on the aforementioned factors and, consequently, the available metals concentrate to different degrees along the depth of the soil. It is necessary then to evaluate the relationship among these parameters and heavy metal accumulation in soil.

1.2 PROBLEM STATEMENT

Agrochemicals have since the past decade been applied on almost all cocoa farms in Ghana with the sole aim of boosting crop yield through controlling pests and diseases, and weeds. The Western region is the largest producer of cocoa in Ghana, producing over 50% of the nation's cocoa beans (Anim-Kwapong and Frimpong, 2005; Appiah *et al.*, 1997). Cocoa farmlands in the region receive appreciable fertilizer and/or other agrochemical applications.

The region is also the second highest producer of gold in Ghana and it hosts lots of small scale mining industries locally termed "galamsey". Several studies have shown the invasive effect of mining activities on the environment (Akabzaa *et al.*, 2005; Asante *et al.*, 2005; Bonzongo *et al.*, 2004). Most cocoa farming communities in the Western region are in proximity with active mining areas. Cocoa farms may, therefore, be exposed to a number of heavy metals as a result of the mining processes and agrochemical applications.

A study of the concentrations of various heavy metals and their depth distribution in soils of cocoa farms in the Western region is, therefore, imperative to ascertain whether or not the levels of the metals are above the maximum contaminant levels. It is also equally important to establish the source of these metals if they indeed exist in the soils so as to formulate remedial measures. This thesis, among other things, sought to determine the levels of cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) in soils of cocoa farms.

1.3 HYPOTHESIS

H_0: Soils in cocoa farms in the Western region of Ghana are contaminated with heavy metals from anthropogenic inputs.

H_1: Soils in cocoa farms in the Western region of Ghana are not contaminated with heavy metals.

1.4 OBJECTIVES OF THE RESEARCH

1.4.1 Aim

The aim of this study is to establish the depth distribution of heavy metals in soils of cocoa farms in the Western region of Ghana.

1.4.2 Specific Objectives

The specific objectives comprise the following:

1. To determine the total concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in soils of cocoa farms in the Western region of Ghana.
2. To determine the exchangeable (mobile) concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in soils of cocoa farms in the Western region of Ghana.
3. To establish the relationships among the heavy metals on one hand, and also between the heavy metals and physicochemical properties of the soils.
4. To determine the sources of the heavy metals in the soils.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 ESSENTIALITY OF ELEMENTS

The ions in the soil solution and in the solid phase that are of primary interest to soil chemists are those essential or toxic to life and those important to soil development (which are also important for plants and animals). Resultantly, elements (including heavy metals) are classified essential or toxic by many studies (Gomes and Silva, 2007; Brady and Weil, 1999; Bohn *et al.*, 1985).

Several definitions exist for essential elements. According to Lindh (2005), an element is essential if: it is present in living tissues at a relatively constant concentration; it provokes similar structural and physiological anomalies in several species when removed from their organisms and these anomalies are prevented or cured by the supplementation of the element. For the World Health Organization (WHO, 2002), an element is considered essential to an organism when the reduction of its exposure below certain limit results consistently in a reduction in a physiologically important function, or when the element is an integral part of an organism structure performing a vital function in the organism.

Sodium, F, Si, Cr, Ni, Co, As, Se, Cl and Sn are essential to only animals, Mo is essential to only plants while H, C, N, O, Mg, Ca, P, S, K, B, V, Mn, Fe, Zn and Cu are considered essential elements to all animals and plants.

However, not all essential elements are needed in large quantities. H, C, N, O, Mg, Ca, Na, P, S and K are referred to as macro-elements because they are required in large quantities by humans whereas B, V, Mn, Fe, Zn, Cu, Mo, Si, Cr, Co, As, Se, Sn and I are required in small quantities and so are termed micro-elements. Chlorine is, however, considered macro and

micro element to animals and plants, respectively (Bohn *et al.*, 1985). Hydrogen, O, C, and N may be classified as major elements because they make up approximately 96% of the human body mass. Sodium, K, Ca, Mg, P, S, and Cl make up 3.78% of the body mass and thus classified minor elements (with their concentration being expressed in gkg^{-1}). The remaining elements and others (about 70) are called trace elements (with their concentration being expressed in $mgkg^{-1}$), (Bohn *et al.*, 1985). The World Health Organization (WHO, 2002) considers the trace elements: Fe, Zn, Cu, Cr, I, Co, Mo and Se, essential to human health.

In recent years, these trace elements, especially those termed heavy metals, in the soil have received attention as environmental contaminants because of their extended persistence and toxicity to many organisms (Hashem and Al-Obaid, 1996).

2.2 HEAVY METALS

The term "heavy metal" has received several definitions from biologists to toxicologists thereby presenting no coherent scientific basis (Duffus, 2002). Most definitions are on the basis of density (specific gravity) (Morris, 1992; Lozet and Mathieu, 1991; Parker, 1989). However, no relationship can be found between density (specific gravity) and any of the various physicochemical concepts that have been used to define "heavy metals" and the toxicity or ecotoxicity attributed to "heavy metals" (Hodgson *et al.*, 1988; Bennett, 1986; Phipps, 1981).

Nevertheless, understanding bioavailability is the key to assessment of the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters and on the physicochemical properties of metallic elements, their ions, and their compounds.

Heavy metals are totally non-degradable to non-toxic forms, although they may be ultimately transformed into insoluble and hence biologically unavailable forms. They enter the body through the breathing of air, drinking of water and through the eating of contaminated food.

Heavy metals occur naturally in ecosystems with large variations in concentration. In modern times, anthropogenic sources of heavy metals have been introduced to the ecosystem. There are 35 metals of environmental concern because of occupational or residential exposure; twenty three of these are "heavy metals" and are antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium and zinc (Glanze, 1996).

Some heavy metals are nutritionally essential for a healthy life whereas large amounts of any of them may cause acute or chronic toxicity (Coen *et al.*, 2001; Vernet, 1992). It should, however, be stressed that metals like cadmium, lead, beryllium and mercury have no biological functions and are highly toxic disrupting bodily functions to a large extent (Phipps, 1981). They, therefore, need close scrutiny. The applications and properties of these heavy metals are as follows:

2.2.1 Cadmium

Cadmium is produced mainly as a by-product from mining, smelting, and refining sulfidic ores of zinc, and, to a lesser degree, lead and copper (Fthenakis, 2004).

Cadmium exists in low concentrations in all soils. It is spread by air and water (sewage sludge) far over sea and land, but especially in the vicinity of heavy industrial plants. Cadmium emission also occurs from the production of artificial phosphate fertilizers and upon addition the element ends up in the soil (Jennings, 2005).

Cadmium is today regarded as the most serious contaminant of the modern age. It is absorbed by many plants and sea creatures and, because of its toxicity, presents a major problem in foodstuffs (Concon, 1998; Das *et al.*, 1997). Contamination through fertilisers becomes an increasing problem. Cadmium contamination cannot be removed from plants by washing them; it is distributed throughout the organism. It is often difficult to ascertain the cause of a Cd content in fruits or vegetables, as the substance in its natural form exists everywhere in the soil and is absorbed by the roots. It has been possible, however, to show that the increased Cd content in Central American cocoa was related to the specific local constituency of the soil. As opposed to African cocoa kernels, which contain 0.08-0.14 mg/kg, values from 0.18-1.5 mg/kg are found in the fine cocoa varieties from Venezuela and Ecuador (Vitošević *et al.*, 2007). Thus, site or vicinity or geographical location is an important factor when dealing with Cd contamination.

Cadmium is a highly toxic element that accumulates in biologic systems and has a long half-life. Its toxicity is manifested by a variety of syndromes: side effects include kidney dysfunction (necrotic protein precipitation), hypertension, hepatic injury, reproductive toxicity, lung damage after inhalation exposure, and bone effects such as “itai-itai” sickness in Japan. The kidney is a critical target-organ for Cd accumulation, and the half-life of the element in this tissue is about 30 years (Robards and Worsfold, 1991; Concon, 1998).

Cadmium is easily transferred from soil to plants, with absorption and accumulation of the element in plant to varying degrees. This process is favoured by low soil pH values, probably as a result of the increase in the exchangeable portion of Cd (Creaser and Purchase, 1991; Reilly, 1980). Cadmium accumulation is a continuous process that requires no particular threshold value of the element in soil and is influenced by physicochemical factors (Cabrera *et al.*, 1994; Zurera *et al.*, 1987; Haghiri, 1973)

During weathering, Cd goes directly into soil solution and, although known to occur as Cd^{2+}, it may also form complex ion such as $CdCl^{+}$, $CdOH^{+}$, $CdCl_3^{-}$, $Cd(OH)_3^{-}$, and $Cd(OH)_4^{2-}$. Oxidation potential and pH are the principal factors controlling Cd ion mobility in soil. Under conditions of of strong oxidation, Cd is however, likely to form CdO and $CdCO_3$, and is likely to be accumulated in phosphate and in biolith deposites (Kabata-Pendias, 2000).

Cadmium concentrations in soil solutions are controlled by adsorption rather than precipitation until a threshold pH value is exceeded (Soon, 1981; Tiller *et al.*, 1979). The solubility of $CdCO_3$ and possibly $Cd_3(PO_4)_2$ may control the Cd mobility in soil (Kabata-Pendias, 2000).

2.2.2 Chromium

Chromium is mined as chromite ($FeCr_2O_4$) ore (Emsley, 2001) and it enters the air, water and soil in the Cr (III) and Cr (VI) forms through natural processes and human activities. According to Kotaś and Stasicka (2000), volcanic eruptions and erosion of Cr containing rocks constitute the natural sources whereas steel, leather and textile manufacturing are, among other things, the predominant human activities that increase Cr concentrations in the environment especially in water. Through coal combustion, however, Cr ends up in the air whereas waste disposal deposits Cr in soils. In soils, Cr^{2+} strongly attaches to soil particles and as a result does not move towards groundwater (Kotaś and Stasicka, 2000).

The metal is known to enhance the action of insulin, the hormone critical to the metabolism and storage of carbohydrate, fat, and protein in the body (Emsley, 2001). Chromium toxicity symptoms, according to Stoecker (2001), include allergic dermatitis, skin lesions and

increased incidence of lung cancer. Toxicity also causes respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation (Myers *et al.*, 1997).

Chromium shows complex anionic and cationic ions in soil such as $Cr(OH)_2^+$, CrO_4^{2-} and CrO_3^{3-}. Under progressive oxidation, Cr forms chromate ion (CrO_4^{2-}) which is readily mobile and also is easily sorbed by clays and hydrous oxides. It has been shown that most of the soil Cr occurs as Cr^{3+} and it is within the mineral structures or forms of mixed Cr^{3+} and Fe^{3+} oxides. Cr^{3+} is is slightly mobile only in very acidic media, and at pH 5.5, it is almost completely precipitated. Consequently, its compounds are considered to be very stable in soils. Cr^{6+}, on the other hand, is very unstable in soils and is easily mobilised in both acid and alkaline soils (Kabata-Pendias, 2000).

2.2.3 Copper

Copper is a very common substance that occurs naturally in the environment. Copper enters food materials from soil through mineralisation by organic matter, food processing or environmental contamination, as in the application of agricultural inputs, such as Cu-based pesticides example fungicides. Kies and Harms (1989) state that adult human body contains about 1.5 ± 2.0 ppm of Cu which, according to Underwood (1977) and Schroeder (1973), is essential as a constituent of some metalloenzymes and required in haemoglobin synthesis and in the catalysis of metabolic oxidation. Symptoms of Cu deficiency in humans include bone demineralisation, depressed growth, depigmentation and gastro-intestinal disturbances. However, reports by Graham and Cordano (1976), Lucas (1974) and Somers (1974) indicate that Cu toxicity due to excessive intake causes liver cirrhosis, dermatitis, neurological disorders, brain damage, demyelization and renal disease. Copper toxicity is also usually characterized by metallic taste, chronic and intermittent nausea, headaches, abdominal

cramping and diarrhea, irritation of the nose, mouth and eyes, dizziness and vomiting, and deposition of the element in the cornea (Garrow and James, 1993; Davidson *et al.*, 1975).

When Cu ends up in the soil, it strongly attaches to organic matter and soil minerals. As a result, it does not travel very far after release and it hardly ever enters groundwater. It does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils, only a limited number of plants have a chance of survival. Due to the effects on plants, Cu is a serious threat to crop production on farmlands. The metal can seriously influence the productivity of certain farmlands, depending upon the acidity of the soil and the presence of organic matter (Patnaik, 1999).

Copper forms quite easily soluble minerals in weathering processes and release Cu ions, especially in acid environments. These Cu ions can readily precipitate with various anions such as sulphide, carbonate and hydroxide. The metal is therefore rather immobile in soils and shows relatively little variation in total content in soil cores. The common characteristic of Cu distribution in soil cores is its accumulation in the top horizon. Its accumulation in surface soils thus reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element (Kabata-Pendias, 2000).

Adsorption, occlusion and coprecipitation, organic chelation and complexing, as well as microbial fixation constitute the processes controlling fixation of Cu by soil constituents. The specific sorption of Cu is related to the reaction with electron-pair donors, and therefore forms strong bonds of high covalency (Kabata-Pendias, 2000).

Though the most mobile form of Cu in the soil is the cation with the valence of +2, several ionic species may also exist in the soil (Cu^{2+}, CuO, Cu, $CuCO_3$, $Cu(CO_3)_2^{2-}$, $CuOH^+$, $Cu(OH)_3^-$,$Cu(OH)_4^{2-}$ and $Cu_2(OH)_2^{2+}$). All these species may be adsorbed by soils but the hydroxide forms are the most readily adsorbed (Bodek *et al.*, 1988). At high pH, more of the

hydroxide species are formed due to the increase in OH^- concentration and hence more of the Cu ions get adsorbed and/or precipitated. Consequently, the Cu content in the soil solution become considerably reduced making less available for plant uptake.

All soil minerals are capable of adsorbing Cu ions but this property depends on the surface charge carried by the adsorbents which invariably is dependent on pH. Hence, the adsorption of Cu is a function of pH. Stevenson and Fitch (1981) indicate, in this regard, that the maximum amount of Cu^{2+} that can be bound to humic and fulvic acids is approximately equal to the content of acidic functional groups.

2.2.4 Iron

Iron is released into the environment by natural processes such as weathering, erosion, forest fires and wind-blown dust. It is also released by human activities such as mining, agriculture, rusting of automobile parts and factory machinery among others.

Iron is essential to most life forms and to normal human physiology. It is an integral part of many proteins and enzymes that maintain good health. Dallman (1986) explains that, in humans, Fe is an essential component of proteins and is involved in oxygen transport. It is also essential in the regulation of cell growth and differentiation (Andrews, 1999; Bothwell *et al.*, 1979).

Iron deficiency limits oxygen delivery to cells, resulting in fatigue and weakness, decreased ability to concentrate, hair loss, dizziness, headaches, brittle nails, apathy, depression and decreased immunity (Bhaskaram, 2001; Haas and Brownlie, 2001). In general, thus, adequate Fe in the body enhances oxygen distribution throughout the body, keeps the immune system healthy and helps the body produce energy.

Despite the seemingly overwhelming importance of Fe, Corbett (1995) explains that excess amounts of Fe can result in toxicity and even death as it exerts its most profound effects on the cardiovascular system. Toxicity results in fatty necrosis of the myocardium, postarteriolar dilatation, increased capillary permeability, and reduced cardiac output (Greentree and Hall, 1995). Excess amount also interferes with clotting mechanisms, augmenting hemorrhagic processes (Myers *et al.,* 1997; Goyer, 1996; Greentree and Hall, 1995; Osweiler *et al.*,1985) and has also been reported to cause thrombocytopenia (Hillman, 1995).

Iron poisoning due to the ingestion of large quantities causes nausea, vomiting, damage to the lining of the intestinal tract, shock and liver failure, loss of appetite, fatigue, weight loss, headaches, bronze or gray hue to the skin, dizziness and shortness of breath. In recent years, excess Fe intake and storage, especially in men, has been implicated as a cause of heart disease and cancer and its overdose has been reported by Corbett (1995) to be one of the leading causes of fatality from toxicological agents in children younger than 6 years.

The reactions of Fe in processes of weathering are dependent largely on Eh-pH system of the environment and on the stage of oxidation of the Fe compounds involved. The general rule governing the mobilization and fixation of Fe are that oxidizing and alkaline conditions promote the precipitation of Fe, whereas acid and reducing conditions promote the solution of Fe compounds. The released Fe readily precipitates as oxides and hydroxides, but it substitutes for Mg and Al in other minerals and often complexes with organic ligands (Kabata-Pendias, 2000).

Both mineral and organic compounds of Fe are easily transformed in soils, and organic matter appears to have a significant influence on the formation of Fe oxides. These metals may be amorphous, semicrystalline, or crystalline, even under the same conditions. The

content of soluble Fe in soils is extremely low in comparison with the total Fe content. Soluble inorganic forms include Fe^{3+}, $Fe(OH)_2^+$, $FeOH^{2+}$, Fe^{2+}, $Fe(OH)_3^-$ and $Fe(OH)_4^{2-}$.

In well aerated soils, however, Fe^{2+} contributes little to the total soluble inorganic Fe, except under high soil pH conditions. The concentration of Fe in soil solutions within common soil pH levels ranges from 30 to 550 µg/L, whereas in a very acid soil it can exceed 2000 µg/L. Acid soils are therefore higher in soluble inorganic Fe than are neutral and calcareous soils. Thus, Fe^{2+} cations when in acid anaerobic soils may become toxic, but in alkaline well-aerated soils, the low concentration of soluble Fe species may not meet plant requirements for this metal (Kabata-Pendias, 2000).

2.2.5 Manganese

Manganese occurs principally as pyrolusite (MnO_2) and to a lesser extent as rhodochrosite ($MnCO_3$) (Emsley, 2001). Manganese is naturally present in rocks, soil, water, and food. It is naturally present in food, with the highest concentrations typically found in nuts, cereals, legumes, fruits, vegetables, grains, and tea. It is also present at low levels in drinking water (Agency for Toxic Substances and Disease Registry (ATSDR), 2000; Pennington et al, 1986).

Manganese is required for growth, development and maintenance of health. It is necessary for skeletal system development, energy metabolism, activation of certain enzymes, nervous system function, immunological system function, reproductive hormone function and is an antioxidant that protects cells from damage due to free radicals (IOM, 2001; ATSDR, 2000).

Despite its use, Mn is toxic at high levels and causes various adverse effects in the respiratory tract and in the brains. Studies in animals have shown that very high levels of Mn in food or

water can cause changes in the brain. This suggests that high levels of Mn in food or water might cause brain injury but it does not appear that this is of concern to people exposed to the normal amounts of Mn in food, water or air. The USEPA has, however, determined that Mn is not classifiable as a human carcinogen (ATSDR, 2000).

In soils, the negatively charged $Mn(OH)_4^{2-}$ and MnO_2^{2-} are responsible for the high degree of association of Mn concretions with some heavy metals, in particular with Co, Ni, Cu, Zn,Pb, Ba, Tl, W and Mo. Additionally, the oxidation of As,. Cr, V, Se, Hg and Pu by Mn oxide is likely to control the redox behaviour of these elements in soils (Bartlett, 1986).

The solubility of Mn in soils is highly dependent on the pH and redox potential. Therefore, the most common reactions occurring in soils are oxidation-reduction and hydrolysis. The solubility of soil Mn is of significance since the plant supply of Mn depends mainly on the soluble Mn pool in the soil. In well-drained soils, the solubility of Mn always increases with the increase of soil acidity. However, the ability of Mn to form anionic complexes and to complex with organic ligands may contribute to increased Mn solubility in the alkaline pH range.

2.2.6 Nickel

Organic matter has a strong ability to adsorb nickel and as a result coal and oil contain considerable amounts of Ni. Nickel is released into the air by power plants and trash incinerators. It is also released by the combustion of fuel by automobiles. The larger part of all Ni compounds that are released to the environment are adsorbed to sediment or soil particles and become immobile. The element is not known to accumulate in plants or animals.

As a result, it does not biomagnify up the food chain (Yaman, 2000; Rasmussen *et al.*, 1988; Grandjean, 1984).

Nickel plays important roles in the biology of microorganisms and plants: Urease (an enzyme which assists in the hydrolysis of urea) contains Ni; the NiFe-hydrogenases contain Ni in addition to iron-sulfur clusters; a nickel-tetrapyrrole coenzyme, F430, is present in the methyl coenzyme M reductase which powers methanogenicarchaea; one of the carbon monoxide dehydrogenase enzymes consists of an Fe-Ni-S cluster; and other Ni-containing enzymes include a class of superoxide dismutase and a glyoxalase (Szilagyi *et al.*, 2004; Thornalley, 2003).

Excess of Ni can be very dangerous. Symptoms of Ni toxicity include skin rash (called nickel dermatitis), nausea, dizziness, diarrhea, headache, vomiting, chest pain, weakness and coughing. Contact with nickel vapor can lead to swelling of the brain and liver; degeneration of the liver; irritation to the eyes, throat and nose; and various types of cancer. The most common harmful health effect of Ni in humans is an allergic reaction (Grandjean, 1984).

Nickel is easily mobilised during weathering and then is coprecipitated mainly with Fe and Mn oxides (Kabata-Pendias, 2000). However, unlike Mn^{2+} and Fe^{2+}, Ni^{2+} is relatively stable in aqueous solutions and is capable of migration over a long distance. In surface soil horizons, Ni appears to occur mainly in organically bound forms, a part of which may be an easily soluble chelate (Bloomfield, 1981).

Nickel distribution in soil cores is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types. Concentrations of Ni in natural solutions of soil horizons of different soils vary from 3 and 25 µg/L at the boundary and at the centre of the affected area, respectively (Anderson *et al.*, 1973). Information on Ni ionic species in the soil

solution is rather limited but the Ni species described by Garrels and Christ (1965) such as Ni^{2+}, $NiOH^{+}$, $HNiO_2^{-}$, $Ni(OH)_3^{-}$ are likely to occur when the Ni is not completely chelated.

Generally, the solubility of soil Ni is inversely related to the soil pH. The Ni sorption on Fe and Mn oxides is especially pH dependent probably because the $NiOH^{+}$ is preferentially sorbed and also because the surface charge on the sorbent is affected by pH (Bodek *et al.*, 1988).

2.2.7 Lead

Lead pollution in the environment is primarily known to be sourced from industrial production processes and their emissions, road traffic with leaded petrol, the smoke and dust emissons of coal and gas-fired power stations, the laying of lead sheets by roofers as well as the use of paints and anti-rust agents (Ve´ron *et al.*, 1999).

Basically, as a result of their comparatively high affinity for proteins, Pb ions, when ingested, bond with the haemoglobin and the plasma protein of the blood. This leads to inhibition of the synthesis of red blood cells and thus of the vital transport of oxygen. If the bonding capacity is exceeded, Pb passes into the bone-marrow, liver and kidneys. Chronic intoxication leads to severe complications such as encephalopathies in the central nervous system (CNS), disturbances in kidney and liver functions progressing as far as necrosis, damage to the reproductive organs, anaemia and many metabolic deficiency symptoms (Vitošević *et al.*, 2007). Little is known about the excretion of Pb, once it has been absorbed. Thus, a large percentage of the metal accumulates in the body (ATSDR, 2000).

Lead is the least mobile of all heavy metals. A high soil pH may precipitate Pb as hydroxide, phosphate or carbonate. The metal forms Pb^{2+} though its oxidation state is +4. The natural Pb

content is strongly related to the bedrock and this is supported by the relatively low concentration in natural soil solutions. For instance, in a study of heavily Pb polluted soils, the formation of pyromorphite, $Pb_5Cl(PO_4)_3$, was observed. It was also observed that the concentration of the mineral was mainly close to the grass (*Agrostis capillaris*) and hence indicated an influence of the rhizoshere on the process of its formation (Kabata-Pendias, 2000). Therefore, natural systems are known to contribute to the formation and distribution of Pb.

2.2.8 Zinc

Zinc ores include Zinc blende or sphalerite (a form of zinc sulfide), wurzite, smithsonite and hemimorphite (Emsley, 2001). It is the 24th most abundant element in the earth crust and it is no surprise it occurs in air, water and soil due to natural processes such as weathering and erosion. The addition of Zn through human activities such as mining, coal and waste combustion and steel processing has increased its concentration in the environment.

Zinc metal is included in most single tablets and it is believed to possess anti-oxidant properties which protect against premature aging of the skin and muscles of the body (ATSDR, 2000).

However, zinc deficiency usually results from poor diet, alcoholism and malabsorption. Zinc deficiency symptoms include decreased sense of taste and smell, dwarfism, hypogonadism and dermatitis whereas toxicity of Zn may lead to electrolyte imbalance, nausea, anaemia, birth defects and lethargy (Dibley 2001; Garrow and James, 1993; Fairweather-Tait, 1988; Prasad, 1984 and 1976).

Zinc accumulates in surface soils as it is easily adsorbed by mineral and organic components. On weathering, Zn^{2+} is released. However, ZnO_2^{2-}, ZnO_2^{-}, $Zn(OH)_3^{-}$, $ZnCl^{+}$ and $ZnHCO_3^{+}$ are some of the other ionic species in which Zn may exist in the soil. Though the factors controlling the mobility of Zn are similar to that of Cu, the metal appears to occur in more readily soluble forms (Kabata-Pendias, 2000).

Two different mechanisms of Zn adsorption are known. Firstly, in acid media, it is related to cation exchange sites, and in alkaline media it is considered to be chemisorptions and is highly influenced by organic ligands (Lindsay, 1972). Nucleation of Zn hydroxide on clay surfaces may produce a strongly pH-dependent retention of Zn whereas the adsorption of Zn^{2+} can be reduced at lower pH (< 7) by competing cations and this will result in easy mobilisation and leaching of Zn from light acid soils (McBride and Blasiak, 1979).

2.3 HEAVY METALS AND SOIL

Soils contain trace levels of metals due mostly to the natural abundances of some metals (McLean and Bledsoe, 1992). Soil, being the interface between the atmosphere and the earth crust as well as the substrate for natural and agricultural ecosystems, is open to inputs of heavy metals from many sources. Concentration of metals in uncontaminated soils has been primarily related to the geology of the parent material from which the soil is formed (McLean and Bledsoe, 1992). Relatively, pristine soils normally contain low background levels of heavy metals as compared to soils in areas where agricultural, industrial or municipal wastes are land-applied as fertilizer. Thus, depending on the surrounding geological environment and anthropogenic and natural activities occurring or once occurred, many soils contain a wide range of heavy metals with varying concentration ranges.

Principally, the sources of heavy metals in the soil are natural processes such as weathering and, also human activities such as mining and application of fertilizers and pesticides. Mining, manufacturing and the use of synthetic products (e.g. pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge) have resulted in heavy metal contamination of urban and agricultural soils. Potentially, contaminated soils may occur at old landfill sites, particularly those that accepted industrial wastes, old farms that used insecticides, fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites (Akabzaa *et al.*, 2005; Asante *et al.*, 2005; Bonzongo *et al.*, 2004; Vernet, 1992; Ahenkorah *et al.*, 1982).

2.3.1 Agrochemicals and Heavy Metals in Soil

According to Foster Wheeler Environmental Corporation (1998), a wide variety of unsafe metals may exist in fertilizers and fungicides which may include: arsenic, lead, cadmium, copper and mercury. This is validated by many studies (Dubey and Townsend, 2004; Wilcke and Döhler, 1995; Faβbender and Bornemisza, 1987; Lepp *et al.*, 1984; Cordero and Ramirez, 1979).

Giuffre *et al.* (1997) also found out that continuous application of fertilizers to the soil may increase the heavy metal concentration thereby exceeding the natural abundances in soils, and transfer of these metals to the human food chain despite the fact that these heavy metals may be present in minute quantities in fertilizers.

Nevertheless, fertilizers are basically chemicals applied to the soil to promote plant growth (McLaughlin *et al.*, 1996). The main nutrients (macronutrients) present in fertilizers include

nitrogen, phosphorus and potassium. Other secondary macronutrients which include sulphur, calcium and magnesium are sometimes added in minute quantities. Additionally, there are micronutrients which are added in smaller amounts such as boron, chlorine, manganese, iron, zinc, copper, molybdenum, selenium and cobalt (Fertilizer Industry Federation of Australia (FIFA), 2008; Mills and Jones, 1996).

Commercial fertilizers have been used for decades and will continue to be used for years to come. Some commercial fertilizers, however, are made from recycled hazardous waste materials including highly toxic metals and chemicals produced for public use (Heckman and Barbour, 2005). Phosphorus fertilizers contain varying amounts of heavy metals and other rare earth elements as contaminants. These contaminants may either come from the phosphate rock ores or other ingredients used in the phosphate fertilizer industry. According to Taylor (1997), application of phosphate fertilizers is the main pathway through which Cd accumulates in the soil. He also noticed that the concentration of up to 100 mg/kg of Cd in phosphate minerals increased the contamination of soil with Cd in New Zealand. Syers *et al.* (1986) and Trueman (1965) found similar observations in soils of Nauru and the Christmas Island, respectively. Hence, even low annual accumulations of metals may finally build up undesired concentrations in soils, especially where fertilizers with high heavy metals or rare earth element concentrations are used.

In Ghana, two main types of fertilizer formulations are used in the Hi-Tech Programme undertaken by Ghana Cocoa Board. These fertilizers have been tested and approved to be used on cocoa by Cocoa Research Institute of Ghana (CRIG). They include: granular fertilizers – "Asaasewura" and "Cocofeed", and liquid fertilizer – "Sidalco". Table 2.1 presents fertilizers, fungicides and insecticides (including their active ingredients) that are recommended by Ghana Cocoa Board.

Table 2.1: Recommended agrochemicals in Ghana

Agrochemical type	Trade name	Active ingredient (a.i.)
Fertilizer	Asasewura	NPK: 0-22-18 + 9CaO + 6S+ 5MgO
	Cocofeed	NPK: 0-30-20
	Sidalco NPK	NPK:15-15 -15 + 2MgO + 3Zn
Fungicide	Funguran	300 g/L of Cu metal as cupric hydroxide.
	Champion	Cupric hydroxide
	Nordox	Cuprous oxide, Cr_2O
	Ridomil Gold Plus	Metalaxyl and copper oxychloride
	Fungikill	35% Copper + 15% Metaxyl
Insecticide	Confidor	200 g/L Imidacloprid
	Actara	240 g/L Thiamethoxam (a.i.) + 0.03% 1, 2-benzisothiazolin-3-one as a preservative.
	Akatemaster	27 g Bifenthrin

Source: Ghana Cocoa Board, 2011.

Recommendations on the application of these agrochemicals by Ghana Cocoa Board, are as follows: For the granular fertilizers, 1 kg to a hectare of cocoa farm should be applied; spraying of fungicides must be done at three weekly intervals for six to nine times in the crop season (the crop year begins in October, when purchases of the main crop begin, while the smaller mid-crop cycle starts in July); from August, spraying should be done against capsids using the recommended insecticides only – spraying should be done once in August, September, October and December (Ghana Cocoa Board, 2011). From Table 2.1, agrochemicals applied in cocoa farms in Ghana have some heavy metals in them.

The levels of metals in the soil have direct effect on plants (Hall and Robarge, 2004; Kabata-Pendias, 2000). For example, variation in soil nutrient levels, including metals, influences plant species composition and growth (Etherington, 1982). Tudureanu and Phillips (2004) reported that Cd can accumulate in plants and not have any effect on the plants but will be toxic to animals and humans that eat them. Soils can be contaminated by the heavy metals which will bioaccumulate in plants and animals eventually making their way to humans through the food chain of humans (Frink, 1996).

The transport of heavy metals in the soil is not only dependent on the properties of the metals but mostly on the physicochemical properties of the soil, viz. clay content, pH, soil organic matter content, cation exchange capacity and mineralogical composition.

2.4 HEAVY METAL MOBILITY

Generally, metals added to soil will stay at the soil surface. Movement to groundwater, surface water, or the atmosphere is minimal as long as, according to McLean and Bledsoe (1992), the retention capacity of the soil is not exceeded. Normally, metals do not travel downward from the soil surface to any great extent. Their movement in soil is directly related to the surface chemistry of the soil matrix and soil solution (Sposito, 1989). Thus, when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility.

At the same time, metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation/reduction

reactions, precipitation/dissolution reactions, and adsorption/desorption reactions (Wilcke *et al.*, 1996; Kabata-Pendias, 1993).

Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. Metals associated with the aqueous phase of soils are subject to movement with soil water, and may be transported through the vadose zone to groundwater. Metals, unlike the hazardous organics, cannot be degraded. However, some metals, such as Cr, can be transformed to other oxidation states in soil, reducing their mobility and toxicity (Kabata-Pendias, 1993; Bohn *et al.*, 1985).

In general, the mobility of metals from soil to plants is a function of the physical and chemical properties of soil and plant species, and it is altered by environmental and human factors (Wilcke *et al.*, 1998; Cabrera *et al.*, 1992; Basque *et al.*, 1990; Haghiri, 1973).

Adsorption processes are also affected by the form of the metal added to the soil and by the solvent introduced along with the metal. These interactions can either increase or decrease the movement of metals in soil water. Soils with heavier textures and higher pHs are effective in attenuating metals, while sandy soils and/or soils with low pH do not retain the metals effectively (McLean and Bledsoe, 1992). Korte *et al.* (1976), in their research, observed that Pb and Cu are the least mobile cationic metals whereas Cr is considered quite mobile. The principal soil surface that controls the mobility of metals in soils and natural water, according to Blume and Schwertmann (1969), and Jenne (1968), is Fe and Mn oxides.

2.4.1 Effect of Clay content on Heavy Metal Accumulation in Soils

Heavy metals tend to accumulate in the clay fraction of most soil cores (Lee *et al.*, 1997; Boon and Soltanpour, 1992). Boon and Soltanpour (1992) conclude that the concentration of heavy metals in soil is sometimes dependent on clay content because clay-sized particles have a large number of ionic binding sites due to the larger surface area.

The effect of clay mineralogy on heavy metals geochemistry has been shown by many studies (Andras *et al.*, 2009; Onweremadu, 2008; Amusan and Adeniyi, 2005; Sipos and Némeh, 2001; DeMatos *et al.*, 2001; Kabata-Pendias, 1993; McBride, 1991). In several studies, kaolinite was found to be a very good sorbent of the majority of the heavy metals considered in those studies (Gupta and Bhattacharyya, 2008; Wahba and Zaghloul, 2007). A sorption/desorption study of heavy metals on competing clays also showed that Cu, Pb and Zn were preferentially fixed on smectites and that Pb was also fixed on illite (Brigatti *et al.*, 1996; Rybicka *et al.*, 1995; Griffin and Shimp, 1978; Griffin and Au, 1977).

A study by Matini *et al.* (2011) on the clay mineralogy responsible for the vertical distribution of Pb, Zn and Cu in the core of an abandoned treatment plant in Mfouati (south east of Congo-Brazzaville) revealed that Kaolinite (1:1 type clay minerals) was more present in all the soil cores in high amount than chlorite and smectite and could control the vertical migration of Pb, Zn and Cu.

Clay particles are usually negatively charged. This is a very important factor influencing sorption properties of the soil. There are at least two major possibilities as to how these charges are formed (Loughnan, 1969). Firstly, the hydroxyl groups which exist on the edges and on the outer layers of minerals can dispose of hydrogen which is bonded with oxygen probably covalently, not very tight. This is a pH-dependent process and the ability to split the hydrogen atom decreases when pH decreases. When pH is above 6 hydrogen may easily be

replaced by other ions like Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}. The second process of creating negative charges is connected to the isomorphous ion replacement in the minerals. In the silica tetrahedral, Al^{3+} can replace the silicon ion Si^{4+} because these two have a similar ionic radius, whereas Mg^{2+} and Fe^{2+} can exist in the octahedral layers instead of Al^{3+}. The negative charge, which appears as a result of isomorphous ion replacement, is not pH-independent and therefore quite persistent. The ability to create negative charges is highest for 2:1 type of clays (Brown, 1998; Dobrzański and Zawadzki, 1993). Clays thus usually act as adsorbents and play an important role in ion exchange reactions (Barrow, 1999; Brigatti *et al.*, 1996).

2.4.2 Effect of Soil pH on Heavy Metal Accumulation in Soils

The pH of soil affects several mechanisms of metal retention by soils according to several studies (Li and Wu, 1999; Peles *et al.*, 1998; Chen *et al.*, 1997; McLean and Bledsoe, 1992; Cataldo *et al.*, 1981). In general, adsorption of cationic metals increases with increasing pH. A study by Harter (1983) of Pb, Ni, Zn, and Cu concluded that the retention of metals did not significantly increase until the pH was greater than 7.

Li and Wu (1999) explained that as soil pH decreased, heavy metals were desorbed from organic and clay particles, entered the soil solution and became more mobile. However, when the pH was higher (pH > 7) heavy metals remained adsorbed, and those in solution precipitated out in the form of salts (Chen *et al.*, 1997). Consequently, variability in pH affects the amount of heavy metal assimilated by plants. For example, John and VanLaerhoven (1972) showed that higher pH resulted in lower Cd uptake. Peles *et al.* (1998) concluded in his study that the addition of lime to contaminated soils (essentially increasing the pH) decreased the uptake of heavy metals by *Ammbrosia trifida*, while in unlimed soils,

uptake increased – it accumulated 2.5 µgCd/g of tissue in limed soils in contrast to a 13.6 µgCd/g of tissue in unlimed soils.

Johnson (1992) observed that soils became more acid when excess hydrogen (H) and aluminium (Al) ions replaced basic cations such as Ca, Mg, K, and Na on the surface of clays and soil humus. The basic cations were often leached below the root zone, leaving H and Al behind because they were more strongly attached to the negative charges on the soil surface. Conversely, any processes (such as liming, weathering and recycling of cations by deep-rooted plants which brought cations to the surface and incorporated them in the topsoil) that would encourage high levels of the exchangeable base forming cations (Ca, Mg, K, Na) would contribute toward an increase in alkalinity. His research again revealed that when the soil pH was too high, deficiencies of Fe, Mn and other micronutrients occurred. This observation is buttressed by a study by Gauch (1972) which noted that the concentration of Fe in a soil solution was markedly affected by pH, since pH values of 7 or higher drastically reduced the availability of Fe to plants because of the precipitation of Fe in the soil.

McLean and Bledsoe (1992) attributed this pH dependence of adsorption reactions of cationic metals partly to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal ion. The proportion of hydrolyzed metal species increases with increasing pH.

2.4.3 Effect of Organic Matter on Heavy Metal Accumulation in Soils

Soil organic matter (SOM) is a term generally used to represent the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition products, and soil biomass. Thus, this term includes: identifiable, high-molecular weight organic materials such as polysaccharides and proteins, simpler substances such as sugars, amino acids, and

other small molecules and humic substances (Jobbagy and Jackson, 2000; Stevenson, 1992; Schulten *et al.*, 1991). Principally, SOM is frequently said to consist of humic substances and nonhumic substances. Nonhumic substances are all those materials that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fats and so on. Humic substances are the other, unidentifiable components.

Soil Organic Matter may range in soils from 0.1% in desert soils to 90% in organic soils. Humic substances make up approximately 85-90% of the total organic carbon in soils (Giesking, 1975; Grim, 1968). Humic substances consist of a heterogeneous mixture of compounds for which no single structural formula will suffice. There is no strict chemical formula for these materials, though substantial evidence exists that humic materials consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone and quinone groups (Schulten *et al.*, 1991). Humic substances are traditionally defined according to their solubilities. Fulvic acids are those organic materials that are soluble in water at all pH values. Humic acids are those materials that are insoluble at acidic pH values < 2. Humin is the fraction of natural organic material that is insoluble in water at all pH values (Grim, 1968).

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

(CEC) is also very high for soil organic matter, especially for fulvic acids according to clay minerals (Stevenson, 1992).

2.4.4 Effect of Cation Exchange Capacity on Heavy Metal Accumulation in Soils

Cation exchange capacity (CEC) is simply a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged ions (cations) such as Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. It may range from 2.0 cmol/kg for sand to > 50 cmol/kg for some clay, and humus 100-300 cmol/kg under certain soil conditions. Thus, CEC is influenced by pH, clay and organic matter content.

A study by Johnson (1992) concluded that the nutrient holding capacity of soil is largely determined by the cation exchange capacity (CEC). The larger the CEC number, the more cations the soil can hold as a result of the many negative charges available on the soil surface. Thus, soils with higher CEC values are more likely to attenuate cations than those with lower values. In view of this, soils rich in plant nutrients but with very high CEC may not support plant growth due to the almost unavailable or slow release of nutrients into soil solution for uptake by roots of plants. Conversely, soils rich in plant nutrients but with very low CEC values may have most of their nutrients in the soil solution available for uptake by plants but may be greatly at risk of heavy leaching.

2.5 DEPTH DISTRIBUTION OF METALS

Depth distribution of metals in soil cores is indicative of weathering and soil genesis and anthropogenic pollution (Jin *et al.*, 2005). Generally, the distribution of heavy metals in

soil is influenced by the nature of parent materials, climatic conditions and their relative mobility depending on soil parameters such as mineralogy, texture, and classification of soil (Krishna and Govil, 2007; Filipinski and Grupe, 1990).

Heavy metals are more strongly sorbed to Fe oxides (Brummer *et al.*, 1986) and, thus, depending on the distribution of Fe oxides along the depths of tropical soils, the consequence would be a different depth distribution of pedo-/geogenic metals in soil cores of the tropical and the temperate zones, and even in soil cores within the tropics.

Most soil cores have an A horizon, which is primarily topsoil composed of decaying organic matter such as leaves and grass, and a B horizon, which is composed of smaller clay-sized particles. In general, heavy metal concentrations are higher in the B horizons than in the A horizons (Lee *et al.*, 1997). According to Boon and Soltanpour (1992) and Khan and Frankland (1983), due to the immobilization of heavy metals, there is little leaching through the soil core. Immobilization, however, can increase the Cd concentration of soil with a concomitant toxicity of the contaminated soil.

2.6 ANALYTICAL METHODS FOR SOIL ANALYSIS

Elements in soils can be determined in the laboratory using the following fixed laboratory assays: Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X−ray fluorescence (XRF), Electron Microprobe (EM), Flame Photometer (FP) and Instrumental Neutron Activation Analysis (INAA). These instruments accurately measure elements in

environmental sample to parts per billion (ppb) concentrations i.e. µg L^{-1} and µg kg^{-1} solid samples respectively (Melamed, 2005).

The choice of a particular technique, however, depends on factors such as speed of analysis, availability of the instrument, technical expertise of the analyst or technician and the cost of analysis among others (Skoog *et al.*, 1998). In this study, ICP-AES was used to determine the total and exchangeable concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn whereas, for the concentrations of exchangeable bases, AAS (for Ca and Mg) and FP (for Na and K) were used.

Before any element is determined with any of these instruments, pre-treatment of sample with acidic extraction (acidic oxidation digestion) or with target reagents is required. The significance of pre-treatment is that all elemental species is converted into the inorganic form for easier detection and measurement. These laboratory assays measure elements accurately but they are expensive to operate and maintain. They are also bulky, requiring fully equipped and staffed laboratories to maintain and operate. Below is the list of the different instruments employed in this study and their operations:

2.6.1 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Inductively Coupled Plasma-Atomic Emission Spectrometry is a hyphenated analytical technique which measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices (Jeffery *et al.*, 1989).

Background correction is required for trace element determination. Background is measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, is determined by the complexity of the spectrum adjacent to the analyte line (Jeffery *et al.*, 1989). Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed (Jeffery *et al.*, 1989).

2.6.2 Atomic Absorption Spectroscopy (AAS)

It is a technique in which the absorption of light by free gaseous atoms in a flame or furnace is used to measure the concentration of atoms. Atomic Absorption Spectroscopy is based on absorption of monochromatic light by a cloud of atoms of the analyte metal. In AAS, a liquid sample is aspirated into a nebulizer system. The sample then mixes with an oxidant gas which is drawn under pressure into a burner to form an aerosol. The flame which uses either air-acetylene or nitrous-oxide acetylene operates at a temperature of 2400 ^{0}C and 2800 ^{0}C respectively.

Within the flame, the aerosol undergoes processes such as evaporation of the solvent and excitation of the gaseous metallic element. To determine the concentration of the analyte, a light beam from a lamp usually a Hollow Cathode Lamp (HCL) whose cathode is made of the element being determined is passed through the flame. A photomultiplier tube attached to the AAS can detect the amount of reduction of the light intensity due to absorption (absorbance) by the analyte. The absorption is proportional to the concentration of the metal ions following the Beer-Lambert Law (Skoog *et al.*, 1998).

2.6.3 Flame Photometry (FP)

Flame Photometry is simply a modification of flame test. In the instrumental technique of flame photometry, a monochromator replaces the coloured glass filter, and a photocell detector/readout replaces our eye. Also, the burner design is more sophisticated in that the sample is continuously fed into the flame by aspiration.

Since each element emits its own characteristic line spectrum, qualitative analysis can be performed here by observing what wavelengths are emitted and comparing these with various standards. However, since the detector is capable of measuring light intensity, qualitative analysis, as well as, quantitative analysis is possible: the intensity of the emitted light increases with concentration.

In short, FP is an atomic technique which measures the wavelength and intensity of light emitted by atoms in a flame resulting from the drop from the excited state (formed due to absorption of energy from the flame) to lower states. Flame photometry, thus, uses flame atomic emission and a filter to quantify elements like Li, Na, K and Ca in liquid samples. No light source is required since the energy imparted to the atoms comes from the flame and, hence, FP is different from AAS.

CHAPTER THREE

3.0 METHODOLOGY

3.1 INTRODUCTION

Effective pest control and fertilizer application in cocoa production constitute the predominant factors that may lead to heavy metal pollution of cocoa growing soils (Vigneri, 2007). Agrochemicals' application on cocoa farmlands as well as mining activities in and around cocoa communities in the Western Region of Ghana makes soils in this area susceptible to heavy metal contamination as many studies in areas under similar conditions have shown (Faβbender and Bornemisza, 1987). This chapter describes the fieldworks, procedures for sample collection, sample preparation, sample treatment and analysis carried out to ascertain whether long years of agrochemical application may have led to contamination of some selected cocoa growing soils in Western Region.

3.2 SELECTION OF STUDY AREA

Though some overlap, there exist differences in the type of soils in the Western Region. In this study, four major soil types were considered. These are Ferric Acrisol, Dystric Fluvisol, Haplic Luvisol and Haplic Ferrasol, with the selection being based on predominance. In all, the study covered eight (8) major cocoa farming communities in the Western Region of Ghana (Fig. 3.1). The farming communities were selected based on purposive and stratified sampling to reflect the soils'geographical abundance in the Western Region, agrochemicals' application, nearness to mining sites and volume of cocoa production.

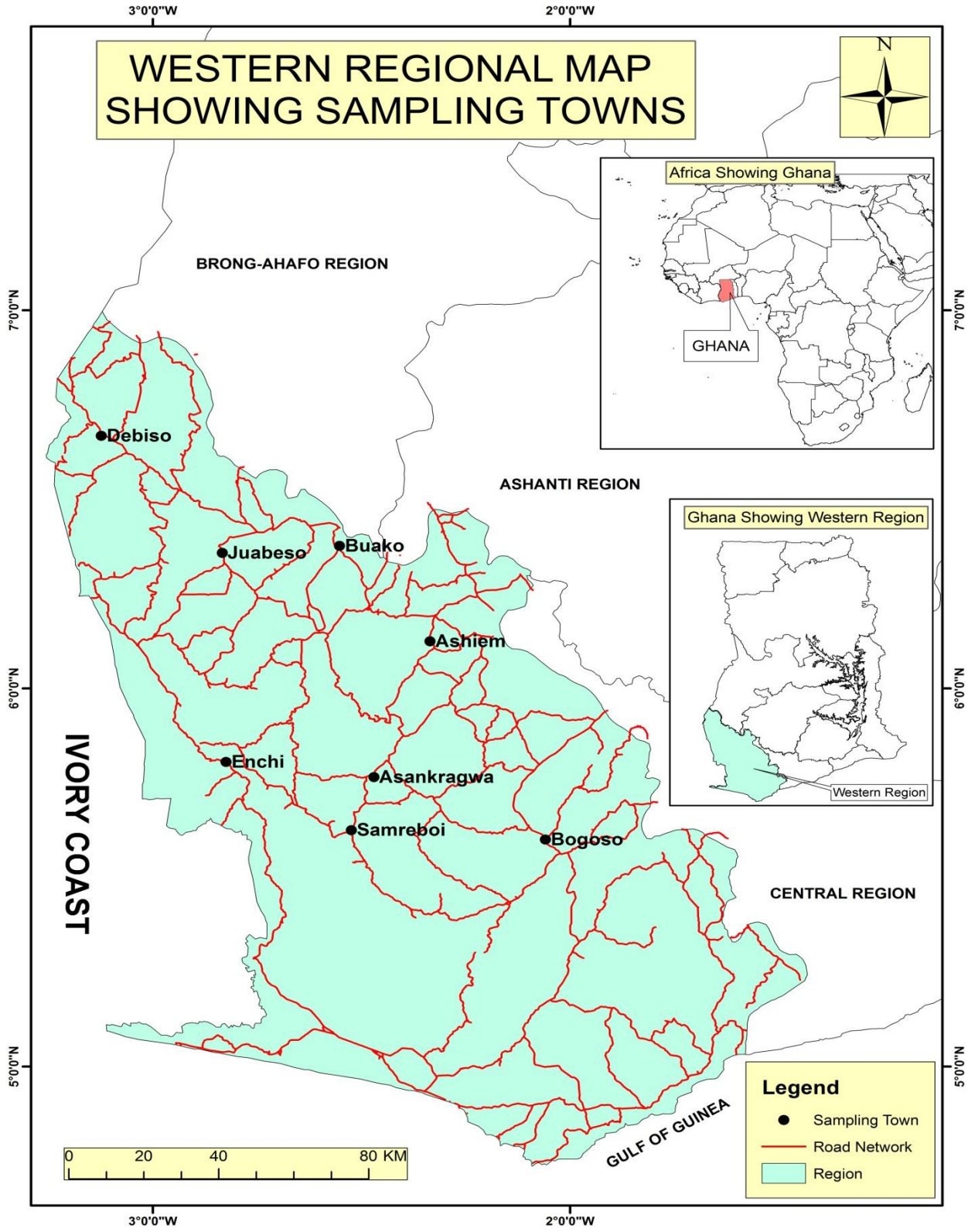


Figure 3.1: Map of Africa, Ghana and Western region indicating the sampling towns

Figure 3.2: A cocoa farm at Asankragwa (Ferric Acrisol)

Figure 3.3: A cocoa farm at Enchi (Dystric Fluvisol)

3.3 PHYSIOGRAPHY OF STUDY AREA

The Western Region of Ghana has over 75% of its vegetation within the high forest zone of Ghana. Agriculture thus, is the biggest industrial activity employing a large majority of workers in the region.

The climate is characterized by moderate temperatures ranging from 22 ^{o}C at nightfall to 34 ^{o}C during the day. The region is the wettest part of Ghana with a double maxima rainfall pattern averaging 1600 mm per annum. The two rainfall peaks fall between May–July and September/October. In addition to the two major rainy seasons, the region also experiences intermittent minor rains all the year round. This high rainfall regime creates much moisture culminating in high relative humidity, ranging from 70 to 90% in most parts of the region. It is a major cocoa growing region and because of the high humidity, the crops are prone to fungal attack, particularly the Black Pod disease. A lot of fungicides are therefore used.

The region is characterised by Tarkwaian and Birrimian rocks. These rocks are believed to have resulted from folding, faulting, metamorphosis, igneous activity, erosion and sedimentary process giving rise to the region's gold belts that exist today (Brash, 1962). Most soils in the region developed over lower Birrimian phyllites and greywacke, such as Nzima-boi, which consists of yellowish brown silty clay loam, with few quartz gravels and stones overlying yellowish red, very gravelly and stony silty clay (*Nzima series*), while others developed over Tarkwaian sandstones, quartz and phyllites (such as the Juaso and Bompata series – *Juaso series* occur on summits and upper slopes. The profile consists of deep, dark reddish brown, sandy clay loam topsoil. This overlies dark red or red sandy clay loam having abundant ironstone concretion and quartz gravels, overlying decomposing rock, and *Bompata series* consist of deep, reddish brown sandy loam topsoil overlying very deep, medium sub-angular blocky, red clay; grading into red, firm clay with few ironstone concretions and

quartz gravels) (Brammer, 1962). Others also developed over alluvial deposits as both small and large flowing water bodies are prevalent in the region. The predominant soil association is Nzima-Boi and the predominant soil type is the Acrisols. These soils have great agriculture value – they support all forms of arable crops such as cocoa, coffee, oil palm and cassava, and hence the region's overwhelming success in cocoa production.

3.4. SOIL SAMPLING

Soil samples were collected from the study area in October 2011. Samples were collected from the eight (8) cocoa farming communities with history of at least ten years of agrochemical application. Samples from Asankragwa and Bogoso were close to small scale mining sites but the rest were not. Additionally, soil samples were taken from three (3) natural forests (sites ABA, JUD and SEN) as pristine reference not directly affected by agrochemical inputs (Table 3.1).

Each chosen farm was divided into grids using poles (sticks) on one side and some cocoa trees perpendicular to the poles. Labels of A1, A2, A3, B1 etc were used to identify the quadrants formed. The various quadrant names were written on pieces of papers, folded, thoroughly mixed and five (5) were picked (Carter, 1993). Soil samples were taken at increasing defined depths of 0-10, 10-30, 30-50, 50-80 and 80-100 cm at each quadrant.

Five (5) soil core samples from each of the randomly selected quadrants at the respective aforementioned depths were taken with a pre-calibrated 1-metre auger. The core samples from each of the corresponding same depths of the five quadrants were bulked to form a composite sample. These culminated in five composite core samples per farm. Samples were then put into well labelled polypropylene zip-loc bags (Figs. 3.3 - 3.6). In order to distinguish the different depths of a site from each other, 1, 2, 3, 4 and 5 were used to indicate depths 0-

10, 10-30, 30-50, 50-80 and 80-100 cm, respectively. However, at some sites, not all the depths were accessible to be sampled due to the presence of gravels and stones at deeper depths. A Global Positioning System (GPS) device was used to map out the sampling sites (Table 3.1). All samples were then transported to the Ecological laboratory of the University of Ghana, Accra for sample preparation.

Table 3.1: Location and soil type of sampling sites

Farm (code)	Code Interpretation	Location	Latitude	Longitude	ᵅSoil association	ᵅSoil type
ABA*	ACf Pristine	Asankragwa	05º45.940'N	002º28.219'W	Nzima – boi	ACf
ASA	Asankragwa	Asankragwa	05º45.960'N	002º28.236'W	Nzima – boi	ACf
ASH	Ashiem	Ashiem	06º07.495'N	002º20.168'W	Nzima – boi	ACf
BOG	Bogoso	Bogoso	05º36.032'N	002º03.557'W	Juaso–bompata	ACf
BUA	Buako	Buako	06º22.631'N	002º33.182'W	Sefwi	FRh
DEB	Debiso	Debiso	06º40.098'N	003º07.436'W	Subin	LVh
ENC	Enchi	Enchi	05º48.364'N	002º49.483'W	Alluvial	FLd
JUA	Juabeso	Juabeso	06º21.516'N	002º50.024'W	Subin	LVh
JUD*	LVh Pristine	Debiso	06º40.277'N	002º50.423'W	Subin	LVh
SAM	Samreboi	Samreboi	05º37.534'N	002º31.460'W	Alluvial	FLd
SEN*	FLd Pristine	Enchi	05º48.228'N	002º49.650'W	Alluvial	FLd

* = natural forest as pristine reference; ACf = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol;

ᵅ. sources: 1. Ahenkorah (1981); 2. Adu and Mensah-Ansah (1969).

Figure 3.4: Taking soil samples from ASH (Ashiem, Ferric Acrisol) with an auger

Figure 3.5: Taking soil samples from SAM(Samreboi, Dystric Fluvisol) with an auger

Figure 3.6: Soil sample in a well labelled polypropylene zip-loc bag

3.5 SAMPLE PREPARATION

The soils were air-dried at room temperature for three (3) weeks. They were then disaggregated using porcelain pestle and mortar, and sieved with a 2-mm nylon mesh to give the fine earth fraction. The fine earth fraction (< 2mm) was then used for the various analytical determinations.

3.5.1 Containers and Cleaning Process

All glassware and high density polyethylene containers to be used in the analytical determinations were immersed in a warm liquid soap bath for two days. They were then rinsed with deionised-water (DI-water) and left immersed in 10% HNO_3 at room temperature for three days. Flasks were again rinsed three times with DI-water and afterwards immersed

in 50% HNO_3 bath at 90 ºC for 24 hours. They were further rinsed with DI-water several times and placed overnight in a clean oven at 60 ºC, then removed from the oven and allowed to cool down. They were then double bagged in new polyethylene bags and stored under room temperature.

3.6 SOIL ANALYSES

3.6.1 Soil Particle Size Analysis

Forty grams of the fine earth fraction of the soil was weighed into a plastic bottle and 100 mL of 5% calgon (sodium hexametaphosphate) solution was added. The content of the bottle was then shaken on a mechanical shaker for 2 hours after which it was transferred into a 1.0 litre measuring cylinder and topped up to the mark with distilled water. The suspension was then agitated with a plunger and five minutes thereafter, the density of the suspension (silt and clay) was taken using a hydrometer. The hydrometer reading of the suspension was taken again after eight hours (clay). The temperatures of the suspensions, T_1 and T_2, were respectively recorded during the 5 minute and 8 hour hydrometer readings. The contents of the cylinder after the eight hour reading were emptied onto a 47-µm sieve. The sand retained on the sieve was then washed off into a moisture can and dried at 105 ºC for 24 hours, after which the dry weight of the sand was recorded (FAO, 1974; Day, 1965). Blank sample hydrometer readings at five minutes and eight hours were also taken for the 5% calgon solution topped up to 1.0 L. The particle size distribution was then determined using the formulae below.

Temperature of the suspensions at T_1 and T_2 = 28 °C

$$\% \text{ Clay and Silt} = \frac{5 \text{ minute reading} - \text{correction for temperature}}{\text{oven dry mass of soil sample}} \times 100\% \quad \text{..... Equation 3.1}$$

$$\% \text{ Clay} = \frac{8 \text{ hour reading} - \text{correction for temperature}}{\text{oven dry mass of soil sample}} \times 100\% \quad \text{..... Equation 3.2}$$

$$\% \text{ Silt} = \% \text{ (Clay and Silt)} - \% \text{ Clay} \quad \text{..... Equation 3.3}$$

$$\% \text{ Sand} = \frac{\text{oven dry weight of particles retained on the 47 } \mu\text{m sieve}}{\text{oven dry mass of soil sample}} \times 100\% \quad \text{..... Equation 3.4}$$

Temperature effect on density of the soil particles was accounted for using the relation provided by Day (1965): for every 1 °C increase in temperature, above 19.5 °C, there is an increase of 0.3 in the density of the particles in suspension.

Hence, increase in weight = $(T_2 - T_1) \times 0.3 = (28 - 28) \times 0.3 = 0$

Correction for temperature = blank hydrometer reading – increase in weight of particles

= blank hydrometer reading – 0

Hence, Correction for temperature = blank hydrometer reading

With the percentages of sand, silt and clay, each soil sample was assigned a textural class using the United States Department of Agriculture textural triangle. Average proportions of the soil types in each soil core were determined and the corresponding average textural class was determined.

3.6.2 Soil pH

The pH of the fine earth fraction (<2mm) of each air-dried soil sample was determined in a 1:1 soil to distilled water ratio (McLean, 1982; McKeague, 1978). A 10 g soil was weighed and 10 mL of distilled water added, stirred vigorously and allowed to stand for 30 minutes. A microprocessor pH 213 meter was calibrated, and then inserted into the supernatant of the soil solution and the pH read. The pH in 1.0 M KCl solution of the soil samples was similarly determined using a 1:1 soil to solution ratio (ISO 10390, 1994).

3.6.3 Soil Organic Carbon

The organic carbon content of the soil was determined using the wet combustion method of Walkley and Black (1934). Ten millilitres of 0.167 M potassium dichromate ($K_2Cr_2O_7$) solution and 20 ml of concentrated sulphuric acid (H_2SO_4) were added to a 0.5 g soil which had been passed through a 0.5 mm sieve in an Erlenmeyer flask. The flask was then swirled to ensure full contact of the soil with the solution after which the mixture was allowed to stand for 30 minutes. The unreduced $K_2Cr_2O_7$ remaining in solution after the oxidation of the oxidizable organic material in the soil sample was titrated with 0.2 M ferrous ammonium sulphate solution after adding 10 mL of orthophosphoric acid and 2 mL of barium diphenylamine sulphonate indicator from a dirty brown colour to a bright green end point. A standardization titration of the $K_2Cr_2O_7$ with the ferrous ammonium sulphate was done and the amount of oxidizable organic carbon calculated by subtracting the moles of unreduced $K_2Cr_2O_7$ from that of $K_2Cr_2O_7$ present in the standardized titration.

Again, the amount (in moles) of oxidizable organic carbon was converted to mass (in grams) by multiplying it by 12 (molar mass of C). Then, the mass was expressed as a percentage of 0.5 g (mass of soil used) to obtain percentage oxidizable organic carbon.

Thus, $\%OC = \frac{n[OC] \times M[C] \times 100\%}{m[C]}$, where OC = oxidizable organic carbon

This was finally converted to percentage total organic carbon by multiplying it by a constant factor (1.333) on the assumption that only 75% of total organic carbon is oxidizable (FAO, 1974; Walkley, 1947).

Hence, $\%TOC = \frac{100}{75} \times \%OC = 1.333 \times \%OC$, where TOC = total organic cabon

3.6.4 Cation Exchange Capacity and Percent Base Saturation

Five grams of the fine earth fraction of the soil was weighed into an extraction bottle and 50 mL of 1.0 M ammonium acetate at pH 7.0 added. The contents were then shaken for 30 minutes and filtered through a Number 42 Whatman filter paper. The filtrate was collected with a well labelled high density polypropylene container and reserved for the determination of exchangeable bases. The soil mass on the filter paper was then leached with methanol to wash off the non-adsorbed NH_4^+ and the NH_4^+ saturated soil leached four times with acidified 1.0 M KCl. A 10 mL aliquot was transferred into a distillation flask and distilled to liberate NH_3 into boric acid. The ammonium ion concentration (mol/L) in the KCl filtrate was determined by titration of the solution with 0.01 M HCl and the CEC of the soil in cmol/kg estimated (Horneck *et al.*, 1989; Schollenberger and Simon, 1945). For quality control purposes, two blank tests in which the same procedure was performed without the soil were

carried out to ensure accuracy and to detect any contamination during the analytical procedure.

$$\text{CEC in cmol/kg of soil} = (\text{mol } L^{-1} \text{ of } NH_4\text{-N in distillate}) \times 10 \text{ mL} \times \frac{100}{5 \text{ g}}$$

where mol L^{-1} NH_4-N in distillate was determined from the titration.

For the exchangeable bases, Na and K concentrations (in mg/L) were read on Flame Photometer (Model: JENWAY PFP7), and Ca and Mg concentrations (in mg/L) were determined by Atomic Absorption Spectroscopy (Model: Perkin Elmer, AAnalyst 400). The values were then converted to cmol/kg as below:

$$\text{Exchangeable base in cmol/kg of soil} = (\text{mg/L of base}) \times \frac{50 \text{ mL}}{\text{Molar mass of base cation} \times 5 \text{ g}} \times \frac{1}{10}$$

The percent base saturation for each soil sample was also estimated by expressing the sum of the exchangeable bases (in $cmolkg^{-1}$) as a percentage of the cation exchange capacity.

$$\%\text{Base saturation} = \frac{[Na^+] + [K^+] + [Ca^+] + [Mg^+] \text{ in cmol/kg}}{\text{CEC in cmol/kg}} \times 100\%$$

3.6.5 Total Elemental Analysis

About 1 g of each air-dry soil sample (< 2mm) was weighed into a digestion flask and 30 mL of ternary mixture ($HClO_4$: HNO_3: H_2SO4 = 1:3:0.5) was added. The mixture was heated at 150 ^oC on a digestion rack. Boiling was continued until the digestion mixture became clear. It was then removed from the digestion rack and allowed to cool. About 20 mL of de-ionised water was added and the mixture was then filtered through a Whatman No. 1 filter paper in a

funnel into a 100 mL volumetric flask. About 30 mL of de-ionised water was then used to rinse the digestion flask and then poured onto the filter paper. The solution was then made to the 100 mL mark of the volumetric flask with de-ionised water and then transferred into a well labelled high density polyethylene (HDPE) container. For quality control purposes, reagent blanks and certified reference soils obtained from Wepal ISE of known composition were analysed with each batch of samples to ensure accuracy and to detect any contamination during the analytical procedure. The concentration of heavy metals in the digested samples was read using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) at the Tema Oil Refinery laboratory in triplicates.

3.6.6 Exchangeable Heavy Metal Determination

About 1 g of each air-dry soil sample (< 2mm) was weighed into a 100 mL conical flask and 10 mL of 0.01 M calcium chloride solution was added to generate a 1 : 10 (soil : solution) mixture. Using a glass rod, the mixture was stirred for 5 minutes and then allowed to stand for 2 hours at room temperature (Maiz *et al.*, 1997; Novozamsky *et al.*, 1993; Houba *et al.*, 1990; Tessier *et al.*, 1979). The suspension was then filtered through a Whatman No. 1 filter paper in a funnel into a 100 mL volumetric flask. About 50 mL of de-ionised water was then used to rinse the conical flask and then poured onto the filter paper. The clear filtrate was then made to the 100 mL mark of the volumetric flask with de-ionised water and then transferred into a well labelled high density polyethylene (HDPE) container. For quality control purposes, two blank tests in which the same procedure was performed without the soil were carried out to ensure accuracy and to detect any contamination during the analytical procedure. The concentration of exchangeable heavy metals extracted from the samples was

read by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) at the Tema Oil Refinery laboratory at least three times with precision of less than 5% for all elements.

The percent bioavailability of each element in each soil sample was obtained by expressing the exchangeable value of an element for the sample as a percentage of its total concentration.

3.7 DATA ANALYSIS

To investigate whether there were differences in the heavy metal concentrations among the eight sites, discriminant analysis was used. The results of this analysis were assessed by examining the canonical correlation statistic, the Wilk's lambda and the significance level (Qishlaqi and Moore, 2007).

To assess the relationship among heavy metal concentrations and four factors (pH, Total Organic Carbon content, Clay content and Cation Exchange Capacity), depth fuction plots were used. The results of this analysis revealed the most significant factor in terms of heavy metal distribution.

In order to quantitatively analyse and confirm the relationship among the soil properties (pH, Organic Carbon content, Clay content and Cation Exchange Capacity) and heavy metal contents, a two-way ANOVA test and a Pearson's correlation analysis were applied to dataset (Facchinelli *et al.*, 2001).

Besides the statistical analysis of data, heavy metal concentrations were compared with standard values of heavy metals for soils (Kabata-Pendias, 1992; Rademacher, UN/ECE, 2001).

In order to evaluate if the present-day heavy metal content in soil derives from natural or anthropogenic sources, enrichment factor was calculated for all the studied soils using Fe as a reference element (Hernández *et al.*, 2003). Accumulation/depletion ratio where the concentration of each metal in each depth of a core was divided by the concentration of that metal for the deepest depth in that core was also calculated (Matini *et al.*, 2011). Finally, principal component analysis was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different groups of metals that correlate and thus can be considered as having a similar behaviour and common origin (Tahri *et al.*, 2005). The combined results from the enrichment factor analysis, accumulation depletion ratio and the principal component analysis was used to predict the sources of the heavy metals.

CHAPTER FOUR

4.0 RESULTS

4.1 INTRODUCTION

The results of total and exchangeable heavy metal concentrations and physicochemical properties of the soils under investigation are presented in Tables 4.1-4.6 and illustrated in Figures 4.1-4.7. Additionally, enrichment factors and accumulation-depletion ratios have been calculated to predict the sources of the metals. Other statistical analyses such as discriminant analysis, two-way ANOVA, Pearson correlation and principal component analysis are applied to the results (using SPSS ver. 17.0) to highlight the relationship between metals and soil physicochemical properties as well as to further validate the deductions from the enrichment factors and the accumulation-depletion ratio. The statistical results are summarized in Tables 4.7-4.9 and Figures 4.8-4.12.

4.2 PHYSICOCHEMICAL CHARACTERISTICS OF THE SOILS

The texture of the individual depths for each sampling site is presented in Table 4.1a-d whereas presents the overall texture of the different soil depths for each sampling site is shown in Table 4.2. The Ferric Acrisols (ASH and BOG) showed increasing clay content but decreasing sand content with depth. The two soils had similar silt contents which were relatively uniform with depth. The clay contents which ranged from 40 and 60% in the Ferric Acrisol (ASH) were higher than in the Ferric Acrisol (BOG) where the small sized fraction was between 26 and 39%. Conversely, sand content was higher in the Ferric Acrisol (BOG) (46-55) than the Ferric Acrisol (ASH) (26-41%). The Haplic Ferrasol (BUA) also had its sand content decreasing from 41% at the top 10 cm to 19% at lower depths with clay content

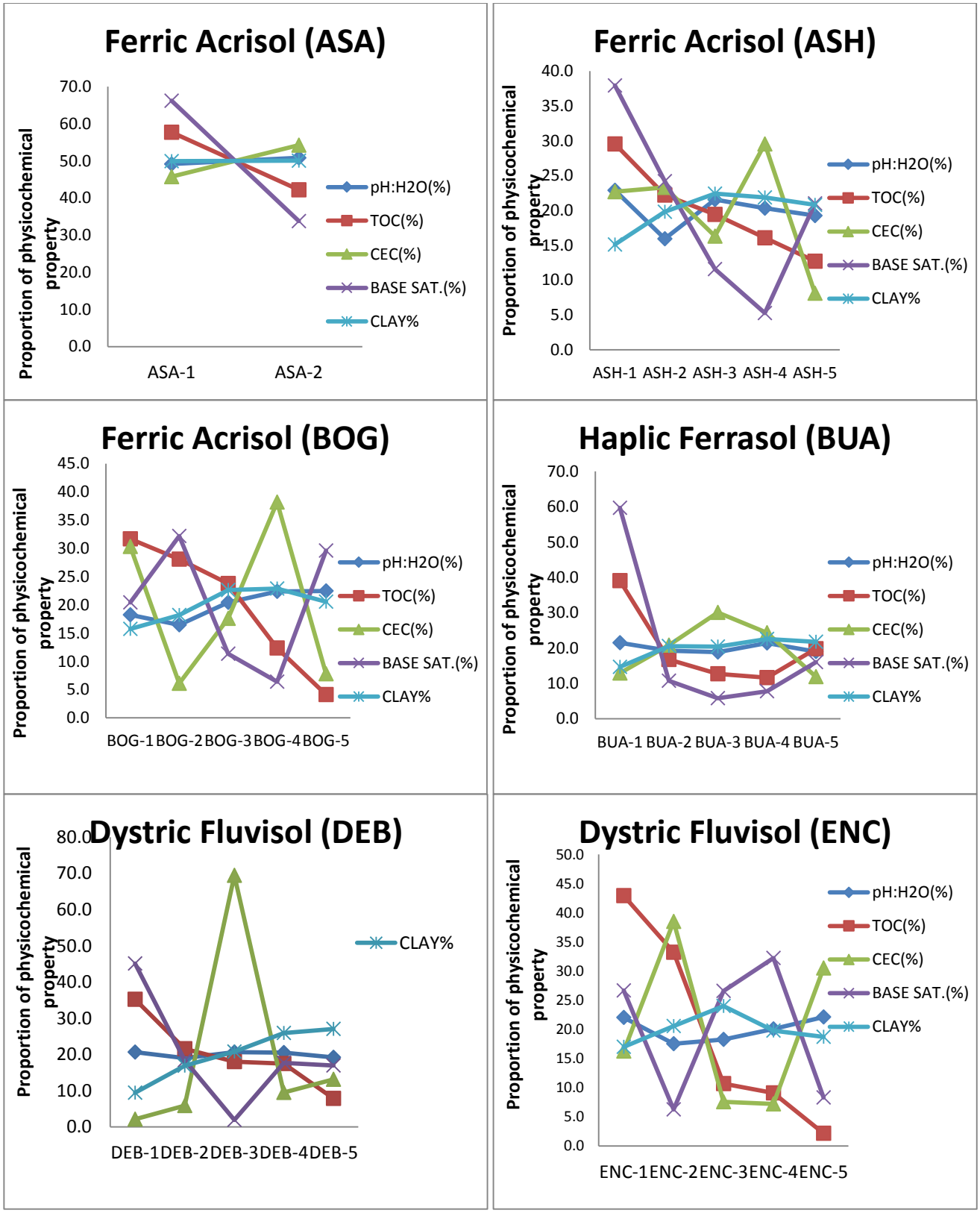
increasing with depth. Unlike the other two soils, the silt content of BUA decreased marginally with depth

By examining the textural classes, it was realised that the Haplic Luvisols (JUA and DEB, including the pristine reference, JUD), presented same textural distribution – their texture ranged from a sandy clay loam end-member to a sandy clay end-member. The cluster of points for the Dystric Fluvisols (ENC, SAM and SEN) ranged from a sandy clay loam end-member to a clay end-member. Also, for the Ferric Acrisols (ASH, BOG, ASA and ABA), the texture ranged from sandy clay loam end-member to a clay end-member.

The textural distributions in the soils from the various farms are, therefore, similar to those presented by their respective pristine references (natural forests). This may indicate that, from the results, weathering processes for the respective soil groups in the Western Region of Ghana are uniform.

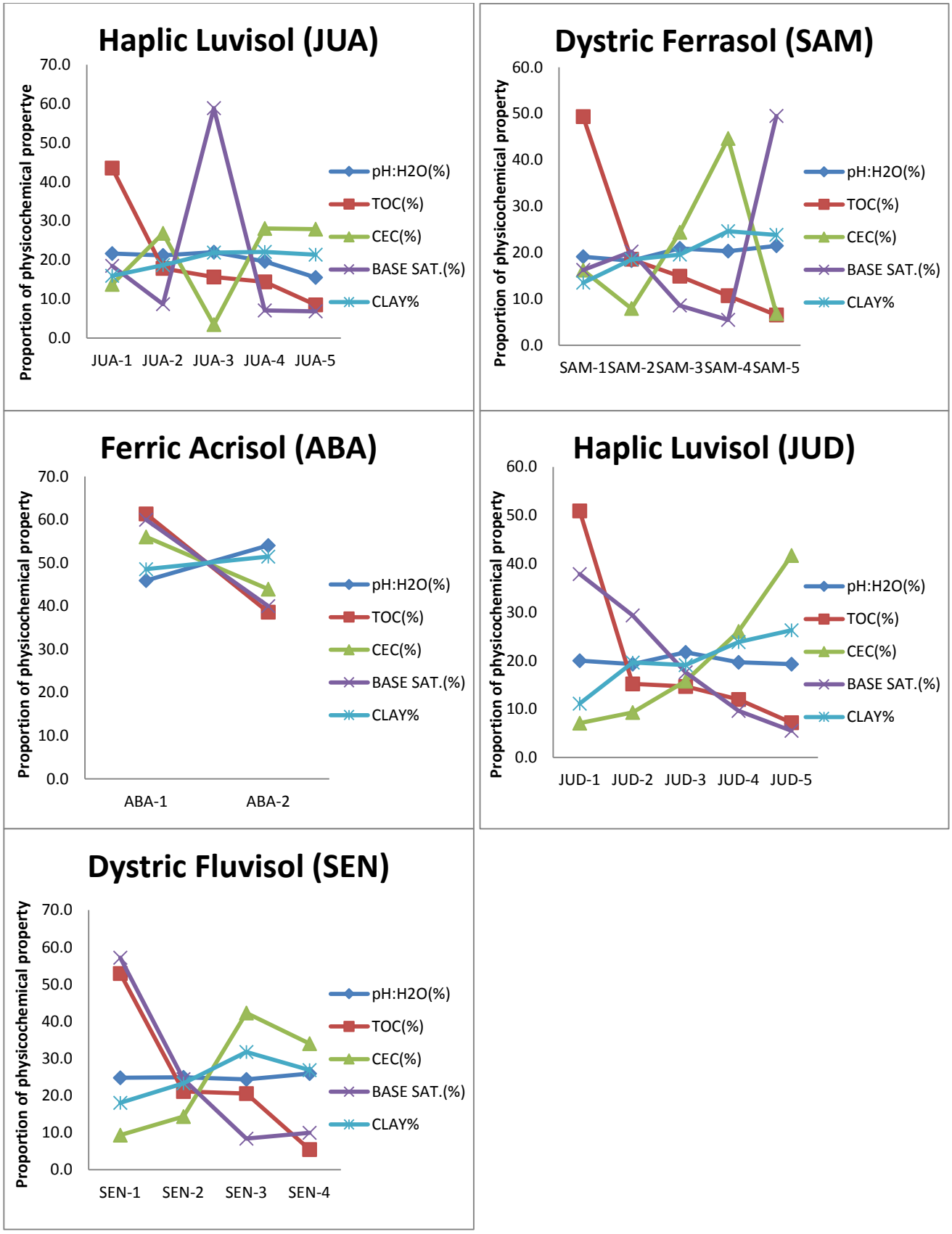
In summary, the cluster of points in Table 4.2 and its illustration in APPENDIX A showed that the soil texture in the cocoa growing areas under study regularly ranged from a sandy clay loam end-member to a clay end-member.

Figures 4.1a and b, which illustrate the trend of the physicochemical characteristics of each soil, showed that the clay proportion increased with depth in the Ferric Acrisols (ASH, BOG and ABA), in the Haplic Ferrasol (BUA), in the Haplic Luvisols (DEB, JUA and JUD) and in the Dystric Fluvisol (SAM) whereas in the Dystric fluvisols (SEN and ENC), it increased from 0 – 50 cm and then began to decrease. The surface layers of these soils (0 – 20 cm) had a significant proportion of loam. In Ferric Acrisol (ASA), however, the proportion of clay was uniform for the two sampled depths (0 – 10 cm and 10 – 30 cm).



On *x-axis*: 1= 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm.

Figure 4.1a: Relative distribution of physicochemical properties along the depth of each sampling site. Each physicochemical parameter is percent-wise normalised for each site [(x / S) × 100, where x = physicochemical value, and S = sum of physicochemical values of the various depths of a site].



On *x-axis*: 1= 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm.

Figure 4.1b: Relative distribution of physicochemical properties along the depth of each sampling site. Each physicochemical parameter is percent-wise normalised for each site [(x / S) × 100, where x = physicochemical value, and S = sum of physicochemical values of the various depths of a site].

Table 4.1a: Soil physicochemical properties for Ferric Acrisols (ASA, ASH and BOG)

Soil type	Depth (cm)	%Particle size by weight			Textural Class	pH (H_2O)	pH (KCl)	ΔpH	TOC (g/kg)	Exchangeable cations (NH_4OAc, pH7), cmol/kg				CEC (cmol/kg)	%BASE SAT.
		Sand	Silt	Clay						Na	K	Ca	Mg		
ACf (ASA)	0 – 10	36.3	25.2	38.5	CL	5.7	4.4	- 1.3	12	0.05	0.05	0.67	0.43	7.88	15.25
	10 – 30	39.2	22.3	38.6	CL	5.9	4.1	- 1.8	09	0.17	0.18	0.11	0.27	9.34	7.79
ACf (ASH)	0 – 10	41.2	18.5	40.3	C	6.4	4.5	- 1.9	16	0.06	0.04	1.01	1.68	15.42	18.04
	10 – 30	33.2	14.0	52.8	C	4.5	4.2	- 0.3	12	0.14	0.09	0.79	0.81	15.86	11.50
	30 – 50	26.8	13.4	59.8	C	6.0	4.0	- 2.0	10	0.00	0.03	0.21	0.38	11.10	5.50
	50 – 80	27.9	13.8	58.3	C	5.7	4.1	- 1.6	09	0.06	0.03	0.21	0.21	18.10	2.82
	80 – 100	28.4	16.1	55.5	C	5.4	4.2	- 1.2	07	0.10	0.12	0.08	0.25	5.52	9.98
ACf (BOG)	0 – 10	55.3	18.2	26.5	SCL	5.2	4.3	- 0.9	15	0.06	0.07	0.47	0.85	6.16	23.65
	10 – 30	54.1	15.3	30.6	SCL	4.6	4.4	- 0.2	13	0.01	0.04	0.20	0.21	1.24	37.32
	30 – 50	46.3	15.6	38.1	SC	5.8	4.1	- 1.7	11	0.03	0.01	0.04	0.40	3.58	13.15
	50 – 80	45.7	15.8	38.6	SC	6.3	4.3	- 2.0	06	0.00	0.01	0.15	0.41	7.76	7.43
	80 – 100	46.4	19.0	34.6	SC	6.3	4.3	- 2.0	02	0.07	0.03	0.04	0.40	1.58	34.30

ACf = Ferric Acrisol; CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; ΔpH = $pH_{(KCl)} - pH_{(H2O)}$; TOC = total organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg; %BASE SAT. = percent base saturation.

Table 4.1b: Soil physicochemical properties for Haplic Ferrasol (BUA), Haplic Luvisol (DEB) and Dystric Fluvisol (ENC)

Soil type	Depth (cm)	%Particle size by weight			Textural Class	pH (H_2O)	pH (KCl)	ΔpH	TOC (g/kg)	Exchangeable cations (NH_4OAc, pH7), cmol/kg				CEC (cmol/kg)	%BASE SAT.
		Sand	Silt	Clay						Na	K	Ca	Mg		
FRh (BUA)	0 – 10	41.3	12.5	46.3	C	6.7	5.4	- 1.3	38	0.05	0.10	1.93	3.27	6.66	80.35
	10 – 30	27.3	7.7	65.0	C	6.1	4.8	- 1.3	16	0.15	0.15	1.47	1.53	10.76	30.73
	30 – 50	24.8	10.7	64.5	C	5.9	4.8	- 1.1	12	0.03	0.02	1.20	1.33	15.54	16.66
	50 – 80	19.1	9.6	71.3	C	6.7	4.9	- 1.8	11	0.05	0.01	1.40	1.32	12.56	22.17
	80 – 100	21.0	10.4	68.6	C	6.0	5.0	- 1.0	19	0.06	0.02	10.21	1.52	6.14	45.72
LVh (DEB)	0 – 10	71.8	13.4	14.8	SL	6.8	5.2	- 1.6	11	0.10	0.12	0.95	0.90	2.48	83.63
	10 – 30	65.9	7.4	26.7	SCL	6.3	5.0	- 1.3	07	0.03	0.03	1.08	1.23	2.76	86.22
	30 – 50	56.8	10.4	32.8	SCL	6.8	4.8	- 2.0	06	0.11	0.06	1.15	1.60	20.70	14.11
	50 – 80	54.8	4.4	40.8	SC	6.8	4.8	- 2.0	06	0.06	0.02	1.37	2.28	4.48	83.06
	80 – 100	49.7	7.6	42.7	SC	6.3	4.8	- 1.5	03	0.12	0.10	1.56	3.13	6.18	79.63
FLd (ENC)	0 – 10	49.1	18.0	32.8	SCL	7.1	5.7	- 1.4	20	0.04	0.12	1.87	2.61	4.98	93.08
	10 – 30	46.6	13.7	39.7	SC	5.7	5.0	- 0.7	16	0.06	0.08	1.15	1.84	11.80	26.56

FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; ΔpH = $pH_{(KCl)} - pH_{(H2O)}$; TOC = total organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg; %BASE SAT. = percent base saturation.

Table 4.1c: Soil physicochemical properties for Dystric Fluvisols (ENC and SAM) and Haplic Luvisol (JUA)

Soil type	Depth (cm)	%Particle size by weight			Textural Class	pH (H_2O)	pH (KCl)	ΔpH	TOC (g/kg)	Exchangeable cations (NH_4OAc, pH7), cmol/kg				CEC (cmol/kg)	%BASE SAT.
		Sand	Silt	Clay						Na	K	Ca	Mg		
FLd (ENC)	30 – 50	42.8	10.8	46.4	C	5.9	4.6	- 1.3	05	0.19	0.22	0.65	1.06	3.32	63.81
	50 – 80	45.7	16.1	38.2	SC	6.5	5.0	- 1.5	04	0.06	0.02	0.89	2.04	3.20	94.03
	80 – 100	47.3	16.6	36.2	SC	7.2	6.2	- 1.0	01	0.10	0.01	0.73	2.46	9.36	35.24
LVh (JUA)	0 – 10	49.9	22.4	27.6	SCL	6.3	4.6	- 1.7	23	0.00	0.03	0.60	0.58	1.74	69.99
	10 – 30	63.6	4.0	32.4	SCL	6.2	4.4	- 1.8	09	0.01	0.01	0.46	0.63	3.40	32.86
	30 – 50	54.8	7.3	37.9	SC	6.4	4.3	- 2.1	08	0.03	0.01	0.35	0.58	3.44	28.48
	50 – 80	54.9	6.8	38.2	SC	5.8	4.3	- 1.5	08	0.05	0.02	0.29	0.60	3.56	26.84
	80 – 100	56.4	6.6	37.0	SC	4.5	4.3	- 0.2	05	0.05	0.02	0.28	0.57	3.54	25.85
FLd(SAM)	0 – 10	49.4	23.0	27.6	SCL	5.8	4.8	- 1.0	16	0.07	0.16	0.11	0.59	4.42	20.98
	10 – 30	50.2	12.0	37.7	SC	5.5	4.2	- 1.3	06	0.01	0.02	0.04	0.49	2.16	26.06
	30 – 50	43.2	16.9	39.9	C	6.3	4.5	- 1.8	05	0.04	0.03	0.21	0.46	6.64	11.11
	50 – 80	32.5	17.3	50.2	C	6.2	4.5	- 1.7	03	0.09	0.14	0.02	0.60	12.16	7.04

FLd – Dystric Fluvisol; LVH = Haplic Luvisol; CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; ΔpH = $pH_{(KCl)} - pH_{(H2O)}$; TOC = total organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg; %BASESAT. = percent base saturation.

Table 4.1d: Soil physicochemical properties for Dystric Fluvisols (SAM and SEN), Ferric Acrisol (ABA) and Haplic Luvisol (JUD)

Soil type	Depth (cm)	%Particle size by weight			Textural Class	pH (H_2O)	pH (KCl)	ΔpH	TOC (g/kg)	Exchangeable cations (NH_4OAc, pH7), cmol/kg				CEC (cmol/kg)	%BASE SAT.
		Sand	Silt	Clay						Na	K	Ca	Mg		
FLd (SAM)	80 – 100	34.6	16.7	48.6	C	6.5	4.4	- 2.1	02	0.07	0.05	0.24	0.83	1.86	63.89
ACf (ABA)	0 – 10	41.0	23.9	35.1	CL	4.7	4.0	- 0.7	21	0.10	0.09	0.03	0.50	6.30	11.32
	10 – 30	44.3	18.6	37.2	CL	5.6	4.5	- 1.1	13	0.06	0.06	0.00	0.26	4.94	7.54
LVh (JUD)	0 – 10	60.1	19.1	20.8	SCL	6.6	6.4	- 0.2	16	0.07	0.15	1.82	1.72	4.18	89.87
	10 – 30	54.9	8.3	36.7	SC	6.3	6.0	- 0.3	05	0.03	0.03	1.67	2.09	4.46	85.55
	30 – 50	52.8	11.4	35.8	SC	7.2	5.2	- 2.0	05	0.01	0.03	1.48	2.35	4.84	80.09
	50 – 80	46.8	8.6	44.6	SC	6.5	4.6	- 1.9	04	0.03	0.07	1.22	2.18	7.98	43.84
	80 – 100	39.3	11.5	49.2	C	6.4	4.1	- 2.3	02	0.11	0.08	1.01	2.01	12.78	25.07
FLd (SEN)	0 – 10	56.6	15.6	27.8	SCL	6.9	5.7	- 1.2	15	0.09	0.05	1.11	2.01	3.64	89.62
	10 – 30	43.0	21.2	35.8	CL	6.9	5.3	- 1.6	06	0.08	0.01	1.03	1.53	4.06	65.60
	30 – 50	42.4	8.7	48.9	C	6.7	5.1	- 1.6	06	0.08	0.16	0.74	1.72	11.94	22.59
	50 – 80	44.4	14.3	41.3	SC	7.2	5.6	- 1.6	02	0.02	0.01	0.93	1.60	9.60	26.77

FLd = Dystric FLuvisol; ACf = Ferric Acrisol; LVh =Haplic Luvisol; CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; ΔpH = $pH_{(KCl)} - pH_{(H2O)}$; TOC = total organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg; %BASESAT. = percent base saturation.

The pH (pH_{H2O}) varied between 4.5 and 7.2. On the whole, 75.00% of the samples had pH values less than 6.5. Approximately, 8.30% of the soil samples were strongly acidic ($4.0 \leq pH \leq 5.0$), 27.07% were slightly acidic ($5.5 \leq pH \leq 6.0$) and none was alkaline ($pH \geq 7.5$), (McLean, 1982). Hence, the study area is composed mainly of acid soils.

The Dystric Fluvisols (ENC, SAM and SEN) recorded pH values ranging from slightly acidic to neutral ($5.5 \leq pH \leq 7.5$). This group also presented the least proportion of clay as earlier indicated and this observation is in agreement with Hernández *et al.* (2003).

Except for Dystric FLuvisol (ENC), where pH (pH_{H2O}) dropped sharply from depth 0 – 30 cm before a steady increase began, the pH_{H2O} generally increased with depth (Fig. 4.1a-b).

All pH_{KCl} values obtained were less than their respective pH_{H2O} (Table 4.1a-d). It is thus an ndication that the soils had net negative charges on their colloidal surfaces becausee $\Delta pH = pH_{(salt)} - pH_{(water)}$ was negative (Tan, 1998). It is observed that 60.00% of all soil samples with pH_{H2O} values below 6 had pH_{KCl} values 0.5 or more units less than their respective pH_{H2O} ($\Delta pH \geq 0.5$). This implies that significant amount of exchangeable Al and/or its derivatives were present (Peverill *et al.*, 1999).

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \quad \text{..... Equation 4.1a}$$

$$Al(OH)^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+ \quad \text{..... Equation 4.1b}$$

Meanwhile, apart from the pH_{KCl} presenting same trend in Dystric Fluvisol (ENC) core as pH_{H2O}, the surface layer (0 – 10 cm) recorded a pH_{H2O} value of 7.1 making it less likely to even possess any exchangeable Al, and so the effect of exchangeable Al is null. The qualitative test for the presence of calcium carbonate ($CaCO_3$) with 10% hydrochloric acid solution (HCl) was positive for the surface (0 – 10 cm) and the deepest (80 – 100 cm) soil samples of the Dystric Fluvisol (ENC) core (APPENDIX B).

Calcium carbonate is, however, known to increase the pH levels of soils owing to the release of more OH^- from the two-step hydrolysis of the CO_3^{2-} group (Equation 4.2a-b) and hence may explain the high pH value for the ENC surface soil sample.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad \text{.....Equation 4.2a}$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \quad \text{.....Equation 4.2b}$$

It is also observed from Fig. 4.1a-d that in all the soils except in the Haplic Ferrasol (BUA), the total organic carbon (TOC) was highest in the surface soils (0 – 10 cm) and sharply decreased from the next sampled-depth (10 – 30 cm). Subsequently, the total organic content then decreases gradually. The decreasing total organic carbon with depth is as a result of litter accumulation in the surface or plough layer of the soil as also indicated by Hernández *et al.* (2003**)**.

The total organic content of the surface soil (0 – 10 cm) in Haplic Ferrasol (BUA) (38 g/kg) was quite high for tropical soils and would indicate high level of N and P should there be mineralisation. This high surface organic carbon is a reflection of the high litter fall and canopy cover of the area which minimises mineralisation and hence accumulation of organic carbon in the soil (Table 4.1a-d). It then decreased drastically in depth 10 – 30 cm (16 g/kg) and thereafter decreases gradually to depth 50 – 80 cm (11 g/kg) beyond which it experienced an unexpected rise in the deepest depth 80 – 100 cm, (19 g/kg). The highest organic carbon contents at lower depth were consequently recorded for Haplic Ferrasol (BUA).

On the average, the Haplic Ferrasol (BUA) was the most enriched in organic carbon whereas the Dystric Fluvisols (ENC, SAM and SEN) had the least organic carbon content.

The cation exchange capacity (CEC) for all the soils was within a range of 1.2 – 20.6 with most of the surface soils having CEC less than 10 cmol kg^{-1} (Table 4.1a-d). This low CEC of

the surface soils despite medium to high organic carbon contents of the soils reflect their highly weathered nature. Except for the Haplic Luvisols (JUD, DEB and JUA), all the other soil did not show any clear trend of CEC with depth (Fig. 4.1a-b). The CEC for the Haplic Luvisols, generally, tended to increase with depth and zones of high accumulation of clay coincided with high CEC.

On the average, the highest CEC values were found fin the Ferric Acrisol at Ashiem (ASH) with a range of 5.52 – 18.10 cmol kg^{-1} (Table 4.1a) whereas the lowest values were found in the Haplic Luvisol at Juabeso (JUA) with a range of 1.74 – 3.56 cmol kg^{-1} (Table 4.1c).

Three soils, Haplic Luvisol pristine reference (JUD), Dystric Fluvisol pristine reference (SEN) and Ferric Acrisol at Ashiem (ASH), presented a relatively higher CEC value in the deep (50 – 100 cm) horizons of range 9.60 – 18.10 cmol kg^{-1}. This has to be related to the relative abundance of clay in those depths.

The percent base saturation for each soil has been calculated from the concentrations of the exchangeable bases and the CEC values, and has been reported in Table 4.1a-d. Generally, the values ranged from 2.82 – 94.03%. The Ferric Acrisols (ABA, ASH, ASA and BOG) presented very low to low base cation contents ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$: 2.82 – 37.33%) whereas the Haplic Luvisols (DEB, JUA and JUD) presented medium to very high base cation contents ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$: 14.11 – 89.87%). The relatively low base saturation of the Acrisols may be due to the fact that the basic cations have been washed out of the soils due to the heavy rainfall regime that pertains in the area.

From Figs.4.1a and b, it is observed that in all the soils but Ferric Acrisol pristine reference (ABA), the erratic lines for percent base saturation were the exact inverse of the CEC lines. Cation exchange capacity is an intrinsic property which is a measure of negative charges on soil colloids that hold onto positively charged ions and, therefore though it is reversible, a

greater portion of the exchange complex might be exchanged with Al^{3+} which is known to dominate acid soils and hence only a small portion might be reserved for the exchange of the less easily exchanged bases like Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. A greater proportion of these bases could thereby be leached. Thus, the dominance of exchangeable aluminium in acid soils might tend to decrease the calculated percent base saturation.

4.3 HEAVY METAL CONTENT AND DISTRIBUTION IN THE SOILS STUDIED

4.3.1 Validation of Analytical Method

To assess how well the whole method (digestion, clean-up and instrumental analysis) was performing, the analytical procedure was validated using WEPAL (Wageningen Evaluating Programs for Analytical Laboratories) soil reference material ISE sample 918 of sandy soil from Sinderen / Netherlands. The results obtained by the analysis are shown in Table 4.3a.

To compare the means of the measured and certified values, a paired-sample T test was applied to the data. The measured and certified values were entered as paired variables and the confidence interval set at 95%. The test output is presented in APPENDIX C1. It was observed that there was no significant difference between the paired values (P = 0.325) and hence the measured values were statistically the same as their respective certified values.

The results were further substantiated using the WEPAL soil reference material ISE sample 998 of organic Ferrasol from Sumatra Barat, Indonesia and the results summarized in Table 4.3b (test output in APPENDIX C2). The result also showed no significant difference between the two compared values (P = 0.200). The accuracy of the analytical procedure was, therefore, good for all the metals under study.

Table 4.2: Soil physicochemical properties for the averaged cores

Soil type	%Particle size by weight			Textural Class	pH (H_2O)	pH (KCl)	ΔpH	TOC (g/kg)	Exchangeable cations (NH_4OAc, pH7), cmol/kg				CEC (cmol/kg)	%BASE SAT.
	Sand	Silt	Clay						Na	K	Ca	Mg		
ACf (ASA)	37.7	23.7	38.6	CL	5.8	4.3	1.5	11	0.11	0.11	0.39	0.35	8.61	11.20
ACf (ASH)	31.5	15.2	53.3	C	5.6	4.2	1.4	11	0.07	0.06	0.46	0.66	13.6	9.22
ACf (BOG)	49.6	16.8	33.7	SCL	5.6	4.3	1.3	09	0.04	0.03	0.18	0.45	4.06	17.27
FRh (BUA)	26.7	10.2	63.1	C	6.3	5.0	1.3	19	0.07	0.06	1.44	3.00	10.33	44.21
LVh (DEB)	59.8	8.6	31.6	SCL	6.6	4.9	1.7	07	0.08	0.07	1.22	1.83	9.42	34.02
FLd (ENC)	46.3	15.1	38.6	SC	6.5	5.3	1.2	09	0.09	0.09	1.06	2.30	6.13	57.72
LVh (JUA)	55.9	9.4	34.6	SCL	5.9	4.4	1.5	11	0.03	0.02	0.40	0.59	2.54	40.89
FLd (SAM)	42.0	17.2	40.8	C	6.1	4.5	1.6	06	0.06	0.08	0.12	0.60	5.45	15.68
ACf (ABA)*	42.6	21.2	36.1	CL	5.2	4.2	1.0	17	0.08	0.07	0.01	0.38	5.62	9.66
LVh (JUD)*	50.8	11.8	37.4	SC	6.6	5.3	1.3	06	0.05	0.07	1.44	2.07	6.13	59.24
FLd (SEN)*	46.6	14.9	38.4	SC	6.9	5.5	1.4	07	0.07	0.06	1.08	1.79	7.06	42.43

ACf = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; * = Pristine reference; CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; ΔpH = $pH_{(H2O)} - pH_{(KCl)}$; TOC = total organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg; %BASESAT. = percent base saturation.

Table 4.3a: Measured and certified values for standard reference ISE 918

ELEMENT	MEASURED VALUE ± SD (mg/kg)	CERTIFIED VALUE ± SD (mg/kg)
Cd	0.26 ± 0.01	0.28 ± 0.06
Cr	51.01 ± 0.47	52.20 ± 11.72
Cu	18.75 ± 0.10	18.00 ± 2.63
Fe	5956.73 ± 0.29	6100.00 ± 0.33
Mn	220.40 ± 7.12	226.0 ± 16.70
Ni	9.00 ± 0.11	8.76 ± 1.53
Pb	25.44 ± 2.64	26.30 ± 3.41
Zn	46.99 ± 3.11	47.80 ± 5.31

SD = Standard deviation

Table 4.3b: Measured and certified values for standard reference ISE 998

ELEMENT	MEASURED VALUE ± SD (mg/kg)	CERTIFIED VALUE ± SD (mg/kg)
Cr	29.75 ± 3.18	31.30 ± 6.13
Cu	34.03 ± 4.00	36.00 ± 3.66
Fe	90170 ± 2226	90200 ± 3360
Mn	168.90 ± 17.77	174.00 ± 22.10
Ni	16.58 ± 1.01	17.10 ± 2.26
Pb	12.12 ± 2.33	12.20 ± 2.91
Zn	66.87 ± 5.98	68.70 ± 7.06

SD = Standard deviation

4.3.2 Heavy Metals in the Studied Soils

Tables 4.4a-d records the total metal content of the soils and the distribution of the different metals versus depth is illustrated in Figs. 4.2a and b. The average abundance order of the total metal contents in the soils was: Fe > Mn > Cr > Zn > Cu > Cd > Pb > Ni. The high Fe content is due to the fact that it is a major component of sesquioxides which are dominant in Acrisols and Luvisols. It may also be due to the presence of haematite and goethite which are likely to be present in the area.

Table 4.5 presents the standard levels of heavy metals for non- polluted soils (Kabata-Pendias and Pendias, 1992) and for European norms (Rademacher, 2001), and the levels in atmospheric fallout (Allen *et al.*,1995).

For almost all the soils, the total heavy metal content was within the range or less than the standard values proposed for the non- polluted soils and for European norms (Kabata-Pendias and Pendias, 1992; Rademacher, 2001), except Cr for soils Ferric Acrisol at Ashiem – depth 80 – 100 cm (191.9 mg/kg) and Dystric Fluvisol at Enchi – depth 30 – 50 cm (143.0 mg/kg).

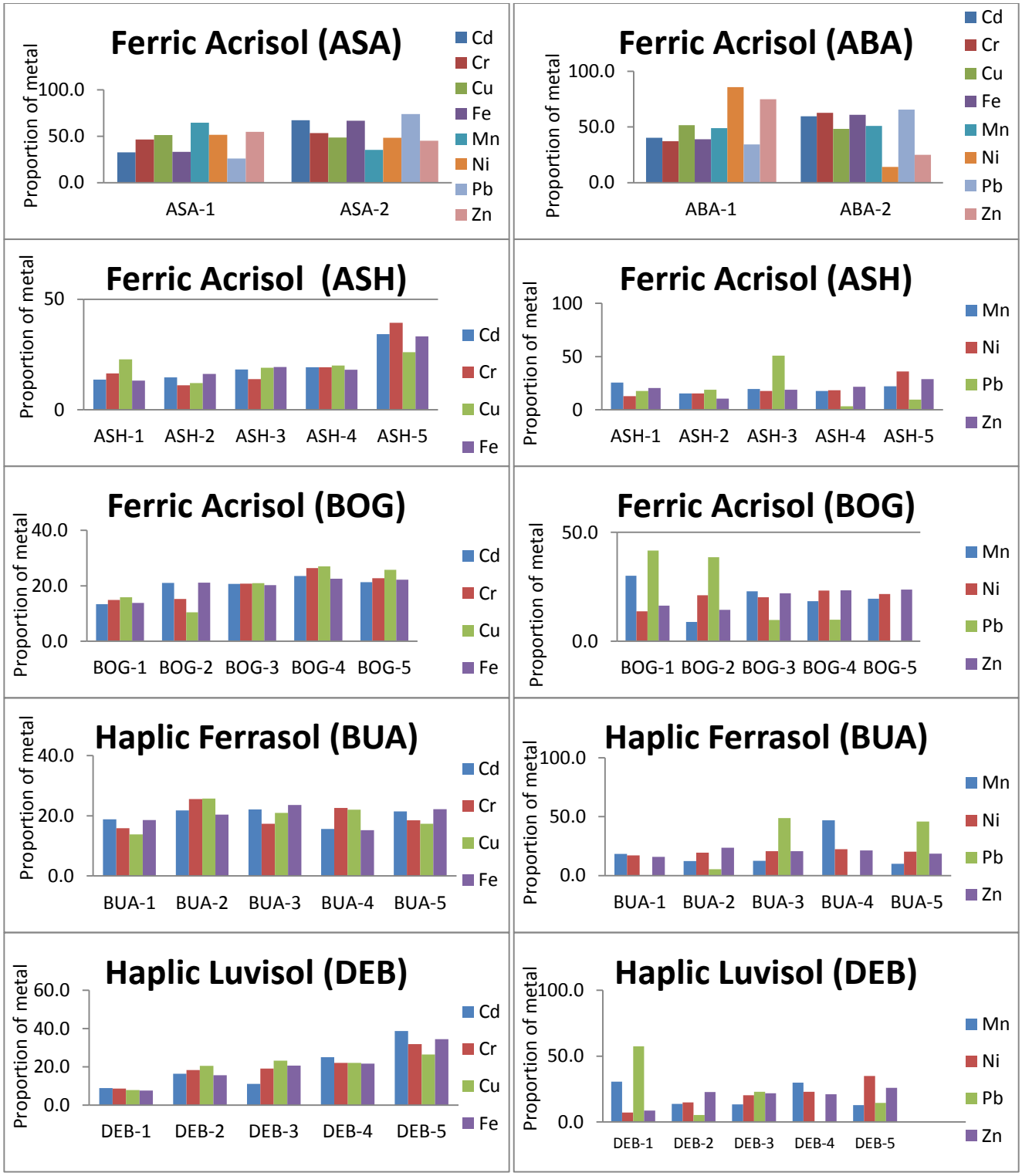
Comparing the mean total heavy metal contents of the surface soil samples (0 – 10 cm) to the values proposed for atmospheric fallout in topsoil (Allen *et al.*,1995), the concentrations of Cd and Cr were high for all surface soils whereas that for Ni was low. This suggests atmospheric deposition of Cd and Cr probably from a common source. The accumulation of Cd especially in the surface soils could be from the P fertilizers used on cocoa farms for years. Cadmium is a known impurity in most P fertilizers. Copper and Pb also presented values above those proposed for atmospheric fallout for all soils but Haplic Luvisols at depth 0 – 10 cm: Juabeso, JUA (6.6 mg/kg) and LVh pristine, JUD (6.3 mg/kg), and Debiso, DEB (11.5 mg/kg), respectively. Most of the fungicides used in cocoa spraying are copper based. It, therefore, stands to reason that the surface soils seemed to have high levels of the metal.

Zinc was, however, low in all surface soils (0 -10 cm) except in Haplic Luvisols at Debiso, DEB (11.5 mg/kg), Juabeso, JUA (16.9 mg/kg) and LVh pristine reference, JUD-1 (14.0 mg/kg), and in Dystric Fluvisol at Samreboi, SAM (28.2 mg/kg).

Also, with the exception of the Haplic Luvisols (JUA, DEB and JUD), all the soils had very high concentrations of Cu and very low concentrations of Pb in their surface soils. This might be an indication of high atmospheric input of Cu and natural occurrence of Pb in the luvisols because this soil group had an elevated Pb content for even the different sites. Thus, the Pb abundance might be from pedogenesis.

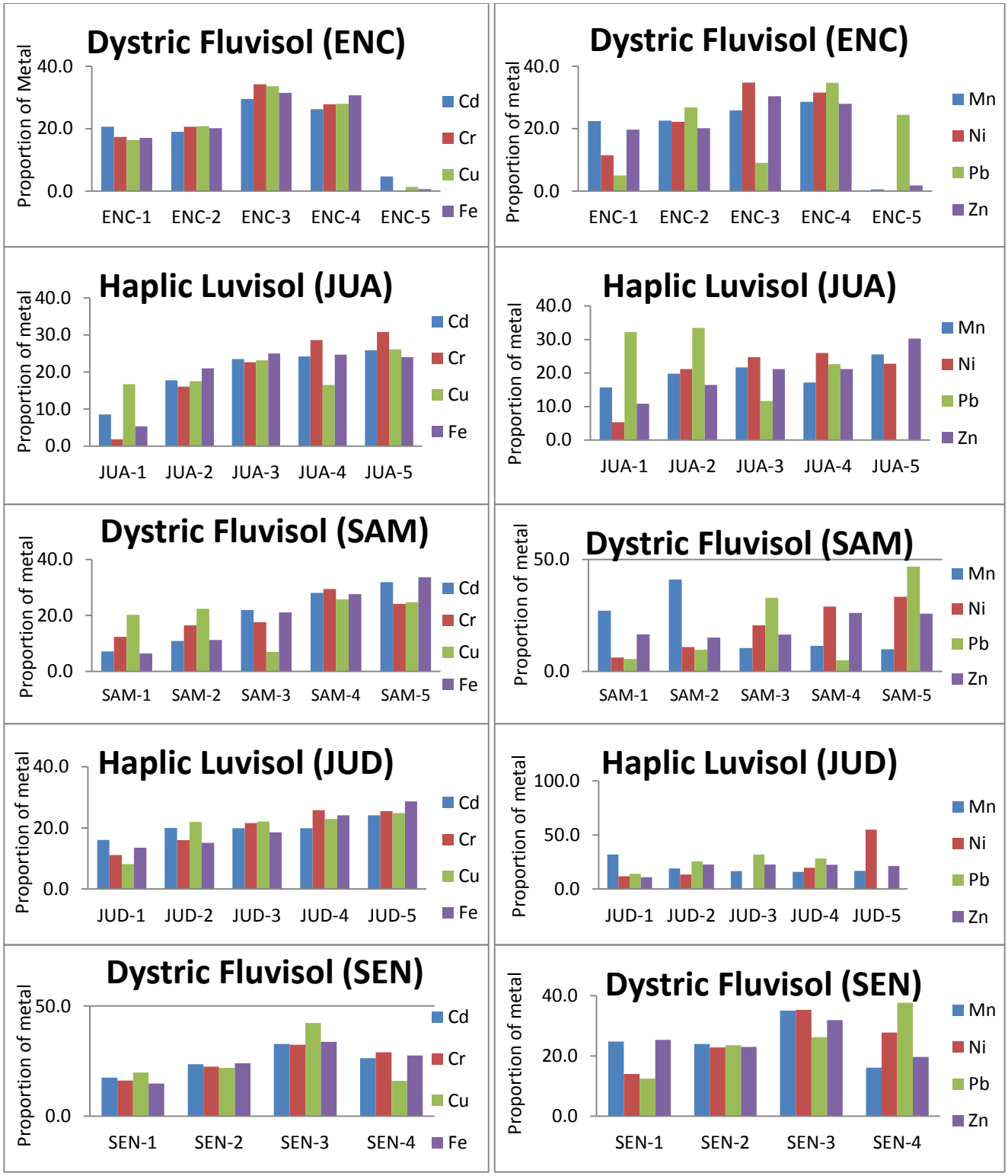
The abundance of Cu in the surface horizons of the other soil samples might be attributed to the high application of agrochemicals especially Cu-containing fungicides. The concentration of Zn was low in the surface soils for Haplic Luvisols (JUA and DEB) and Dystric Fluvisol (SAM) relative to the other soils. The Dystric Fluvisols (ENC, SAM and SEN) and the Haplic Ferrasol (BUA) presented the highest heavy metal content, whereas the lowest concentrations were found in the Haplic Luvisols (JUA, DEB and pristine reference JUD).

The exchangeable (mobile) fractions of all metals which are detailed in APPENDIX D were below all the standard values presented in Table 4.5. The mean concentrations of Mn (range: 23.7 – 1066.0 mg/kg) and Fe (range: 1331.7 – 85688.7 mg/kg) were extremely high as compared to the other metals (range: not detected – 191.9 mg/kg) and this might be as a result of their natural abundance. Lead which is not a plant nutrient is the most exchangeable heavy metal in relation to its total concentration in the soil. It had an exchangeable concentration of range 2.1 – 39.0% and thus, when taken up by crops, it could pose health problems. Contrarily, Cd, Cr and Zn, which had higher total contents in the soils, were the least available.



On *x-axis*: 1= 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm.

Figure 4.2a: Proportional distribution of metals along the depths of each sampling site. The proportion of each metal in each depth is plotted against that depth; to obtain the proportion of each metal per depth, the concentration of the metal is expressed as a percentage of the sum of the metal content of the various depths of that site for that metal.



On *x-axis*: 1= 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm.

Figure 4.2b: Proportional distribution of metals along the depths of each sampling site. The proportion of each metal in each depth is plotted against that depth; to obtain the proportion of each metal per depth, the mean concentration of the metal is expressed as a percentage of the sum of the mean metal content of the various depths of that site for that metal.

Table 4.4a: Total metal concentrations with corresponding exchangeable metal fractions for Ferric Acrisols (ASA, ASH and BOG)

Soil type	Depth (cm)	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
		T (mg/kg)	B (%)	T (mg/kg	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)
ACf (ASA)	0 – 10	4.1	0.1	31.9	0.0	16.5	8.2	25178.7	< 0.1	252.0	19.9	1.9	52.4	1.2	39.0	40.4	2.2
	10 – 30	8.5	0.0	36.8	0.0	15.7	9.0	50498.7	< 0.1	138.5	7.6	1.8	22.2	3.4	8.0	33.2	1.6
ACf (ASH)	0 – 10	6.7	0.0	79.8	0.0	22.0	6.3	34218.7	< 0.1	81.8	13.4	1.2	0.0	3.9	10.6	38.7	0.0
	10 – 30	7.2	< 0.1	54.0	0.0	11.7	16.8	41768.7	< 0.1	49.1	3.4	1.5	0.0	4.2	8.5	20.1	2.2
	30 – 50	8.9	0.1	67.6	0.0	18.3	0.0	49948.7	< 0.1	62.4	5.5	1.7	0.0	11.3	4.4	35.6	0.8
	50 – 80	9.4	0.0	93.7	1.8	19.2	7.9	46758.7	< 0.1	56.5	7.8	1.8	0.0	0.7	13.4	41.3	0.8
	80 – 100	16.7	0.1	191.9	0.0	25.0	5.6	85688.7	< 0.1	71.1	6.6	3.4	0.0	2.1	13.1	54.7	0.3
ACf (BOG)	0 – 10	3.1	1.1	25.5	0.3	14.5	11.6	15798.7	< 0.1	447.7	28.4	0.5	52.3	4.2	16.1	36.5	6.2
	10 – 30	4.9	0.0	26.2	0.0	9.5	13.4	24138.7	< 0.1	133.1	56.4	0.8	0.0	3.9	4.1	32.1	3.0
	30 – 50	4.8	0.1	35.7	0.1	19.1	0.0	23108.7	0.0	342.0	0.0	0.8	12.5	1.0	18.9	49.3	0.0
	50 – 80	5.5	< 0.1	45.4	0.0	24.6	0.0	25788.7	0.0	273.7	0.0	0.9	0.0	1.0	34.0	52.3	0.0
	80 – 100	5.0	0.0	39.0	0.0	23.5	0.0	25387.7	0.0	291.0	0.0	0.9	10.0	ND	-	53.0	0.0

ACf = Ferric Acrisol; T = total metal concentration in mg/kg; B = exchangeable metal fraction in %; ND = not detected. B% is derived by expressing the value of the exchangeable metal concentration (in mg/kg) as a percentage of the total metal concentration (T).

Table 4.4b: Total metal concentrations with corresponding exchangeable metal fractions for Haplic Ferrasol (BUA), Haplic Luvisol (DEB) and Dystric Fluvisol (ENC)

Soil type	Depth (cm)	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
		T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)
FRh (BUA)	0 – 10	9.8	< 0.1	60.3	0.0	19.2	5.9	50678.7	< 0.1	358.3	2.6	1.9	0.0	ND	-	33.5	0.0
	10 – 30	11.4	< 0.1	97.3	0.0	35.7	3.8	55558.7	< 0.1	242.1	8.1	2.1	0.0	1.2	24.3	50.2	0.0
	30 – 50	11.6	0.0	66.1	0.0	29.2	4.6	64418.7	< 0.1	243.6	7.7	2.3	0.0	11.2	4.9	43.8	0.0
	50 – 80	8.2	< 0.1	86.2	0.0	30.7	4.3	41488.7	< 0.1	914.6	1.5	2.4	0.0	ND	-	45.1	0.0
	80 – 100	11.2	0.0	70.3	0.0	24.1	5.6	60508.7	< 0.1	194.0	7.8	2.2	0.0	10.5	3.7	39.3	0.0
LVh (DEB)	0 – 10	2.8	0.2	15.7	0.0	5.9	21.7	14698.7	< 0.1	408.9	14.2	0.5	0.0	11.5	0.4	11.6	0.0
	10 – 30	5.2	0.0	33.5	0.0	15.4	10.5	30088.7	< 0.1	182.7	18.5	1.0	41.3	1.1	21.9	30.5	0.0
	30 – 50	3.5	0.2	35.0	0.0	17.4	7.9	39828.7	< 0.1	176.9	13.2	1.4	0.0	4.6	12.8	29.3	0.0
	50 – 80	8.0	< 0.1	40.4	0.0	16.5	9.2	41848.7	< 0.1	398.3	4.2	1.6	0.0	ND	-	28.3	0.0
	80 – 100	12.4	< 0.1	58.1	0.0	19.9	6.9	66458.7	< 0.1	170.4	5.4	2.4	0.0	2.9	13.0	34.7	0.0
FLd (ENC)	0 – 10	8.9	0.0	72.4	0.0	24.0	5.7	35080.7	< 0.1	909.0	1.1	0.8	25.8	2.1	8.6	55.0	0.0
	10 – 30	8.2	0.2	86.2	0.0	30.7	4.4	41488.7	< 0.1	914.6	2.2	1.5	0.0	11.2	1.6	56.4	0.0

FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; T = total metal concentration in mg/kg; B = exchangeable metal fraction in %; ND = not detected. B% is derived by expressing the value of the exchangeable metal concentration (in mg/kg) as a percentage of the total metal concentration (T).

Table 4.4c: Total metal concentrations with corresponding exchangeable metal fractions for Dystric Fluvisols (ENC and SAM) and Haplic Luvisol (JUA)

Soil type	Depth (cm)	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
		T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)
FLd (ENC)	30 – 50	12.7	0.0	143.0	0.1	49.5	2.9	64678.7	< 0.1	1048.0	2.9	2.4	6.3	3.8	3.7	84.8	0.0
	50 – 80	11.3	< 0.1	116.3	0.1	41.1	3.3	63108.7	< 0.1	1158.0	1.7	2.2	0.0	14.5	1.1	78.2	0.0
	80 – 100	2.0	0.4	ND	0.0	2.0	63.0	1331.7	0.2	23.7	3.1	ND	-	10.2	6.7	5.1	0.0
LVh (JUA)	0 – 10	1.4	1.0	2.6	6.8	6.6	20.2	3716.7	0.0	48.1	140.7	0.1	80.5	10.2	0.0	16.9	1.0
	10 – 30	2.9	0.1	22.3	0.0	6.9	19.2	14648.7	< 0.1	60.7	2.2	0.5	0.0	10.6	3.3	25.5	0.0
	30 – 50	3.8	0.1	31.4	< 0.1	9.2	17.7	17468.7	< 0.1	66.5	10.1	0.6	0.0	3.7	9.2	32.9	3.4
	50 – 80	3.9	< 0.1	39.7	0.0	6.5	22.8	17238.7	< 0.1	52.6	16.3	0.6	8.9	7.2	0.1	32.9	1.1
	80 – 100	4.2	0.3	42.8	0.0	10.3	13.7	16798.7	< 0.1	78.3	13.9	0.5	0.0	ND	-	47.0	1.3
FLd(SAM)	0 – 10	2.5	0.0	23.4	0.0	10.1	13.9	12068.7	< 0.1	210.5	21.8	0.4	0.0	2.0	9.2	28.2	0.0
	10 – 30	3.9	0.0	31.1	0.0	11.2	12.7	21058.7	< 0.1	318.4	6.3	0.7	0.0	3.5	17.8	25.7	0.0
	30 – 50	7.8	0.0	33.2	0.0	3.5	40.0	39438.7	0.0	80.7	20.9	1.4	0.0	11.9	4.6	28.0	0.0
	50 – 80	10.0	0.1	55.6	0.0	12.9	9.3	51798.7	0.0	88.9	16.7	1.9	5.2	1.8	9.1	44.4	0.0

FLd = Dystric Fluvisol; LVh = Haplic Luvisol; T = total metal concentration in mg/kg; B = exchangeable metal fraction in %; ND = not detected. B% is derived by expressing the value of the exchangeable metal concentration (in mg/kg) as a percentage of the total metal concentration (T).

Table 4.4d: Total metal concentrations with corresponding exchangeable metal fractions for Dystric Fluvisols (SAM and SEN), Ferric Acrisol (ABA) and Haplic Luvisol (JUD)

Soil type	Depth (cm)	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
		T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)
FLd (SAM)	80 – 100	11.3	0.1	45.7	0.0	12.4	11.0	62998.7	0.0	76.6	12.5	2.2	9.6	16.9	1.9	43.9	0.0
ACf (ABA)	0 – 10	3.4	0.0	11.4	0.0	15.0	9.3	16118.7	0.1	41.1	20.1	5.2	7.8	4.8	0.0	72.8	3.5
	10 – 30	5.1	0.0	19.1	0.0	14.0	9.8	25098.7	< 0.1	42.7	20.0	0.9	33.0	9.1	3.3	24.4	6.5
LVh (JUD)	0 – 10	2.8	0.0	18.1	0.0	6.3	20.7	11058.7	< 0.1	233.8	4.1	0.4	0.0	1.4	24.9	14.0	0.0
	10 – 30	3.5	0.1	26.0	0.0	16.9	7.8	12398.7	< 0.1	139.2	1.8	0.4	22.2	2.6	23.8	29.2	0.0
	30 – 50	3.5	< 0.1	35.0	0.0	17.0	6.7	15219.7	< 0.1	121.7	2.6	ND	-	3.2	15.2	29.3	0.0
	50 – 80	3.5	0.0	42.0	0.1	17.7	6.5	19768.7	< 0.1	116.6	9.7	0.6	0.0	2.9	23.9	29.0	0.0
	80 – 100	4.3	0.0	41.4	0.0	19.1	6.6	23468.7	< 0.1	122.7	11.1	1.8	60.5	ND	-	27.4	0.0
FLd (SEN)	0 – 10	6.3	0.0	40.2	0.0	22.4	6.5	27558.7	< 0.1	754.0	3.3	0.9	0.0	7.4	2.1	57.8	0.0
	10 – 30	8.5	0.0	55.9	0.0	24.7	6.0	44678.7	< 0.1	727.9	0.4	1.5	0.0	14.0	2.6	52.4	0.0
	30 – 50	11.9	0.0	80.7	0.0	47.6	3.4	62828.7	0.0	1066.0	0.6	2.4	0.0	15.6	3.7	72.7	0.0
	50 – 80	9.5	0.2	72.2	0.0	18.0	8.4	51448.7	0.0	490.7	1.4	1.9	0.0	22.4	3.7	44.9	0.0

FLd = Dystric FLuvisol; ACf = Ferric Acrisol; LVh = Haplic Luvisol; T = total metal concentration in mg/kg; B = exchangeable metal fraction in %; ND = not detected. B% is derived by expressing the value of the exchangeable metal concentration (in mg/kg) as a percentage of the total metal concentration (T).

Table 4.5: Standard values of heavy metals for soils and atmospheric fallout

Element	Standard value[a] (mg/kg)	World range in non-polluted soils[b] (mg/kg)	Atmospheric fallout[c] (mg/kg)
Cd	0.8–1.5	0.07–1.10	0.25
Cr	50–100	5–120	1.4
Cu	30–60	6–60	8.8
Ni	30–60	1–200	7.3
Pb	50–100	10–70	11
Zn	100–200	17–125	29

[a] From European norms (Rademacher, UN/ECE; 2001); [b] Kabata-Pendias and Pendias (1992); [c] In topsoil to 20 cm depth, estimated 100 year accumulation (Allen *et al.*, 1995).

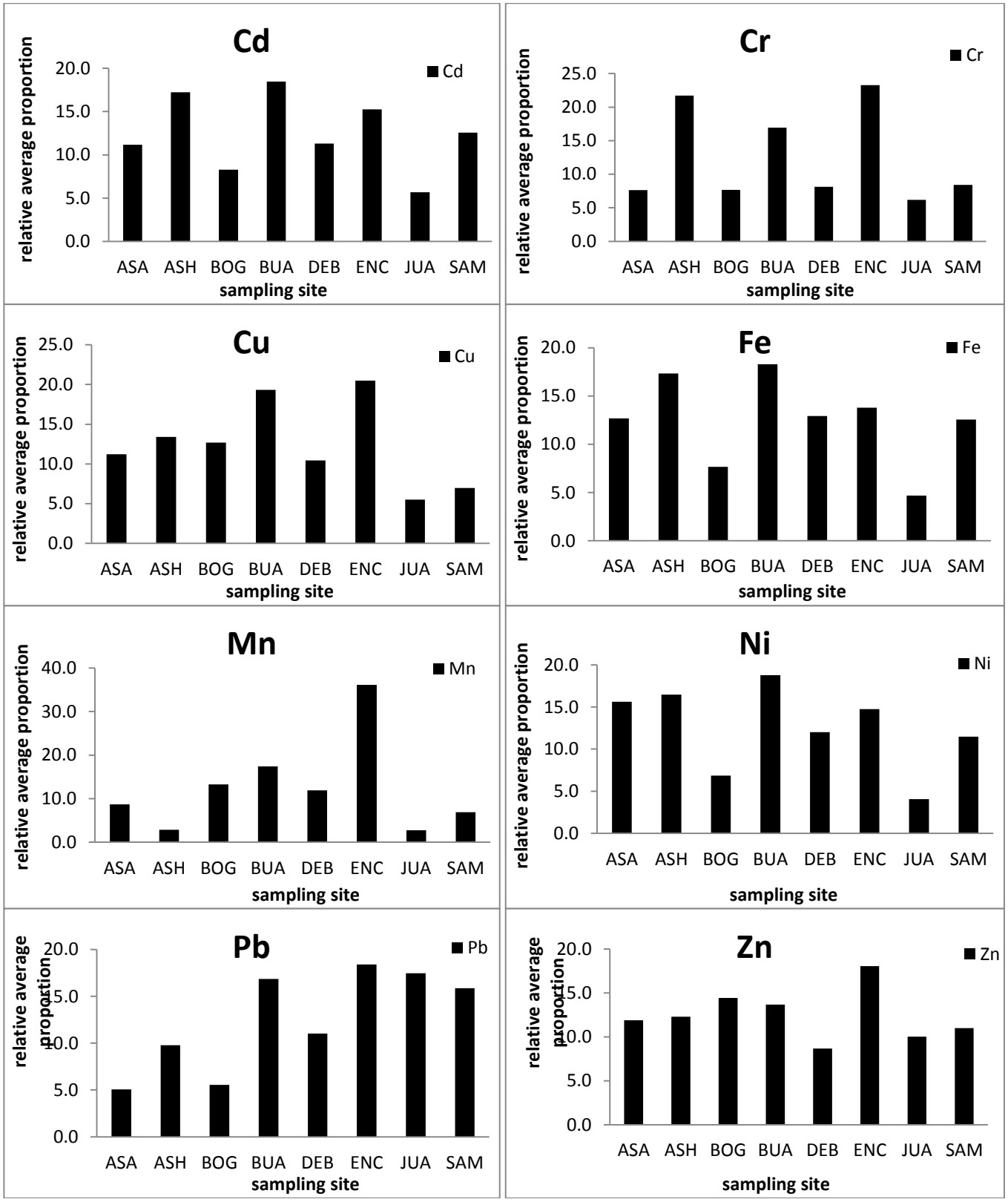
The distribution of the heavy metals with depth varied according to the element and to the soil type (Figs. 4.2a and b). The concentrations of Cd, Cr and Fe in all the soils increased with depth suggesting that the metals might be from lithogenic sources. Nickel content also increased with depth in all the soils except in the Haplic Ferrasol (BUA) and Ferric Acrisols (ASA and ABA) where the Ni concentrations were constant. Also, apart from the Haplic Ferrasol (BUA) and Ferric Acrisols (ASA and ABA), Zn content increased with depth in all the soils – Ferric Acrisols (ASA and ABA) had their Zn concentrations decreasing with depth while in Haplic Ferrasol (BUA), it was constant.

In ENC, Pb content decreased with depth till the 30 – 50 cm depth where it experienced a gradual increase to the deepest layer sampled. The opposite of the latter trend was observed for Ferric Acrisol (ASH). The Pb content in the Haplic Luvisol (DEB) decreased with depth whereas all the other unmentioned soils experienced an increase in Pb content with depth.

The latter observation might be due to the significant increase in clay fraction with depth in those soils.

With the exception of the Haplic Ferrasol (BUA) and the Ferric Acrisols (ASA and ABA) where the concentration of Cu remained unchanged within the soil, Cu content increased with depth for all the soils. The Haplic Ferrasol (BUA), the Haplic Luvisol (DEB) and Dystric Fluvisol (SEN) presented an erratic distribution of Mn; the Ferric Acrisols (ASA and ASH) exhibited constant Mn concentration in their soils while Dystric Fluvisol (ENC) displayed an increasing concentration of Mn with depth.

Figure 4.3 and Table 4.6 present a summary of concentrations for the representative soils. The Dystric Fluvisol (ENC) recorded the highest average concentrations of Mn (810.7 mg/kg) and Cr (104.5 mg/kg). The least average Mn value (61.2 mg/kg) was presented by Haplic Luvisol (JUA) and so was the least average Cr content (27.8 mg/kg). The Haplic Luvisol (JUA) again recorded the least average concentrations of Fe (13974.3 mg/kg), Cu (7.9 mg/kg), Ni (0.5 mg/kg) and Cd (3.2 mg/kg) while their highest concentrations were presented by Haplic Ferrasol - BUA (54530.7 mg/kg), Dystric Fluvisol - ENC (29.5 mg/kg), Ferric Acrisol - ABA, (3.0 mg/kg) and Haplic Ferrasol - BUA (10.4 mg/kg), respectively. The highest average Pb (8.4 mg/kg) and Zn (57.0 mg/kg) concentrations were presented by Dystric Fluvisols (ENC and SEN), respectively, whereas their respective least values were recorded by Ferric Acrisol - ASA (2.3 mg/kg) and Haplic Luvisol - JUD (25.8 mg/kg).



Note: Ferric Acrisols = ASA, ASH and BOG; Haplic Ferrasol = BUA; Haplic Luvisols = DEB and JUA; Dystric Fluvisols = ENC and SAM

Figure 4.3: Comparing the average proportions of metals between the various farms. The average proportion of a metal for a site is obtained by finding the mean of the various proportions of the metal in the different depths of that site; the relative average proportion is obtained by expressing the average proportion of a metal as a percentage of the total average proportion of that metal for the various farms.

Table 4.6: Mean total heavy metal concentrations with corresponding exchangeable metal fractions for the soils studied

Sample (code)	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)	T (mg/kg)	B (%)
ACf (ASA)	6.3	0.1	34.3	0.0	16.1	8.6	37838.7	< 0.1	195.3	13.8	1.8	37.3	2.3	23.5	36.8	1.9
ACf (ASH)	9.8	0.0	97.4	0.4	19.3	7.3	51676.7	< 0.1	64.2	7.3	1.9	0.0	4.4	10.0	38.1	0.8
ACf (BOG)	4.7	0.3	34.4	0.1	18.2	5.0	22844.5	0.0	297.5	17.0	0.8	15.0	2.5	18.3	44.7	1.8
FRh (BUA)	10.4	0.0	76.0	0.0	27.8	4.8	54530.7	< 0.1	390.5	5.5	2.2	0.0	7.7	10.9	42.4	0.0
LVh (DEB)	6.4	0.1	36.5	0.0	15.0	11.2	38584.7	< 0.1	267.4	11.1	1.4	8.3	5.0	12.0	26.9	0.0
FLd (ENC)	8.6	0.1	104.5	0.0	29.5	15.9	41137.7	0.2	810.7	2.2	1.7	8.0	8.4	4.3	55.9	0.0
LVh (JUA)	3.2	0.4	27.8	1.7	7.9	18.7	13974.3	0.0	61.2	36.7	0.5	17.9	7.9	3.2	31.0	1.4
FLd (SAM)	7.1	0.0	37.8	0.0	10.0	17.4	37472.7	0.0	155.0	15.6	1.3	3.0	7.2	8.5	34.0	0.0
ACf (ABA)*	4.2	0.0	15.2	0.0	14.5	9.6	20608.7	0.1	41.9	20.0	3.0	20.4	7.0	1.7	48.6	5.0
LVh (JUD)*	3.5	0.0	32.5	0.0	15.4	9.7	16382.9	< 0.1	146.8	5.8	0.8	20.7	2.5	22.0	25.8	0.0
FLd (SEN)*	9.1	0.0	62.3	0.0	28.2	6.1	46628.7	0.0	759.7	1.4	1.7	0.0	14.9	3.0	57.0	0.0

ACf = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; * = Pristine reference; T = mean total metal concentration in mg/kg; B = exchangeable metal fraction in %. B% is derived by expressing the value of the mean exchangeable metal concentration (in mg/kg) as a percentage of the mean total metal concentration (T).

4.4 PHYSICOCHEMICAL PROPERTIES VERSUS HEAVY METAL CONTENT

Depth function is employed to highlight the behaviour of soil physicochemical properties with heavy metals at each sampling site (Figs. 4.4-4.7).

4.4.1 Clay versus Heavy Metal Distribution

Figures 4.4a and b illustrates the distribution of clay with heavy metals. In the Ferric Acrisol (ASH), clay distribution pattern did not synchronise with that of the metals except for Cd, Fe and Ni for depth 0 – 80 cm. Clay might be responsible for their distribution (Boon and Soltanpour, 1992). At depth 80 – 100 cm, Cd, Fe and Ni experiencea a sharp increase while clay showed the reverse.

With the exception of Mn Fe, and Pb, clay distribution pattern in the Ferric Acrisol (BOG) matched with that of the metals. The distribution of Fe, Mn and Pb might, therefore, be controlled by other physicochemical properties other than clay.

In the Dystric Fluvisol (ENC) and in the Haplic Luvisol (JUA), apart from Pb the distribution patterns of all the metals were similar to that of clay from depth 0 – 80 cm. Zinc showed a reverse pattern with clay from depth 80 – 100 cm in the Haplic Luvisol (JUA). The distribution patterns of clay and Cd, Cu, Cr and Zn were congruent whereas that with Fe, Mn and Pb depicted otherwise as far as Haplic Luvisol (JUA) and Dystric Fluvisol (SAM) were concerned. In the Dystric Fluvisol Pristine reference (SEN), however, clay distribution pattern matched that of all the metals but Pb.

In summary, clay seemed to control the movement and distribution pattern of most of the metals except Pb and to a lesser degree Mn.

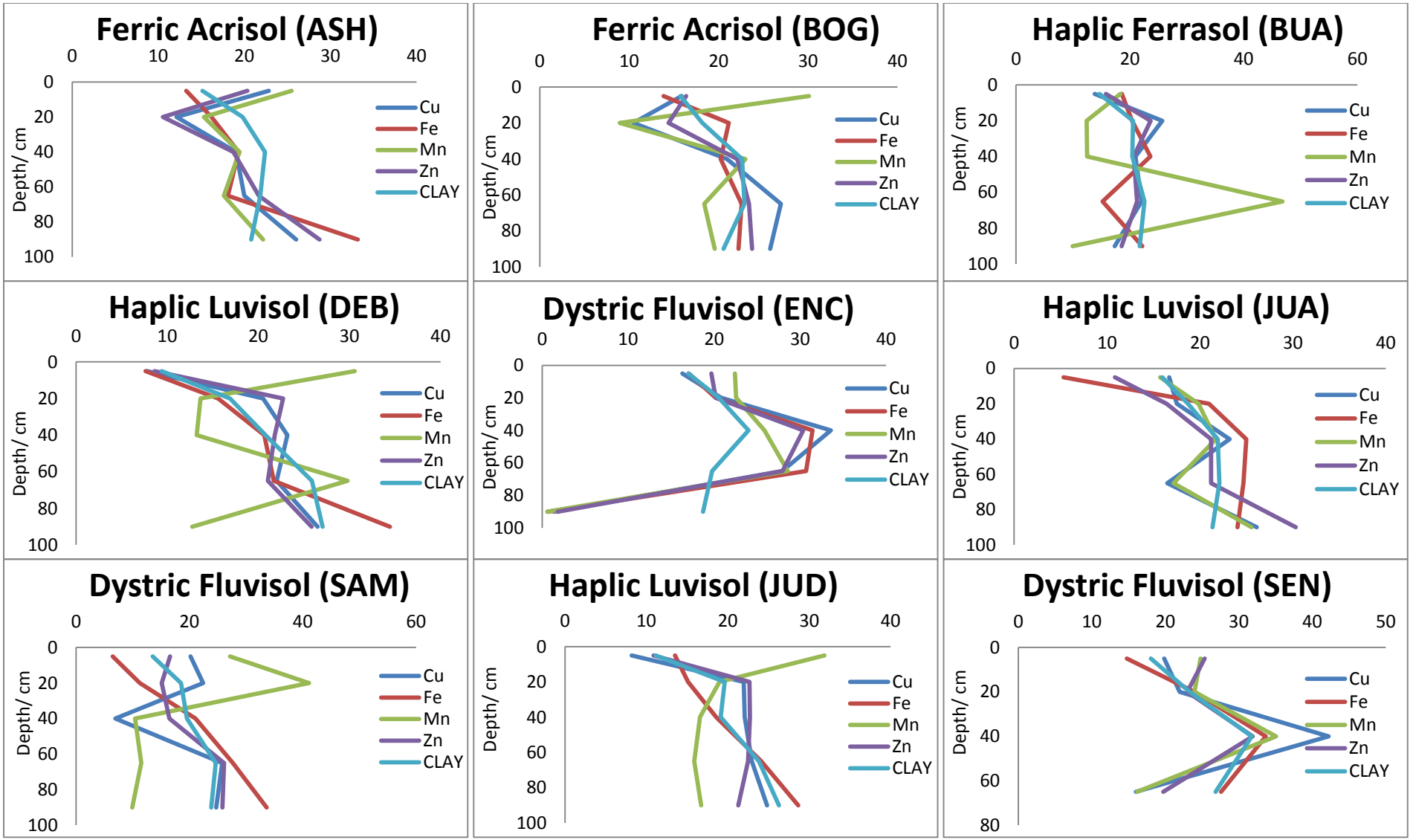


Figure 4.4a: Depth function plots illustrating the distribution of Cu, Fe, Mn and Zn with clay content.

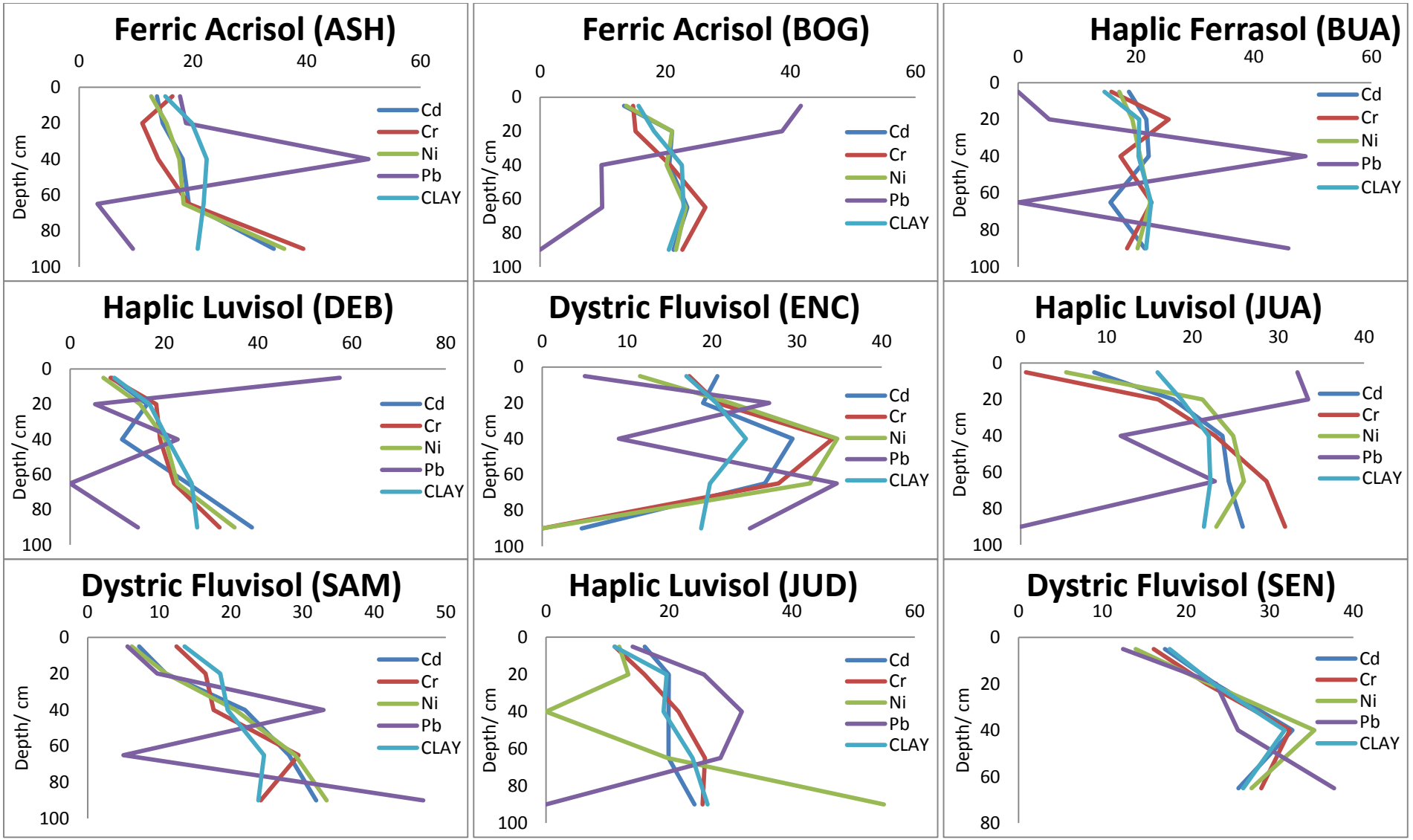


Figure 4.4b: Depth function plots illustrating the distribution of Cd, Cr, Ni and Pb with clay content.

4.4.2 pH versus Heavy Metal Distribution

In the Ferric Acrisol (BOG), the distribution patterns of all the metals except Pb synchronised with that of pH (Figs. 4.5a and b). At high pH, the metals were converted to their hydroxide forms which are the preferred species adsorbed onto clay surfaces (McLean and Bledsoe, 1992; Harter, 1983). This was in agreement with the clay distribution pattern. The distribution pattern at Ferric Acrisol (BOG) was also observed for the Ferric Acrisol (ASH) till depth 80 cm where the opposite was observed. Eluviation of metals might explain the latter observation (Li and Wu, 1999).

The Haplic Ferrasol (BUA) indicated a reverse pattern between pH and Cd, Fe, Mn and Pb. Nonetheless, Cr, Cu, Ni and Zn showed the same distribution pattern as pH. The former observation might be explained as the metals being of lithogenic origin and so their distribution was mostly affected by clay while the latter might be indicative of anthropogenic input. The latter observation could depend on pH and probably organic matter for the metals distribution in the soil as both soil properties are strongly influenced by human and environmental factors such as rainfall and application of manure and agrochemicals.

In the Haplic Luvisol (DEB), pH distribution pattern was only in agreement with Cr, Cu and Fe between depths 10 cm and 50 cm. There was, however, no agreement between pH and any of the heavy metals for the Haplic Luvisol (DEB) studied. The Dystric Fluvisol (SAM) also showed an agreement in distribution pattern between pH and Zn for depth 0 – 50 cm. No metal showed any agreement in distribution pattern with pH for Dystric Fluvisol (SAM). Sites Dystric Fluvisols (ENC and SEN) and Haplic Luvisols (JUA and JUD) indicated no agreement in distribution pattern between pH and any of the heavy metals.

In all, except for the Ferric Acrisol (ASH), pH shows no agreement with any of the metals for the various soils studied.

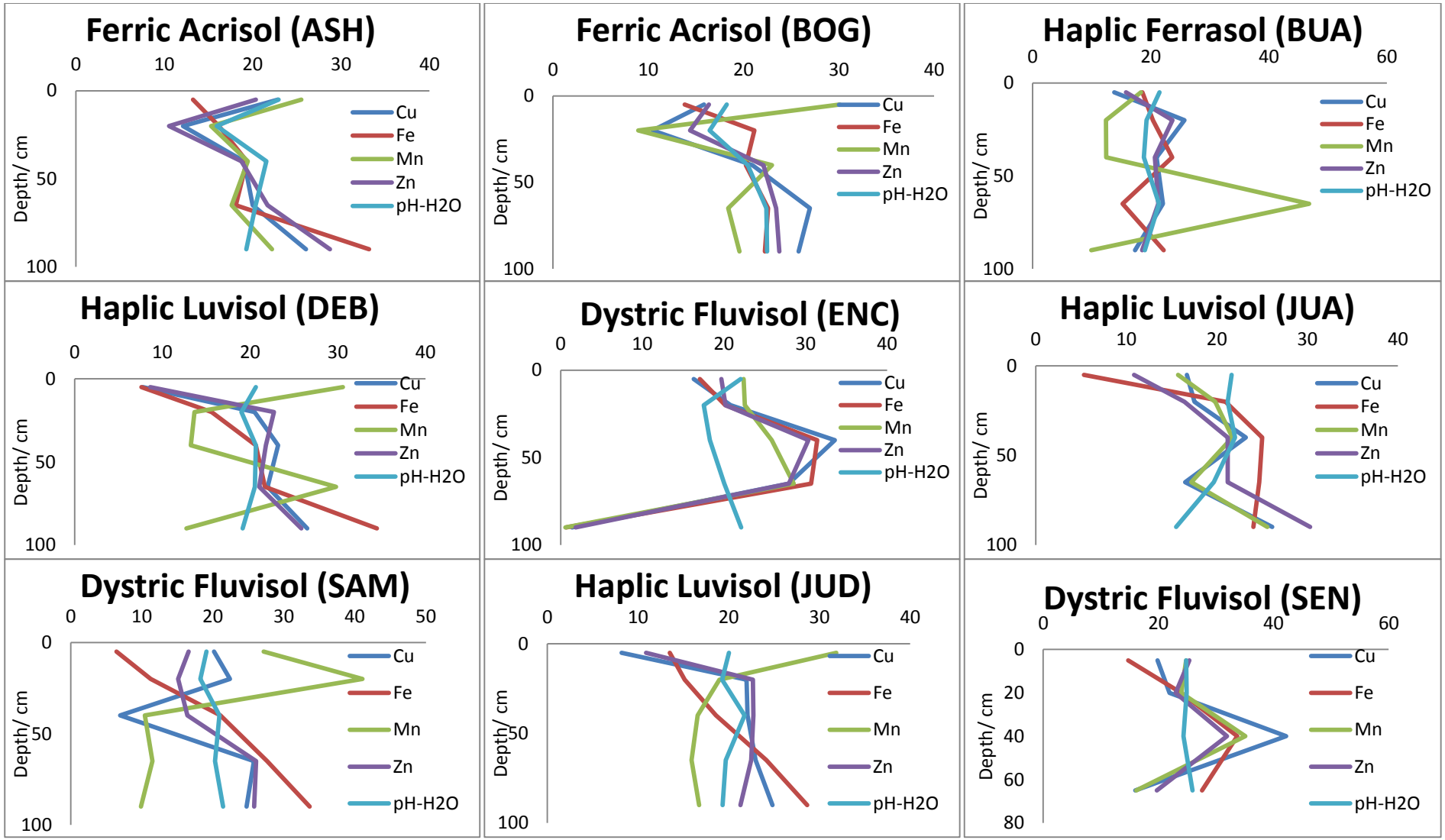


Figure 4.5a: Depth function plots illustrating the distribution of Cu, Fe, Mn and Zn with pH (Soil:H_2O = 1:1).

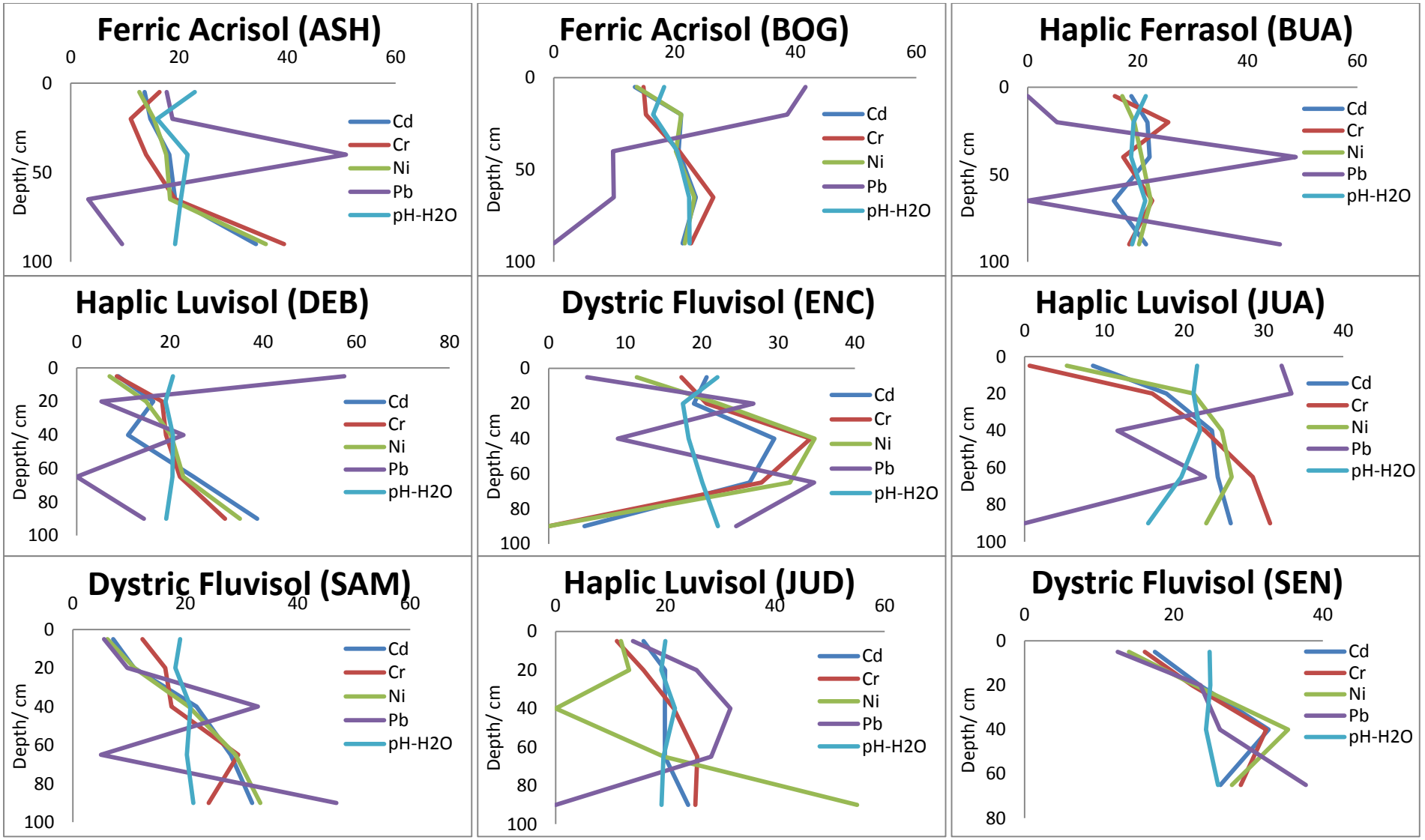


Figure 4.5b: Depth function plots illustrating the distribution of Cd, Cr, Ni and Pb with pH (Soil:H_2O = 1:1).

4.4.3 Total Organic Carbon Content (TOC) versus Heavy Metal Distribution

With the exception of the the Haplic Luvisol (JUD) which showed an agreeable TOC distribution pattern with Mn for depths 0 – 80 cm (Figs. 4.6a and b), the distribution pattern of TOC showed no agreement with that of the heavy metals for all the soils studied.

4.4.4 Cation Exchange Capacity (CEC) versus Heavy Metal Distribution

The Ferric Acrisol (ASH) and Dystric Fluvisol (ENC and SAM) showed no agreement between the distribution patterns of the metals and CEC (Figs. 4.7a and b).

In the Ferric Acrisol (BOG), however, the distribution patterns of Cu and Zn were similar to that of CEC and so were Cr, Cu, Fe and Ni in the Haplic Luvisol (DEB). In the the Haplic Ferrasol (BUA) and in the Haplic Luvisol pristine reference (JUD), Fe exhibited the same distribution pattern with CEC. The distribution pattern of Ni in the Haplic Ferrasol (BUA), though not so close, was more in agreement with CEC than the other metals in that soil. The Haplic Luvisol (JUA) was the only soil that indicated, though slight, a similar distribution pattern between CEC and Pb.

The Dystric Luvisol pristine reference (SEN), however, showed strong similar CEC distribution pattern with Cd, Cr, Cu, Mn, Ni and Zn. In the same soil, Fe presented a slight similar pattern with CEC as compared to the aforementioned metals whereas Pb showed a completely dissimilar pattern.

On the whole, clay content seemed to be the dominant factor that controlled the movement of the metals.

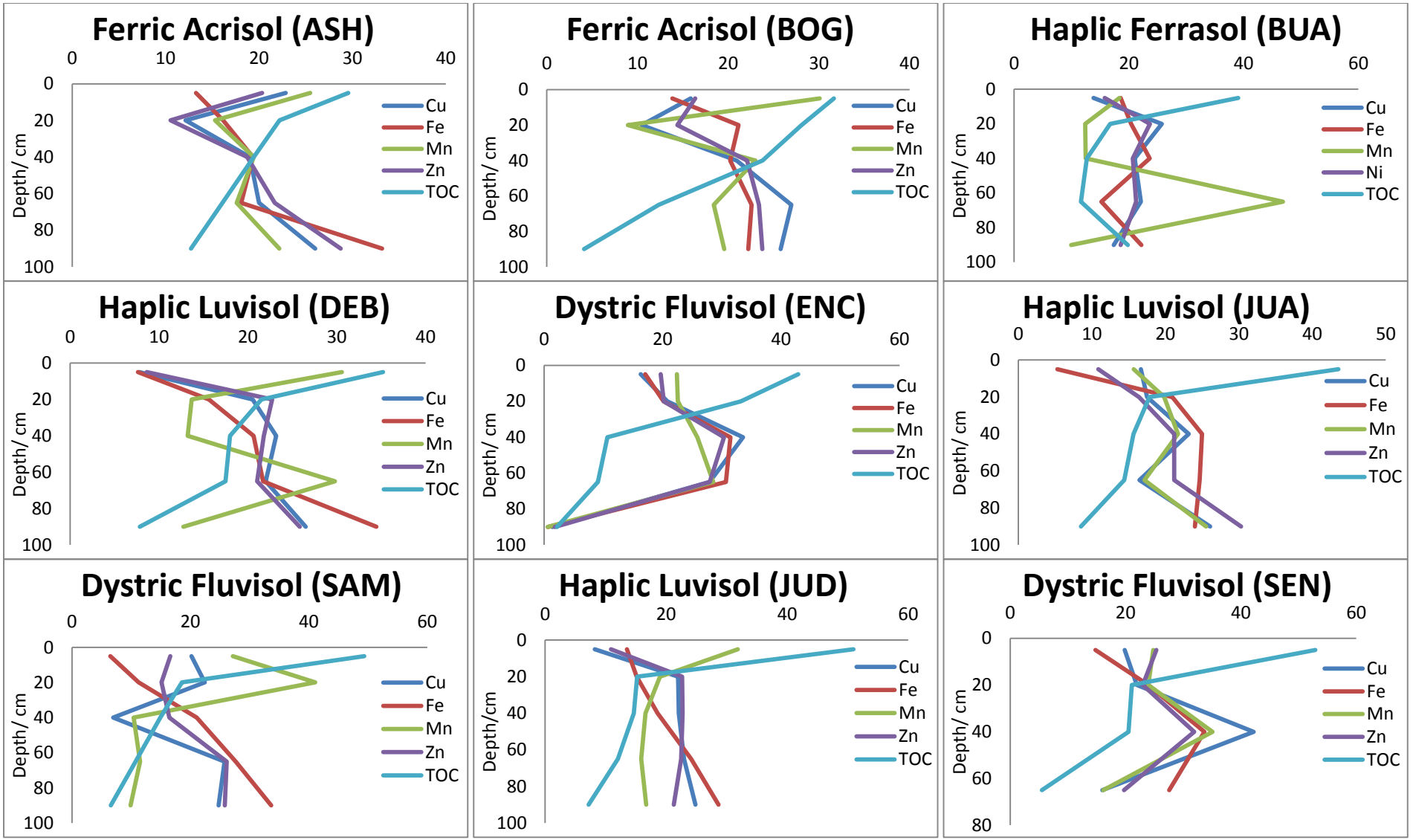


Figure 4.6a: Depth function plots illustrating the distribution of Cu, Fe, Mn and Zn with total organic carbon content (TOC).

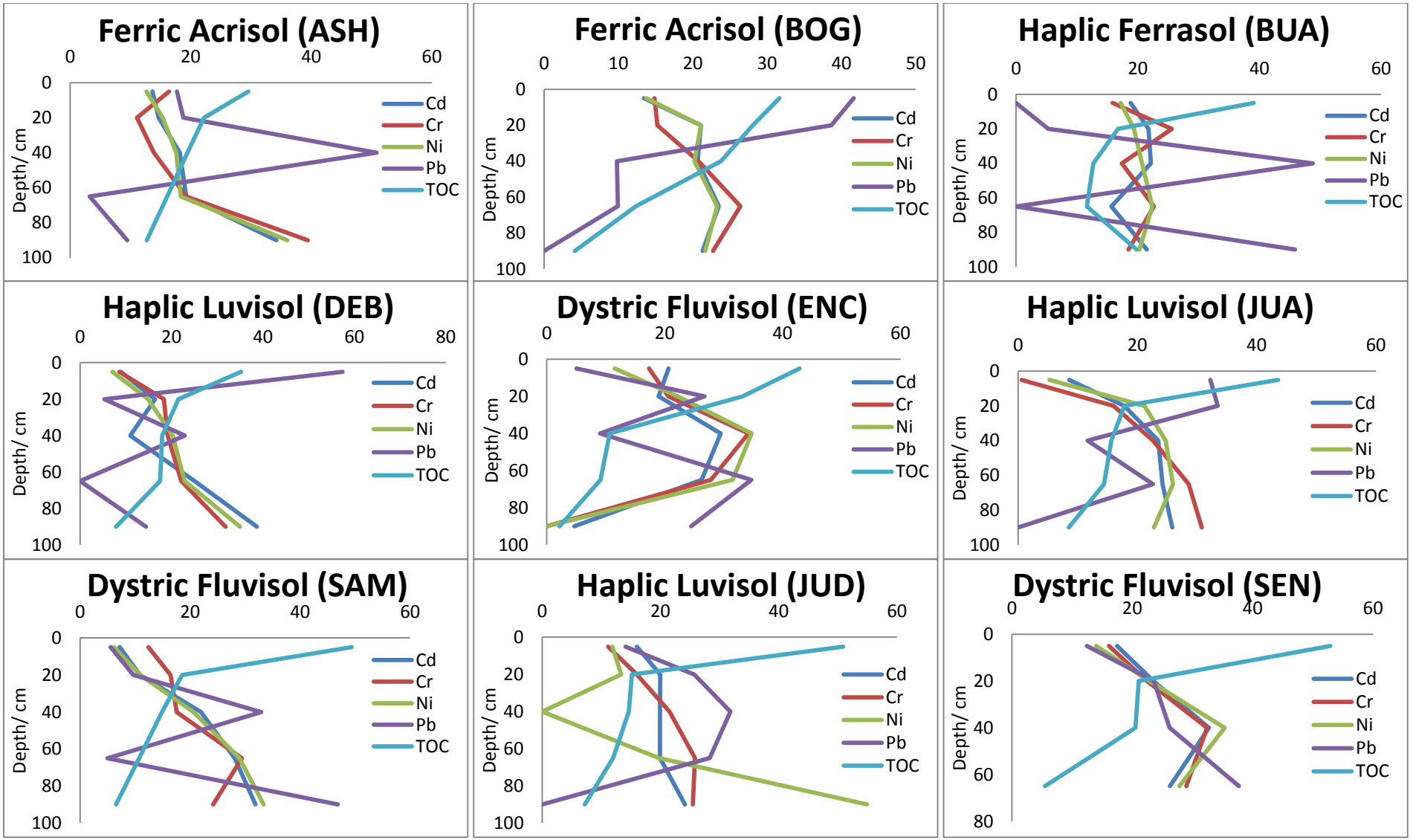


Figure 4.6b: Depth function plots illustrating the distribution of Cd, Cr, Ni and Pb with total organic carbon content (TOC).

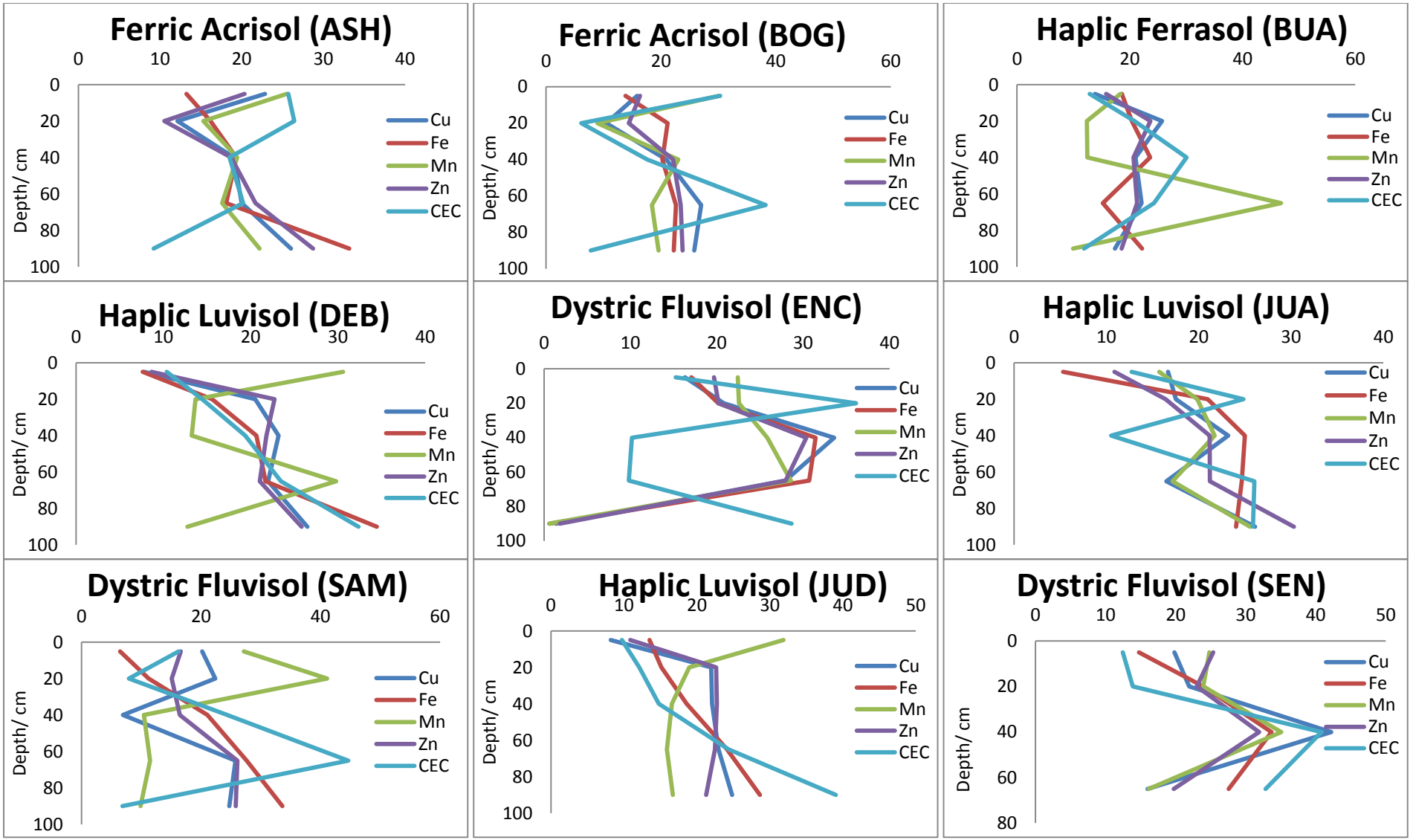


Figure 4.7a: Depth function plots illustrating the distribution of Cu, Fe, Mn and Zn with cation exchange capacity (CEC).

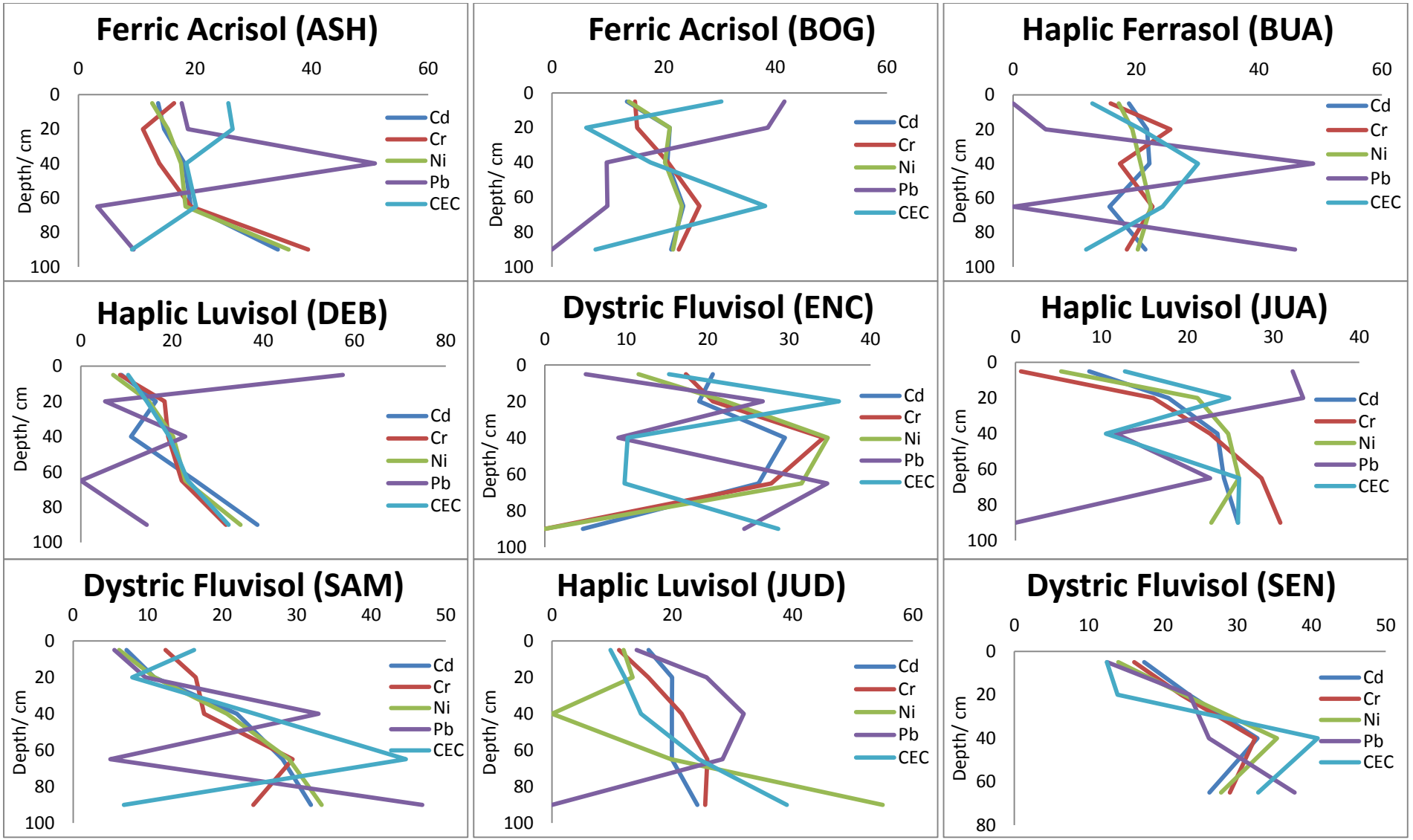


Figure 4.7b: Depth function plots illustrating the distribution of Cd, Cr, Ni and Pb with cation exchange capacity (CEC).

4.5 DISCRIMINANT ANALYSIS

Discriminant analysis was employed to determine whether the investigated soils differ significantly in terms of metal concentration. For this reason, the eleven sampling sites representing the major soils (ABA, ASA, ASH, BOG, BUA, DEB, ENC, JUA, JUD, SAM and SEN) were first entered as grouping variables into SPSS (SPSS for Wndows, Ver. 17.0). The eight heavy metal concentrations were then entered as the independent variables. The canonical correlation statistic, the Wilk's Lambda statistic, the significant level and the percentage of group cases correctly classified were extracted from the SPSS viewer and presented in Table 4.7.

The results indicated that all the soils exhibited different concentrations of heavy metals. Generally, the larger the canonical correlation statistic ($\geq$ 0.45), the greater the between-group variation as compared to the total variation and the larger the Wilk's Lambda statistic ($\geq$ 0.45), the greater is the within-group variation as a proportion of the total variation.

Excluding Fe (0.085), the canonical correlations had values ranging from 0.686 to 0.954. This implies that for each metal under investigation, except for Fe, a high degree of between-site variations existed. Thus, the average concentration of each metal differed appreciably from one soil to the other. The average concentration of Fe, however, did not statistically differ for the different soils. This showed that Fe content in the soils was pedogenic and not anthropogenic.

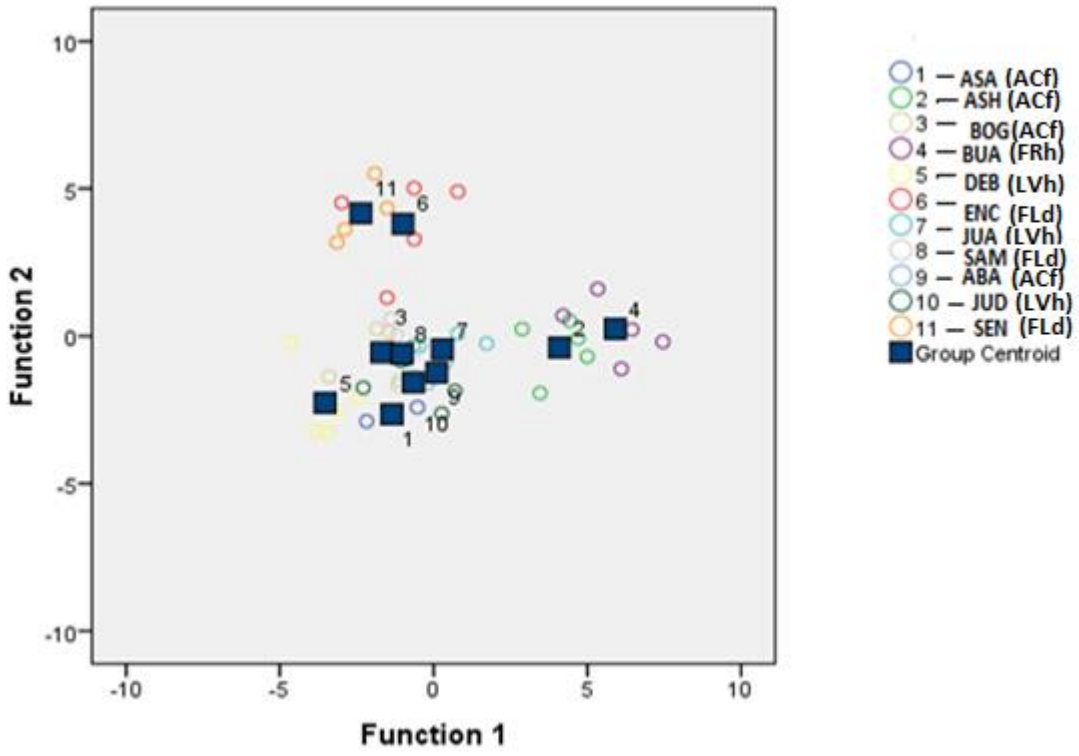
There was also a high degree of within-site variations as indicated by the Wilk's Lambda statistic (range: 0.487 – 0.608) for Cd, Cr, Cu, Fe, Ni, Pb and Zn whereas Mn presented a low degree of within-site variation (0.326). Consequently, all metals but Mn showed differing degrees of accumulation for the various depths in each soil. The statistically significant results (significance range: 0 – 0.027) also demonstrated that the originally grouped cases had

very high percentage (100%). The scatter plot (Fig. 4.8) illustrates the deviations of the individual soils from their group centroid or mean based on the first two extracted eigen functions.

Table 4.7: Discriminant analysis results for the investigated soils

Variable	Canonical correlation	Wilk's Lambda statistic	F	df1	df2	Sig.	Percentage of grouped cases correctly classified
Cd	0.919	0.496	3.762	10	37	0.001	100.0
Cr	0.954	0.487	3.890	10	37	0.001	100.0
Cu	0.877	0.508	3.588	10	37	0.002	100.0
Fe	0.085	0.496	3.756	10	37	0.002	100.0
Mn	0.919	0.326	7.637	10	37	0.000	100.0
Ni	0.701	0.548	3.050	10	37	0.006	100.0
Pb	0.919	0.584	2.640	10	37	0.015	100.0
Zn	0.686	0.608	2.390	10	37	0.027	100.0

F = ratio of between group variability (explained variance) to within group variability (unexplained variance); df – degrees of freedom; Sig. – significance.



ACf = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol

Figure 4.8: Scatter plot showing between-group variations and the deviations of the individual soils from their group centroid or mean (within-group variations).

4.6 ANOVA ANALYSIS

Though discriminant analysis proved to be useful in establishing the fact that there were variations in metal concentrations from the soils, it did not provide information as to why there were differences in metal concentrations among the soils. With the knowledge that the metal concentrations could be associated with high soil pH, total organic carbon content (TOC), cation exchange capacity (CEC) and clay fraction, a two-way analysis of variance was performed to determine which variable was the most important factor in controlling the spatial differences in metal concentration. In this model, Site-Clay was first entered as grouping variable into the SPSS, then Site-pH, then Site-TOC and Site-CEC finally. The

dependent variables (the heavy metals) were subjected to log-normal transformation before being used.

The detailed results of the two-way ANOVA are summarized in APPENDIX E.The results indicated that the concentrations of each of the metals under investigation were significantly different across the eleven soil sampling sites. The results were in agreement with those obtained from the execution of the discriminant analysis and even highlighted which of the independent variables and/or interactions between them could explain the variations in the concentration of metals.

Clay content was observed (APPENDIX E1) to account for significant variations between the group means of Cd (P = 0.042) and Fe (P = 0.042). The variable soil site, however, presented significant variations between the group means of all the metals ($0.000 \leq P \leq 0.041$) except for Cd (P = 0.106) and Pb (P = 0.653). The result was in agreement with that from the depth functions which indicated that clay controlled the distribution pattern of all the metals except Pb. The effects of the interactions between the two independent variables (Site and Clay) highlighted the significant variations in the concentrations of only Cr (P = 0.018), Fe (P = 0.046) and Ni (P = 0.003). Thus, the variations between the group means of Cr, Fe and Ni might be as a result of their different sources at the investigated sites.

It is evident from the test of between-subject effects for Site-pH variables (APPENDIX E2) that pH did not account for any significant variations between the group means of all the metals ($0.157 \leq P \leq 1.000$). This observation agreed with the conclusion from the depth function graphs that pH did not control the distribution pattern of the heavy metals in the investigated soils. It was also observed that variable soil site showed no significant variation between the group means of the metals ($0.101 \leq P \leq 0.399$) except for Fe (P = 0.000), Mn (P = 0.000) and Zn (P = 0.002). The effects of the interactions between the two independent

variables (Site and pH) highlighted the significant variations in the concentration of only Mn (P = 0.011). This was probably due to the different sources of Mn in the investigated soils.

Total organic carbon (TOC) showed significant variations between the group means of Cd (P = 0.000), Cr (P = 0.000), Fe (P = 0.000) and Ni (P = 0.002), (APPENDIX E3). It was observed that variable soil site showed significant variation between the group means of all metals ($0.000 \leq P \leq 0.007$). The interactions between the independent variables (Site and TOC) were only significant for Cd (P = 0.044), Cr (P = 0.007), Fe (P = 0.005), Ni (P = 0.000) and Zn (P = 0.021). This observation could be attributed to different sources of Cd, Cr, Fe, Ni and Zn in addition to the contributions from TOC in the investigated soils. Total OC could, therefore, not be solely responsible for the distribution patterns of the heavy metals.

It was observed that cation exchange capacity (CEC) showed no significant variations between the group means of the metals ($0.116 \leq P \leq 0.914$), (APPENDIX E4). It was also evident that except Ni (P = 0.239) variable soil site showed significant variation between the group means of all investigated metals ($0.000 \leq P \leq 0.047$). The interactions between the independent variables (Site and CEC) were not significant for all metals ($0.560 \leq P \leq 0.949$). The contribution of CEC to the distribution pattern of the metals was thus not significant and so did not agree with the observation from the depth function graphs.

4.7 CORRELATION ANALYSIS

4.7.1 Relationships among the heavy metals

Cadmium, Cu and Fe were significantly related to each other and to all metals but Pb according to Pearson correlation (APPENDIX F). Lead dids not relate to any of the other

seven metals under study. It might be associated with a unique source most probably one from an anthropogenic origin.

The heavy metals were strongly related to the total Fe content ($0.485 \leq r^2 \leq 0.972$, n = 48, P = 0) except for Pb (r^2 = 0.223, n = 48, P = 0.123). Such a relationship was particularly significant for Cd, Cr, Cu, Ni and Zn (r^2 = 0.972, = 0.485, 0.636, 0.651 and 0.524, respectively, n = 48, P = 0) and weakly significant for Mn (r^2 = 0.319, n = 48, P = 0.027). This indicated the strong affinity of these six elements for Fe oxides. Iron content can help in determining the heavy metal background values (Huisman *et al.*, 1997). This strong affinity may also be due to the presence of high levels of sesquioxides in the soils particularly the Acrisols. A lot of Fe coexists with clay and since clay seemed to be controlling the movement of most, it stands to reason that Fe is highly associated with most of the metals.

Chromium, Mn and Ni were not significantly related to each other. The distribution of this group of metals might be explained by different soil physicochemical properties. Probably for the same reason for the different distribution patterns of the latter group of metals; Zn and Cr were observed to have no significant relationship.

4.7.2 Relationships between Metal Content and Soil Physicochemical Properties

The relationships between the main soil properties and metals were also assessed (APPENDIX F). Clay proportion and all the heavy metals but Mn and Pb were positively correlated particularly Cd, Cr, Cu, Fe and Ni (r^2 = 0.659, 0.638, 0.460, 0.651 and 0.516, respectively, n = 48, P = 0). This was in agreement with the results from the depth function graphs and ANOVA.

The Mn content was weakly but significantly correlated to only pH(H_2O) for all the soils (r^2 = 0.305, n = 48, *P* = 0.035). This observation agreed with the ANOVA results.

The relationship between total organic carbon (TOC) and both the metals and any other soil physicochemical properties was not significant. The observation also supported the results from the depth function graphs and ANOVA.

A significant and positive correlation was observed between cation exchange capacity (CEC) and the clay proportion for the different soil horizons (r^2 = 0.422, n = 48, *P* = 0.003). The CEC and Clay content explained the distribution of Cr in the soils (r^2 = 0.487and 0.638, respectively, n= 48, *P* = 0). Chromium was the only metal related to CEC.

4.8 ANTHROPOGENIC VERSUS LITHOGENIC SOURCES OF HEAVY METALS

4.8.1 Accumulation-Depletion Ratio

A relative accumulation ratio of metals in the soil core was determined from the ratio below:

Accumulation-Depletion ratio = $[M]_{depth}$ / $[M]_{deepest\ depth}$.

where, $[M]_{depth}$ = The concentration of a metal M at a given depth

$[M]_{deepest\ depth}$ = The concentration of a metal M at the depth 80 - 100 cm

The results are presented in Figs. 4.9a and b and detailed in APPENDIX G. The following orders of the metal accumulation characterized the specific soils:

In the Ferric Acrisol at Ashiem (ASH),

0 – 50 cm: Pb >> Mn > Cu > Zn > Fe > Ni = Cd > Cr

50 – 100 cm: Zn = Mn = Cu > Cd > Ni = Fe = Cr > Pb

In the Ferric Acrisol at Asankragwa (ASA),

0 – 100 cm: Mn > Zn > Ni = Cu > Cr > Fe = Cd > Pb

In the Ferric Acrisol at Bogoso (BOG),

0 – 10 cm: Pb >> Mn > Zn = Cr > Ni = Fe = Cu = Cd,

10 – 30 cm: Pb >> Cd = Fe > Ni > Cr > Zn > Mn > Cu,

30 – 50 cm: Mn > Pb = Cd > Ni = Zn = Fe = Cr > Cu

50 – 100 cm: Cr > Cd > Cu = Fe = Ni = Pb = Zn > Mn

In the Haplic Ferrasol at Buako (BUA),

0 – 10 cm: Mn > Zn = Ni = Cr = Cd > Fe = Cu > Pb,

10 – 30 cm: Cu > Cr, Zn > Mn > Ni = Cd > Fe > Pb

30 – 100 cm: Mn >> Cu > Cr > Ni = Zn > Fe = Cd >> Pb

In the Haplic Luvisol at Debiso (DEB),

0 – 100 cm: Pb > Mn >> Zn = Cu = Cr > Ni = Fe = Cd

In the Dystric Fluvisol at Enchi (ENC),

0 – 50 cm: Fe > Cu > Zn > Cd > Mn > Pb > Ni = Cr

50 – 100 cm: Fe > Cu > Zn > Cd > Pb > Ni = Cr > Mn

In the Ferric Acrisol pristine reference (ABA) from Asankragwa,

Ni > Zn > Cu > Mn > Cd > Fe = Cr > Pb for the depths sampled

In the Haplic Luvisol at Juabeso (JUA),

0 – 10 cm: Pb > Mn = Cu > Zn > Cd > Ni = Fe > Cr,

10 – 30 cm: Pb > Ni > Fe > Mn > Cu > Cd > Zn = Cr,

30 – 80 cm: Ni > Fe > Cu = Cd > Mn > Zn > Cr >Pb

80 – 100 cm: Ni > Pb = Fe > Cr = Cd > Zn > Mn > Cu

In the Dystric Fluvisol at Samreboi (SAM),

0 – 30 cm: Mn > Cu > Zn = Cr > Ni = Fe = Cd > Pb,

30 – 80 cm: Mn >Pb = Cr = Cd > Zn = Ni = Fe > Cu,

80 – 100 cm: Mn = Cr > Zn = Cu > Ni = Cd > Fe > Pb

In the Haplic Luvisol pristine reference (JUD) from Debiso,

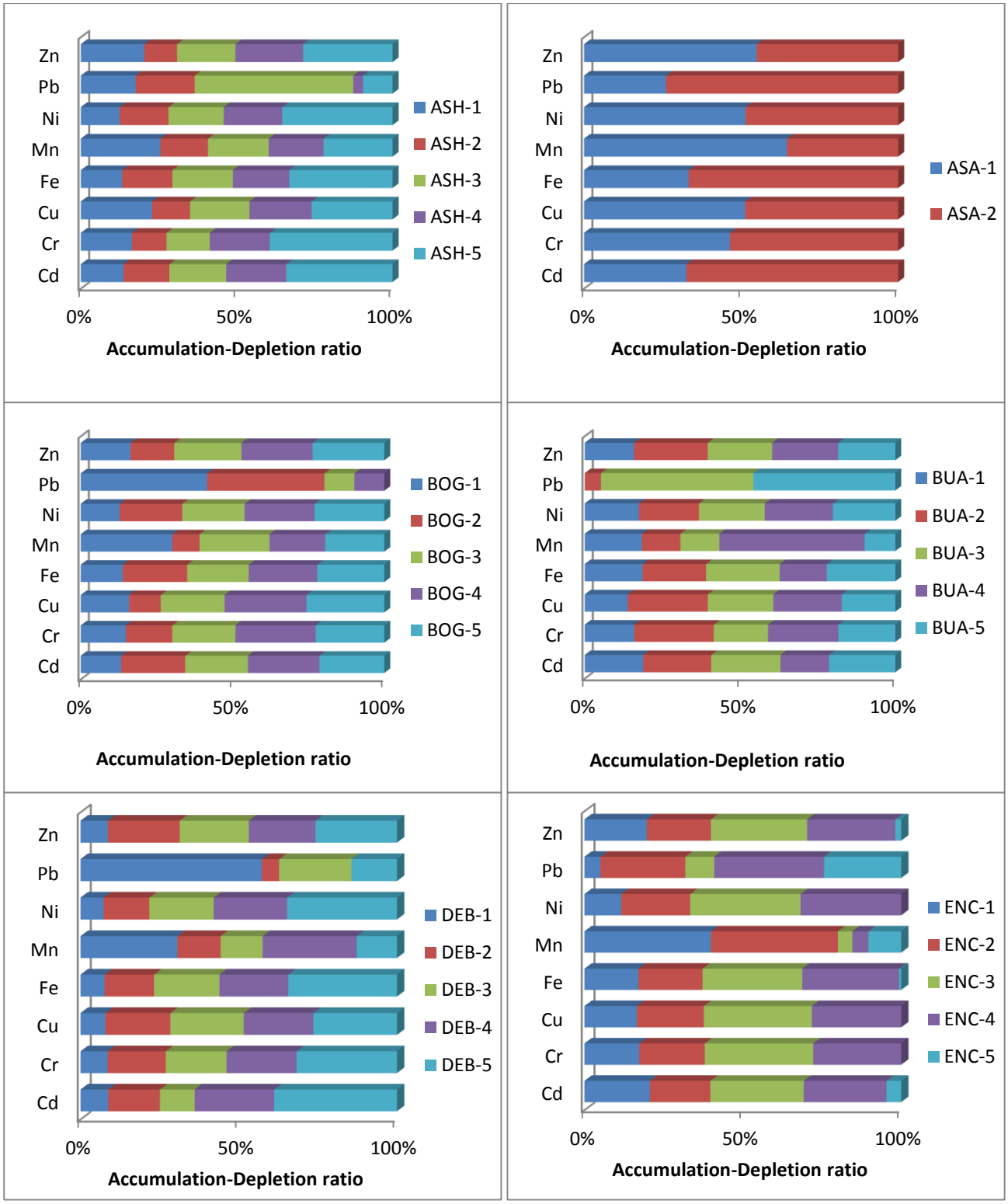
0 – 10 cm: Mn > Cd > Zn = Pb = Fe > Cr > Cu >Ni

10 – 100 cm: Mn = Zn = Pb > Cu = Cd = Cr = Fe > Ni

In the Dystric Fluvisol pristine reference (SEN) from Enchi,

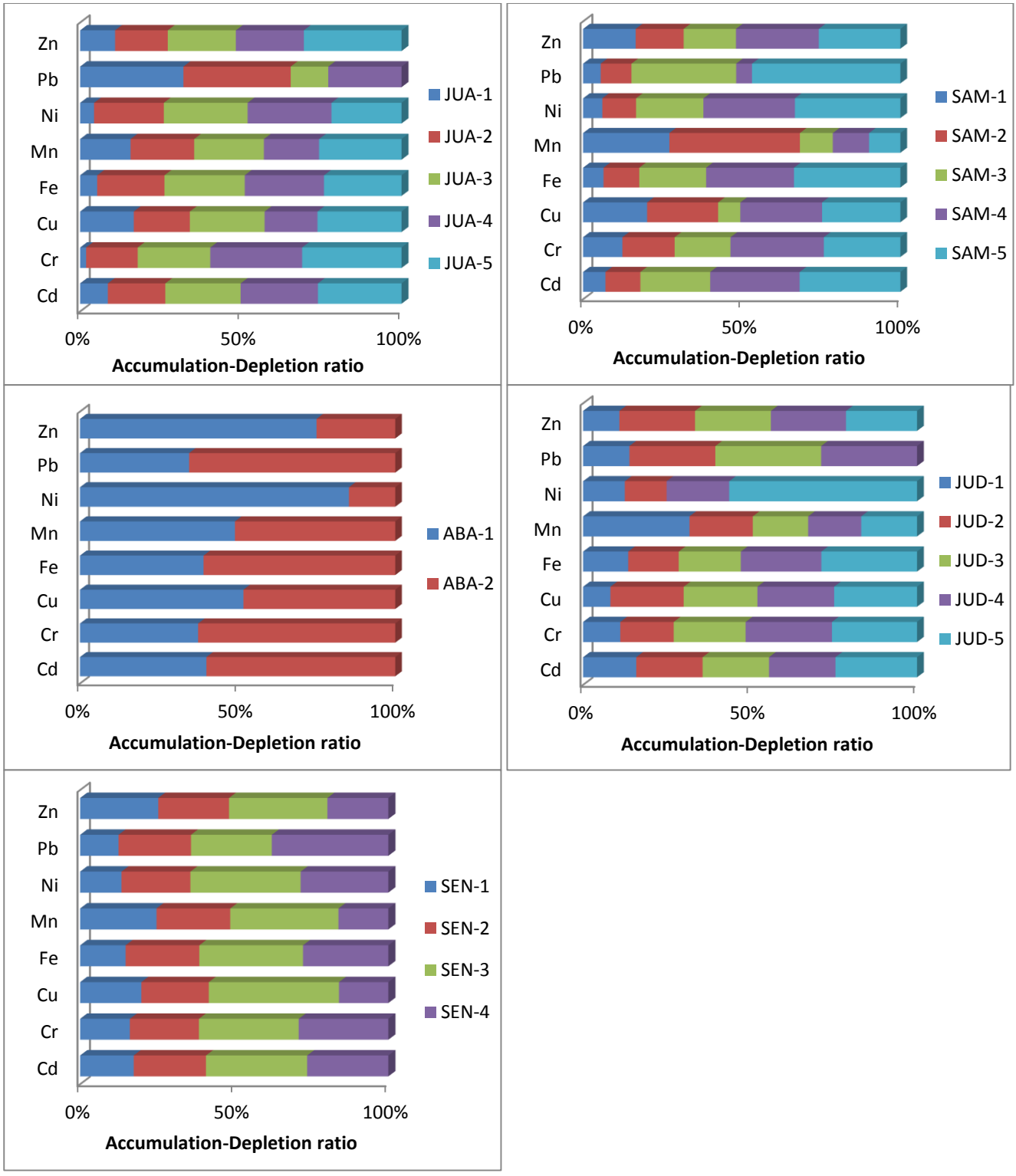
0 – 100 cm: Mn > Cu > Zn > Cd > Fe = Ni > Cr > Pb

With the exception of Cr, each metal seemed to highly accumulate in the 0 – 10 cm depth in at least one soil sampling site. This might be due to anthropogenic inputs (accumulation-depletion ratio > 1). In view of this, metal accumulation probably due to anthropogenic input for specified sites is summarized as ASA (Mn, Zn, Cu and Ni), ASH (Pd and Cu), BOG (Pb and Mn), BUA (Mn), DEB (Pb and Mn), ENC (Cd, Cu, Zn, Mn and Fe), JUA (Pb), SAM (Mn), ABA (Ni, Cu and Zn), JUD (Mn) and SEN (Zn, Cu and Mn). However, generally, the frequency was in the order: Mn > Cu > Pb = Zn > Ni > Cd = Fe.



In the key: 1 = 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm; and Ferric Acrisols = ASA, ASH and BOG; Haplic Ferrasol = BUA; Haplic Luvisols = DEB and JUA; Dystric Fluvisols = ENC and SAM

Figure 4.9a: Relative accumulation ratio of heavy metals in the soils at different depths. Each accumulation-depletion ratio was percent-wise normalised for each site [(a / B) × 100, where a = accumulation-depletion value for a metal, and B = sum of accumulation-depletion values of that metal for various depths of a soil].



In the key: 1 = 0 – 10 cm; 2 = 10 – 30 cm; 3 = 30 – 50 cm; 4 = 50 – 80 cm; 5 = 80 – 100 cm; and Ferric Acrisols = ASA, ASH and BOG; Haplic Ferrasol = BUA; Haplic Luvisols = DEB and JUA; Dystric Fluvisols = ENC and SAM

Figure 4.9b: Relative accumulation ratio of heavy metals in the soils at different depths. Each accumulation-depletion ratio was percent-wise normalised for each site [(a / B) × 100, where a = accumulation-depletion value for a metal, and B = sum of accumulation-depletion values of that metal various depths of a soil].

Figure 4.10 is a graph obtained by plotting the average values of the 0 – 10 cm accumulation-depletion ratios of each metal for the different soil types against that metal. The grouping of the accumulation-depletion ratios according to the soil types showed that the Cd accumulation in the 0 – 10 cm depth was only pronounced in the Dystric Fluvisols. Copper, Zn and Fe accumulations were also most pronounced in the Dystric Fluvisols probably due to fungicide and fertilizer applications and/or the relatively high pH, high CEC and high TOC in their surface soils (0 – 10 cm) which might tend to slow the metals' mobility down their soil profiles (Tables 4.1b-d and 4.2a).

Manganese accumulation was high in the surface soils (0 – 10 cm) of all the soil types.. However, Mn concentration also decreased with depth as TOC indicating an anthropogenic source. In conclusion, Mn occurrence may be due to pooled factors from more of anthropogenic source than lithogenic origins.

Nickel accumulation was high in the 0 – 10 cm depth for only the Ferric Acrisols and Pb was high for both Ferric Acrisols and Haplic Luvisols. The surface layers of these soil types had high clay content and acidic pH thereby facilitating rapid adsorption and desorption processes, respectively (Tables 4.1a-d and 4.2). Therefore, the high accumulations of Ni and Pb in the surface soils of the Ferric Acrisols and Pb in that of the Haplic Luvisols might be explained by the strong retention of the metals deposited from anthropogenic sources into the highly reactive medium of acidic pH clay fractions of the surface soils.

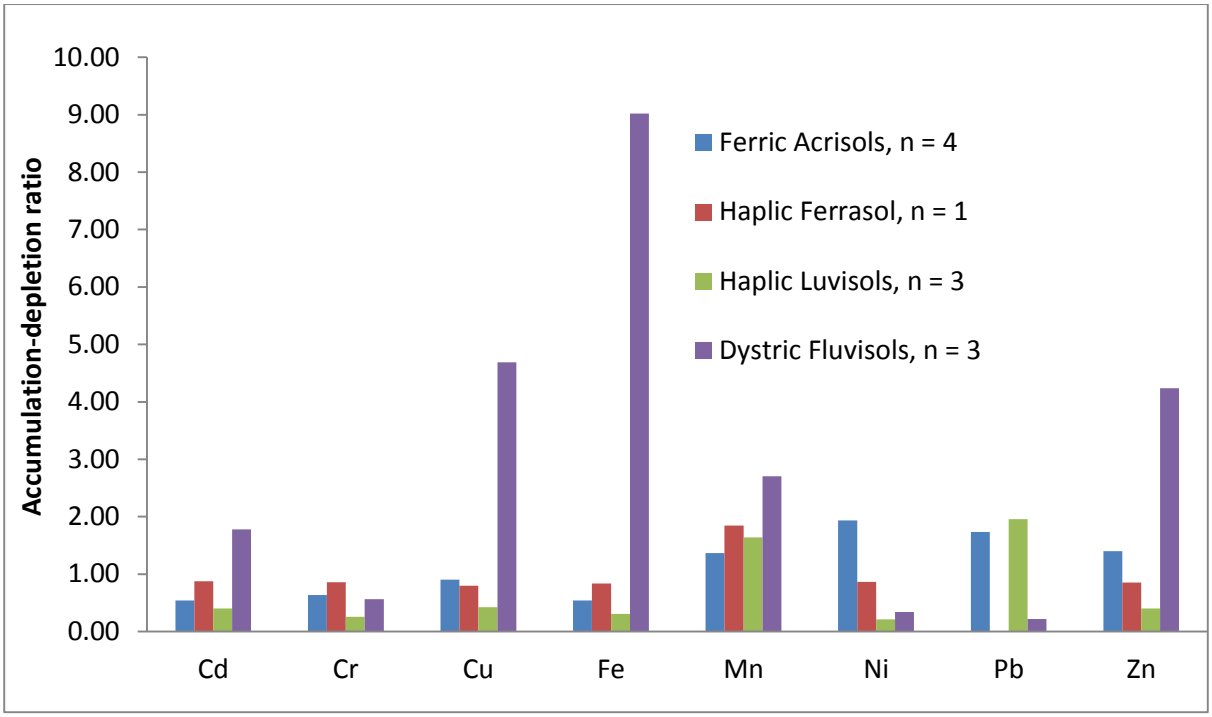


Figure 4.10: Average accumulation-depletion ratios of metals in the surface soils (0 – 10 cm) grouped according to soil types. The graph is obtained by plotting the average values of the 0 – 10 cm accumulation-depletion ratios of each metal for the different soil types against that metal.

4.8.2 Enrichment Factor and Anthropogenic/Lithogenic Contribution

The enrichment factor is the relative abundance of a chemical in a soil compared to the bedrock. Enrichment factor (EF) was calculated using Fe as a reference element (Hernández *et al.*, 2003). Firstly, the reference values were taken for some metals from the respective pristine references (PR) [Eq. 4.3a] and, then for all the considered metals from the concentrations in each deepest soil horizon, 80 – 100 cm (DSH) [Eq. 4.3b]. The purpose was to determine a relative range of enrichment factors.

$$EF_1 = \frac{[M]/[Fe]_{soil}}{[M]/[Fe]_{PR}} \quad \text{..... Equation 4.3a}$$

$$EF_2 = \frac{[M]/[Fe]_{soil}}{[M]/[Fe]_{DSH}} \quad \text{..... Equation 4.3b}$$

where [M] = total heavy metal concentration measured in soil sample (mg/kg)

[Fe] = total concentration of Fe (mg/kg).

The EF values ranging between 0.5 and 2 can be considered in the range of natural variability, whereas ratios greater than 2 indicate some enrichment corresponding mainly to anthropogenic inputs (Qishlaqi and Moore, 2007).

The concentration of lithogenic heavy metal with respect to PR was calculated as follows:

$$[M]_{lithogenic} = [Fe]_{soil} \times [M]/[Fe]_{PR} \quad \text{..... Equation 4.4a}$$

where $[M]/[Fe]_{PR}$ corresponds to the average ratio of the pristine reference (PR)

Then, the anthropogenic heavy metal with respect to PR was estimated as:

$$[M]_{anthropogenic} = [M]_{soil} - [M]_{lithogenic} \quad \text{..... Equation 4.4b}$$

Therefore, %anthropogenic heavy metal with respect to PR was deduced as:

$$\%\text{Anthropogenic} = \frac{[M]\text{anthropogenic}}{[M]\text{soil}} \times 100\% \quad \text{..... Equation 4.4c}$$

Equations 4.4a-c were again used to calculate the %anthropogenic heavy metal but with respect to the deepest soil horizon, DSH (80 – 100 cm).

The results are summarized in Tables 4.8a and b and detailed in APPENDICES H and I for all metals. The results are also illustrated in Figs. 4.11a and 4.11b, respectively, for Pb and Cr taken as examples because Pb is known as partly coming from anthropogenic atmospheric input and on the opposite Cr is often supposed to be of lithogenic origin (Shotyk *et al.*, 2000).

Table 4.8a: Enrichment factors, EF_1 (against the pristine reference value) and EF_2 (against the value of the deepest horizon sampled), and anthropogenic contributions (%) for Cd, Pb, Cr and Ni in the studied soils; (bold: EF>2)

Soil type	Depth (cm)	Cd				Pb				Cr				Ni			
		EF_1	EF_2	%Anthrop.		EF_1	EF_2	%Anthrop		EF_1	EF_2	%Anthrop.		EF_1	EF_2	%Anthrop.	
				PR	DSH			PR	DSH			PR	DSH			PR	DSH
ACf (ASA)	0 – 10	0.8	1.0	-	-	0.2	0.7	-	-	1.8	1.7	44.3	42.6	0.2	**2.1**	-	53.4
ACf (ASH)	0 – 10	0.9	1.0	-	-	0.4	**4.7**	-	78.7	**3.3**	1.0	69.7	4.0	0.1	0.9	-	-
ACf (BOG)	0 – 10	0.9	1.0	-	1.1	0.9	**6.9**	-	85.4	**2.3**	1.1	56.3	4.9	0.1	1.0	-	1.9
FRh (BUA)	0 – 10	-	1.0	-	4.4	-	-	-	-	-	1.0	-	2.4	-	1.0	-	1.2
LVh (DEB)	0 – 10	0.8	1.0	-	3.6	**6.0**	**18.0**	83.0	94.4	0.7	1.2	-	18.2	1.0	0.9	-	-
FLd (ENC)	0 – 10	1.1	0.2	9.4	-	0.2	0.0	-	-	1.4	1.1	29.4	10.8	0.7	0.7	-	-
LVh (JUA)	0 – 10	1.4	1.5	30.9	33.3	**21.0**	**6.6**	95.0	84.9	0.4	0.3	-	-	1.0	1.1	-	4.8
FLd (SAM)	0 – 10	0.9	1.2	-	14.7	0.6	1.3	-	-	1.3	**2.7**	24.9	62.7	1.0	1.0	0.3	-

ACF = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric FLuvisol; %Anthropo. = %anthropogenic contribution; PR = with respect to pristine reference; DSH = with respect to deepest soil horizon

Table 4.8b: Enrichment factors, EF_1 (against the pristine reference value) and EF_2 (against the value of the deepest horizon sampled), and anthropogenic contributions (%) for Cu, Mn and Zn in the studied soils; (bold: EF>2)

Soil type	Depth (cm)	Cu				Mn				Zn			
		EF_1	EF_2	%Anthrop.		EF_1	EF_2	%Anthrop.		EF_1	EF_2	%Anthrop.	
				PR	DSH			PR	DSH			PR	DSH
ACf (ASA)	0 – 10	0.7	**2.1**	-	52.6	**3.9**	**3.6**	74.5	72.6	0.4	**2.4**	-	59.0
ACf (ASH)	0 – 10	0.7	**2.2**	-	54.5	0.9	**2.9**	-	65.3	0.3	1.8	-	43.6
ACf (BOG)	0 – 10	1.0	1.0	-	-	**11.1**	**2.5**	91.0	59.6	0.5	1.1	-	9.7
FRh (BUA)	0 – 10	-	1.0	-	-	-	**2.2**	-	54.7	-	1.0	-	1.6
LVh (DEB)	0 – 10	0.7	1.3	-	24.7	1.3	**10.8**	24.0	90.8	0.6	1.5	-	33.7
FLd (ENC)	0 – 10	0.8	0.5	-	-	0.9	1.5	-	31.3	0.7	0.4	-	-
LVh (JUA)	0 – 10	**3.1**	**2.9**	67.9	65.4	0.6	**2.8**	-	64.0	**3.6**	1.6	72.1	38.3
FLd (SAM)	0 – 10	1.0	**4.3**	3.1	76.5	0.6	**14.4**	-	93.0	1.1	**3.4**	10.3	70.2

ACF = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric FLuvisol; %Anthropo. = %anthropogenic contribution; PR = with respect to pristine reference; DSH = with respect to deepest soil horizon

Figure 4.11 presents two plots: the bar chart presents a plot of the enrichment factor values of Pb (Fig. 4.11a) or Cr (Fig. 4.11b) versus the various sampled depths of each soil and also compares the enrichment factor values EF_1 and EF_2; the pie chart, on the other hand, presents only the anthropogenic and lithogenic proportions of Pb (Fig. 4.11a) or Cr (Fig. 4.11b) in the surface soils (0 – 10 cm).

From Fig. 4.11a, it can be observed that almost all the soils were enriched in Pb when compared to average pristine reference abundances, except Ferric Acrisol (ASA), Haplic Ferrasol (BUA) and Dystric Fluvisols (ENC and SAM). Most of the enriched samples were in the surface horizons (0 -10 cm) from the Haplic luvisols (DEB and JUA). These soils had high Pb anthropogenic contribution (83.5 – 95.3%). For Haplic Luvisol (DEB), when the enrichment was calculated with regard to the deepest soil horizon sampled, enrichment was obvious and so was for JUA, albeit less so. For the Haplic Luvisol (DEB), the enrichment factor calculated with the deep soil layer contents as a reference was higher than that calculated with the pristine reference values. This could be attributed to lower Pb content in the deeper soil layer as compared to the pristine reference. The least Pb enriched soils were the Ferric Acrisol (ASA), Haplic Ferrasol (BUA) and Dystric Fluvisols (ENC and SAM). All of them showed no significant enrichments from anthropogenic contribution.

In all the soils, Cr enrichment values were weak as compared to those calculated for Pb (Fig. 4.11b). The discrepancies between calculated lithogenic contributions using pristine reference and deepest soil horizon reference values were noticeably less important than for Pb. This implies that the reference lithogenic values were quite uniform and that the deep soil core samples were not disturbed by Cr sources other than lithogenic origin. However, relative to the other soil samples, the enrichment factor for Dystric Fluvisol (SAM) was more important using the deep soil horizon as a reference in relation to significantly lower Cr/Fe ratios in the

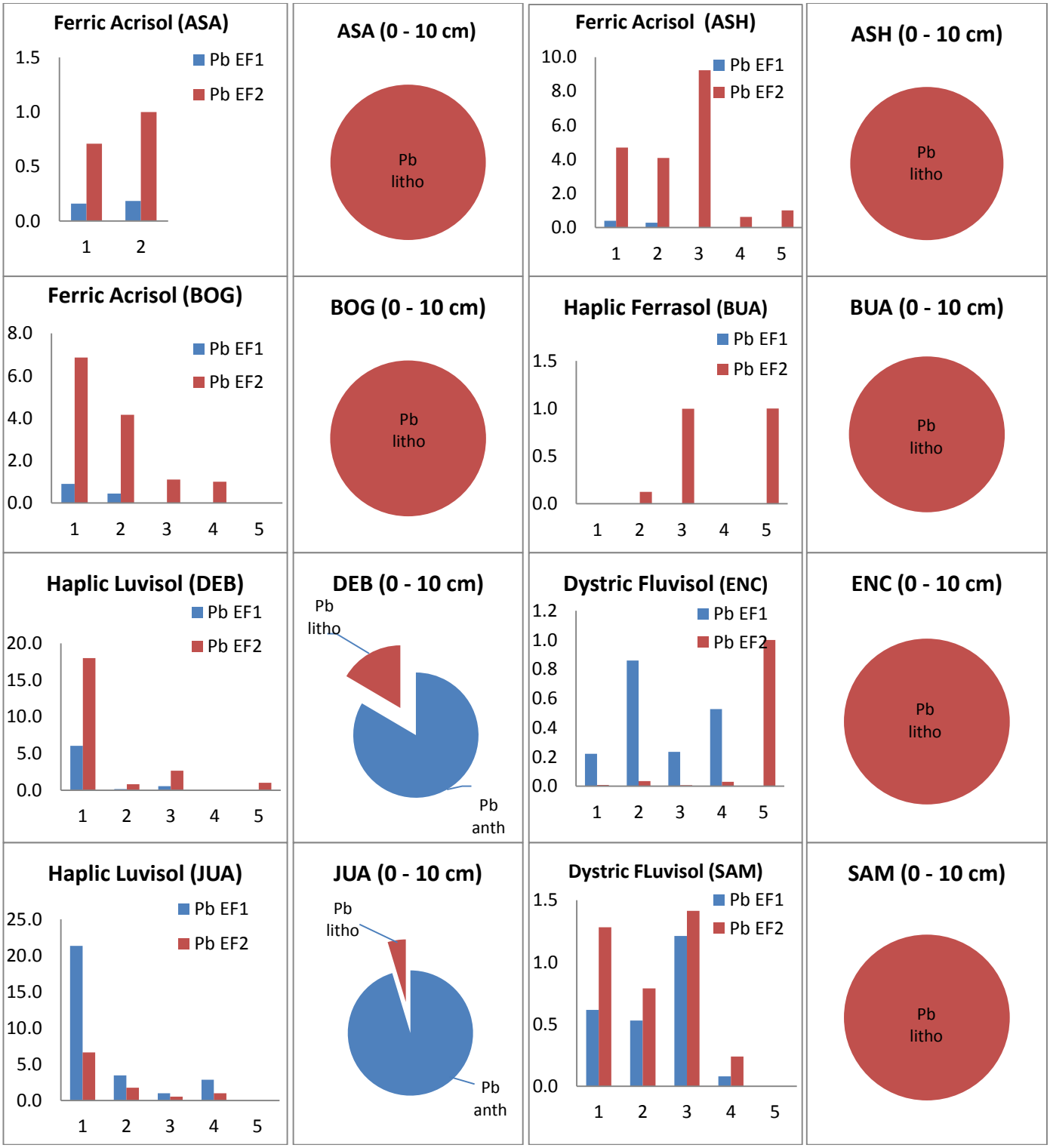
deepest soil horizon than in the pristine reference. Contrary to Pb, Cr in the surface horizons appeared to be mainly of lithogenic origin in all the soils.

For the other metals, except for Mn, almost all the soils were not metal-enriched with reference to the deep soil horizons. The Ferric Acrisol (ASA) was the most highly enriched with Cu, Zn, and Ni with respect to the deepest soil horizon whereas the Haplic Luvisol (JUA) was the most enriched in Cu and Zn with respect to the pristine reference.

Noticeably, with reference to the deepest soil horizons, some surface soils recorded enrichment factors ranging between 2.0 and 4.0, and even greater than 4.0: Cu, Mn, Ni, Zn (2.1, 3.6, 2.1 and 2.4, respectively) for Ferric Acrisol (ASA), Cu, Mn (2.2 and 2.9, respectively) for Ferric Acrisol (ASH), Mn (2.5, 2.2 and 10.8) for Ferric Acrisol (BOG), Haplic Ferrasol (BUA) and Haplic Luvisol (DEB), respectively, Cu, Mn (2.9 and 2.8, respectively) for Haplic Luvisol (JUA) and Cu, Mn, Zn (4.3, 14.4 and 3.4, respectively) for Dystric Fluvisol (SAM) whereas with reference to the pristine reference, some surface soils had enrichment factors above 3.0: Cu (3.1) for Haplic Luvisol (JUA), Mn (3.9 and 11.1) for Ferric Acrisols (ASA and BOG, respectively), and Zn (3.6) for Haplic Luvisol (JUA).

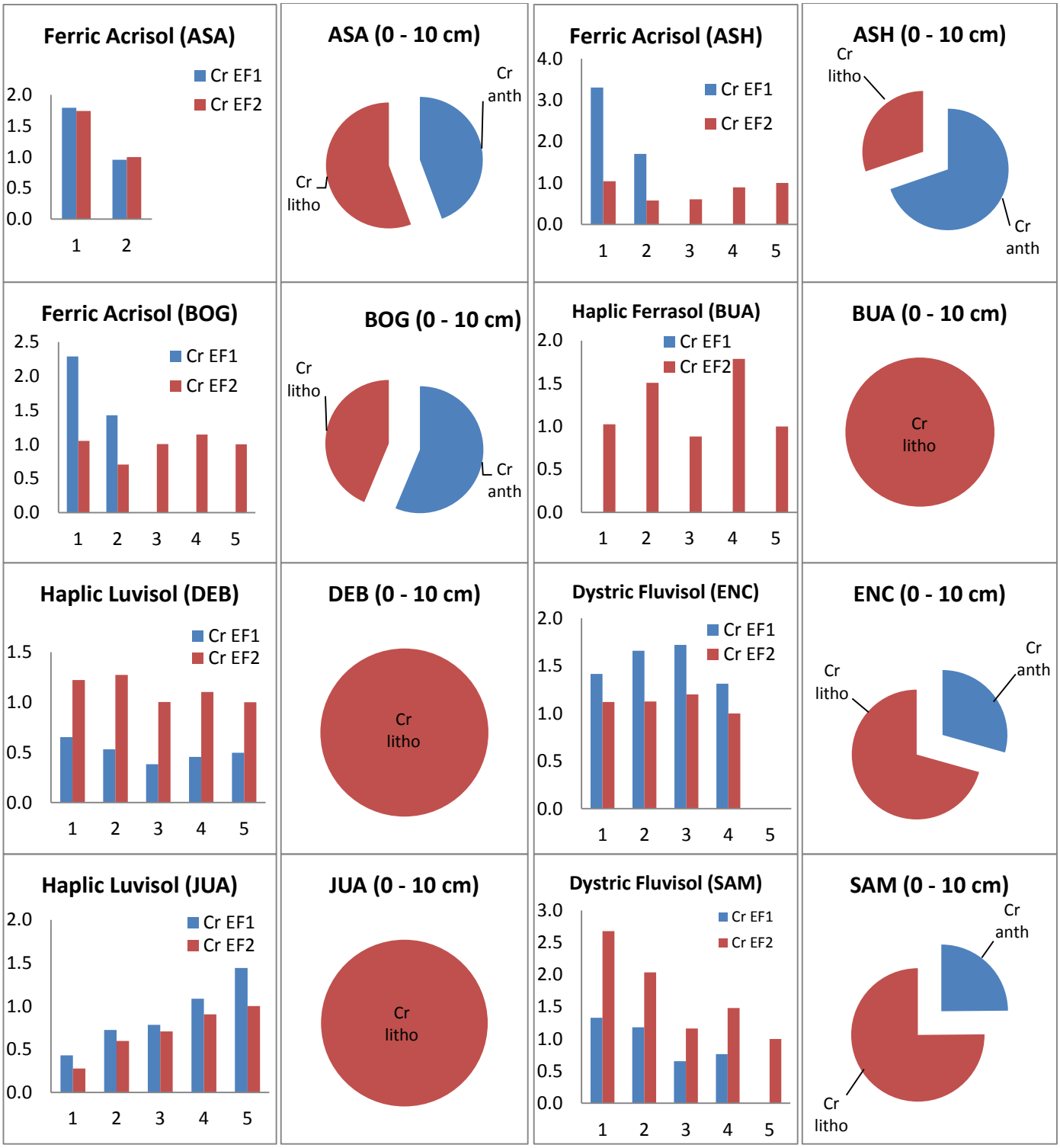
Lead and Mn recorded the highest values for EF_1 (pristine reference) and EF_2 (deepest soil horizon reference): For EF_1, Pb and Mn recorded values of 21.3 (JUA) and 11.1 (BOG) respectively, whereas for EF_2, Pb recorded 18.0 (DEB) and Mn recorded 14.4 (SAM) and 10.8 (DEB). Thus, the corresponding calculated anthropogenic was more important.

All these differences could be attributed to the disparity between the surface and deeper soil horizon concentrations, particularly for Fe concentration which generally increased with depth. Consequently, without bedrock data reference for the studied soils, the accurate value for enrichment factor and anthropogenic contribution was in between the values given in Table 4.10.



Litho = lithogenic; anth = anthropogenic; EF1 = enrichment factor against pristine reference; EF2 = enrichment factor against deepest soil horizon sampled.

Figure 4.11a: Lead enrichment in the different soils and lead anthropogenic proportion with reference to the pristine reference content in surface horizons. The pie chart illustrates the anthropogenic and lithogenic proportions of Pb in the surface soils (0 – 10 cm).



Litho = lithogenic; anth = anthropogenic; EF1 = enrichment factor against pristine reference; EF2 = enrichment factor against deepest soil horizon sampled.

Figure 4.11b: Chromium enrichment in the different soils and chromium anthropogenic proportion with reference to the pristine reference content in surface horizons. The pie chart illustrates the anthropogenic and lithogenic proportions of Cr in the surface soils (0 – 10 cm).

4.8.3 Principal Component Analysis (PCA)

Principal component analysis was applied to the auto-scaled data to present a differentiation between the metals in the soils. About 69.024% of the total variance in the data was found after the variables were correlated with three principal components. The selection of the number of significant principal components was based on the Kaiser criterion with eigen value higher than 1 (Kaiser, 1960). Accordingly, three principal components were selected as subsequent eigen values were all less than 1. Consequently, the descriptor space had a reduced dimensionality of three.

Varimax orthogonal rotation was then applied to the Kaiser-normalised data and three components or factors were extracted. These components were related to the sources of metals in the investigated soils. The results are summarised in Table 4.9 and illustrated in Fig. 4.12. Variables within same principal component group (PC1, PC2 or PC3) were associated and this strongly suggests that they have a similar source.

The first component (PC1) with 43.027% of variance comprised of Cd, Cr, Cu, Fe, Mn and Zn (bold figures in Table 4.9; within green circle and in green shades in Fig. 4.12) with high loadings. This group was not associated with any soil physicochemical properties and so the observation might be attributed to anthropogenic inputs such as agrochemical products (organic fertilizers and Cu-containing fungicides) and probably from the continual use of steel-made farm tools such as cutlasses, axes and hoes.

The second component (PC2) with 14.683% of variance comprised of Cd, Cr, Fe, Ni, CEC and Clay (bold figures in Table 4.9; within blue circle in Fig. 4.12). Cation exchange capacity (CEC) and Clay could be responsible for their distribution. The physicochemical meaning of PC2 also agreed with the results of the depth function graphs and Pearson correlation. From the results of the depth function, ANOVA, Pearson correlation and the Principal component

analysis, TOC was not related to any variable and so CEC was mainly the contribution of the charges on the Clay particles. Resultantly, since Clay is of lithogenic origin, the metals in PC2 might be of lithogenic source and their mobility in the soil could also be controlled by Clay.

Strikingly, Fe, Cr and Cd appeared in both PC1 and PC2 suggesting that their association could be explained by both anthropogenic and lithogenic factors. Nevertheless, Ni was most probably from a lithogenic source whereas Cu, Zn and Mn were of anthropogenic origin.

The third component (PC3) contributed Pb and pH (bold figures in Table 4.9; within red circle in Fig. 4.12) at 11.315% total variance. From the Pearson correlation, pH did not relate to any variable except Mn. It would, however, only be speculative to suggest that Pb was of anthropogenic origin on the basis that Mn was suggested to be of anthropogenic origin. Soil pH might have been a contribution from several sources such as organic matter, clay, soil moisture, acid rain and Al and Fe oxide contents of soil. It was therefore very difficult to ascertain the source of this component.

Table 4.9: Principal component loadings (Varimax with Kaiser Normalisation) for experimented variables in the soil samples (n = 48)

Variable	PC1	PC2	PC3
Cd	**0.587**	**0.708**	0.114
Cr	**0.649**	**0.599**	0.001
Cu	**0.847**	0.330	0.078
Fe	**0.522**	**0.765**	0.147
Mn	**0.861**	-0.171	0.252
Ni	0.439	**0.638**	-0.229
Pb	0.158	0.029	**0.638**
Zn	**0.875**	0.191	-0.109
pH	0.095	-0.155	**0.776**
TOC	0.124	-0.157	-0.562
CEC	-0.215	**0.637**	0.101
CLAY	0.153	**0.850**	-0.044
Eigen values	5.163	1.762	1.358
% Total variance	43.027	14.683	11.315
Cumulative %	43.027	57.710	69.024

TOC = Total organic carbon; CEC = Cation exchange capacity; PC = Principal component

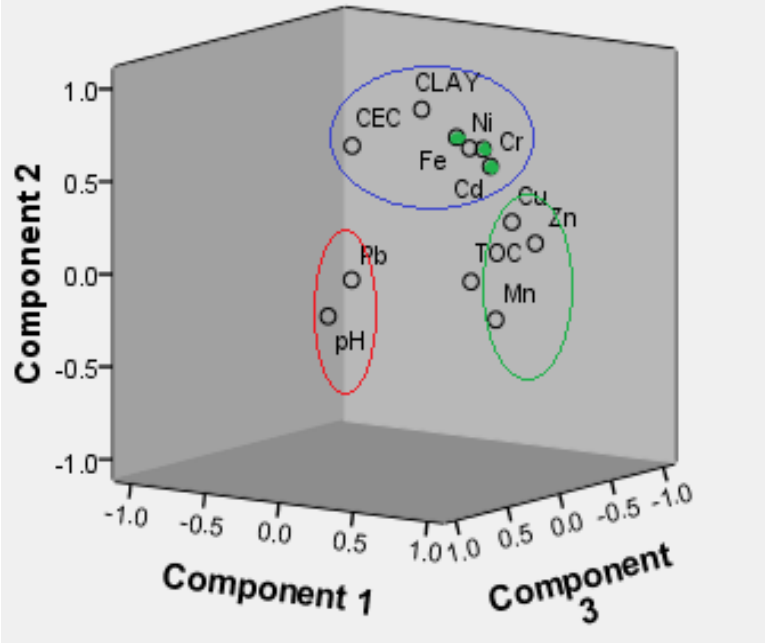


Figure 4.12: Principal component analysis loading plot for the rotated components.

CHAPTER FIVE

1.0 DISCUSSION

The textural distributions in the soils from the various farms were similar to those presented by their respective pristine references (natural forests). This reveals that weathering processes for the respective soil groups in the Western Region of Ghana are uniform.

The clay content increasing with decreasing sand content with depth in most of the soils showed that there was weathering of sand size particles into clay size fractions (Nartey *et al.*, 1997). The increasing clay content with depth might also be due to vertical translocation of clay from the surface to the subsurface. The change in pH values ($\Delta pH = pH_{KCl} - pH_{H2O}$) which were all negative indicates that the soils possess net negative charges on their colloidal surfaces and so might have sorption abilities.

The soils with the exception of Haplic Ferrasol at Buako (BUA) generally contained low levels of organic carbon in the plough layer consistent with values for most cultivated soils in Ghana (Nartey *et al.*, 1997; Jones, 2006). This low organic carbon contents is as a result of high mineralisation rates characteristic of tropical soils. The particularly high organic carbon in the Haplic Ferrasol (BUA) soil (38 g/kg) could be attributed to the high litter fall noticed on that soil and the great canopy covers that could slow mineralisation.

The low exchangeable bases and hence low base saturation of all the soils could be attributed to the high rainfall in the area which leads to leaching of bases out of the top soil into deeper horizons. This might in turn explain the low pH in KCl as the exchange complex might be dominated by the acidic cations Al and H. The low CEC might be as a result of the near removal of weatherable primary minerals under the prevailing tropical environment. The low CEC of the soils also confirms their highly weathered nature and indicates the presence of

low activity clays like kaolinite (Nartey *et al.*, 1997). This low CEC was also confirmed by the low organic carbon contents in the soils. With the high rainfall of the area coupled with the mobility of the basic cations, Ca, Mg, K and Na, it stands to reason that base saturation of most of the soils were very low. In the top soils where base saturation was high such as in Haplic Ferrasol at Buako (BUA) and in the Dystric Fluvisols at Enchi (ENC and SEN), organic carbon contents were particularly high (> 15 g/kg) indicating the positive role that organic matter plays in charge development in soils.

Generally, the soil samples had low metal contents, less than or within the range of concentration for non-polluted soils and for the European norms (Kabata-Pendias and Pendias, 1992, and Rademacher, 2001, respectively). Meanwhile, it is noteworthy to mention that Cr presented high concentration values in the deepest layer of the Ferric Acrisol at Ashiem (ASH, 80 – 100 cm) and in the mid-depth of the Dystric Fluvisol at Enchi (ENC, 30 – 50 cm). In comparison with the atmospheric fallout values from Allen *et al.* (1995), Cd, Cr, Cu and Pb concentrations in surface soils suggested anthropogenic and atmospheric deposition whiles Zn and Ni seemed to be of lithogenic origin.

The exchangeable (or mobile) heavy metal fractions, however, were below the values for non-polluted soils, atmospheric fallout and the European norms according to Kabata-Pendias and Pendias (1992), Allen *et al.* (1995) and Rademacher (2001), respectively. This reveals that only non-alarming concentrations of the heavy metals get into the soil solution. However, not all the mobile metal fractions might even get to plants (uptake by roots): some are leached into deeper soil profile layers beyond the reach of plant roots. Hence, only a small fraction of the mobile metals might enter the food chain posing little or no health risk to humans.

Differences in metal concentrations between soil horizons may result from varying chemical composition of different geogenic layers, pedogenetic redistribution, and anthropogenic input (Wilcke *et al.*, 2000). Most metals showed high accumulation in the first 10 cm of the soils and were gradually leached down into deeper layers, which is the conventional view for the mechanism of metal distribution in soil profiles (Matini *et al.*, 2011).

Iron and Mn were the most abundant metals in the soils. The high Fe content which increased with depth might indicate both the lithogenic weathering origin of Fe and/or a leaching within the profile. Andriesse and Scholten (1982) explained the increasing Fe concentrations with depth in tropical Oxisol by the accumulation of primary quartz being more pronounced than that of the oxides. Clay illuviation might also contribute to increasing Fe concentrations with depth as clay comigrated with Fe.

The high Mn content which decreased with depth might also predict minerals of Mn weathering origin and also probably from an anthropogenic origin. The Ferric Acrisols (at Bogoso and Asankragwa) and the Dystric Fluvisol (at Samreboi) had high Mn loadings in their surface soils (0 – 50 cm). This might be due to the former prediction of weathering origin as they are few kilometers from Nsuta, where there is surface mining of Mn. The Haplic Ferrasol at Buako (BUA) had high levels of Mn in all the soil layers. This might be an indication of the presence of Mn mineral deposites. The increasing Mn content with depth in only the Dystric Fluvisol at Enchi (ENC) cannot be associated with the non-uniform pattern of clay distribution in the ENC profile and this, thus, suggests a contribution from anthropogenic origin, lithogenic origin and/or eluviation of Mn compounds.

The generally increasing concentration of Cd, Cr, Cu and Ni with depth may indicate leaching. Chromium, Cu and Ni like Zn are strongly bound to clay minerals and so can be mobilised within the soil profile during clay leaching process which is associated with Al-Fe

oxide soils (acid soils) (Baize, 1997). According to Rautengarten *et al.* (1995), though Cd distribution is controlled by small mineral particles and organic matter, its mobility is mainly determined by clay content. However, the dominant process in the sorption of heavy metals, in the case of clay minerals, is represented by ionic replacement between solution and solid phase, and physical process of adsorption. Under acid conditions (pH < 6.5), Cd is usually converted to the Cd^{2+}, $CdCO_3$ and possibly $Cd_3(PO_4)_2$ forms which are the soluble forms making Cd very mobile whiles under alkaline conditions (pH > 6.5), it is converted to the $CdOH^+$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$ forms which are the preferred forms adsorbed onto clay surfaces. It also seemed that in the soils, a strong adsorption of Cd was supported by a very high concentration of metal as it is shown on Tables 4.1a-d and 4.4a-d that zones of high accumulation of clay coincided with high levels of Cd.

The inconsistent behaviour of Zn in the soils might be due to several factors: firstly, Ferric Acrisols (ASA and ABA) presenting decreasing Zn concentration with depth suggests an anthropogenic origin most probably from application of fertilizers such as Sidalco NPK. The high clay content in the surface soils of these soils might be attenuating their mobility; secondly, Zn content increasing with depth in the Ferric Acrisols (ASH and BOG), Haplic Luvisols (DEB, JUA and JUD) and in the Dystric Fluvisol (ENC, SAM and SEN) suggests lithogenic origin and/or mobilisation from illuviated clay minerals; and, thirdly, the same Zn concentration present in the Haplic Ferrasol (BUA) is an indication of a contribution from pooled factors from both lithogenic and anthropogenic sources.

Lead distribution in the Dystric Fluvisol at Enchi (ENC) suggests both anthropogenic and lithogenc origins but its distribution in the Ferric Acrisol at Ashiem (ASH) clearly indicates Pb eluviations from soil surfaces laden with atmospheric Pb depositions. The decreasing content of Pb with depth in the Haplic Luvisol at Debiso (DEB) predicts anthropogenic origin whereas that in the remaining soils reflects lithogenic and/or Pb eluviations.

It is evident from the discussions above that the investigated soils presented differing metal concentrations for the different depths of a particular soil for most of the soils. The discriminant analysis substantiated this observation. The canonical correlation statistic established that, apart from Fe, there existed a high degree of between-site variations and the Wilk's Lambda statistic indicated a high degree of within-site variation for all the metals but Mn. The scatter plot from the first two eigen functions clearly illustrated the discriminant analysis results.

Iron showed no variation among the soils indicating a uniform weathering regime in the studied areas and thus suggesting Fe distribution being of lithogenic origin. However, Mn content being statistically the same for each soil signifies that Mn distribution was due to pooled factors from both anthropogenic and lithogenic origins. Thus, anthropogenic inputs which might be different in the different studied areas might be responsible for the differing Mn contents in the different soils.

The depth function plot employed in this study presented very interesting observations as to which soil properties were responsible for the distribution pattern of the heavy metals in the various soils. Clay was found to control the movement of all the heavy metals considered in this study except Pb. Also, except for the Ferric Acrisol at Ashiem (ASH), soil pH which was shown in studies by Kotas and Stasicka (2000) and McBride *et al.* (1997) to have a strong influence on metal adsorption, retention and movement in soil profiles, showed a rather dissimilar distribution pattern with all the heavy metals indicating a zero or probably indirect influence. The contribution of organic matter and pH on heavy metal accumulation in soils is felt more in the plough layer of soils where variability of these two soil parameters is high due to the influence of different management practices. But, the distribution pattern of total organic carbon content (TOC) is only congruent with that of Mn in the Haplic Luvisol

pristine reference (JUD). Cation exchange capacity (CEC), however, showed a rather more similar distribution patterns with the metals than pH or TOC.

The ANOVA and the Pearson Correlation analyses presented worthwhile information to validating the results from the depth function plots.

Again, pH was observed to have no significant relations in the two-way ANOVA analysis. However, the effect of the interaction between site and pH presented a significant variation in Mn content. This is an indication that different soils with different pHs have different Mn content, and this observation buttressed the results of the Wilk's Lambda statistic.

Total organic carbon (TOC), from the ANOVA analysis results, showed a significant association with Cd, Cr, Fe and Ni, and so was the effect of variable soil site. However, the effect of the interaction between soil site and TOC was only significant for Cd. Cadmium input from the application of inorganic fertilizers particularly triple super phosphate and the single super phosphate which may have been adsorbed by organic matter would account for its association with TOC (Canet *et al.*, 1997).

The variation in clay content at each site and between sites respectively showed highly significant associations with the metals except for Cd and Fe, and Cd and Pb. This observation agrees with that of the depth function plot. Cation exchange capacity also showed similar relationship with the heay metals. Thus, clay content and CEC may influence the distribution of most of the metals. Apparently, all cocoa farms use the recommended agrochemicals and so Cd distribution being invariable both within and between sites may support the deductions from the TOC result that anthropogenic input was its most probable source. Meanwhile, Fe association with the clay content suggested it was of lithogenic origin whiles Pb depicted an anthropogenic origin.

In spite of the non-assessment of the reactive fraction of the organic matter (TOC for that matter), its relationship with the heavy metals and other physicochemical properties was expected. However, the correlation results indicated that total organic carbon bore no relationship to any metals or to other physicochemical properties. The results from the depth function plots are again validated by this observation.

Cation exchange capacity and clay content showed significant correlation. This was in agreement with the ANOVA results that CEC and clay content together influenced the distribution of most metals. With the low organic carbon contents of the soils, the main contribution to charge development in the soils would be clay. According to Caravaca *et al.* (1999), clay-size fraction has the highest CEC due to greater surface area per unit of clay mineral mass. The clay fraction, thus, presents a great importance for metal behaviour in the different soils and, consequently, plays a major role in the physicochemical processes to metal retention in the soils. This was particularly true for Cd, Cr, Fe and Ni contents in the studied soils.

Iron content can help in determining the heavy metal background values (Huisman *et al.*, 1997). Except Pb, the heavy metals were strongly correlated with Fe content and weakly correlated with Mn. The strong association of all the metals with the exception of Pb with Fe indicates the strong affinity of these heavy metals for Fe oxides. Once Fe co-migrates with clay and Fe can coat clay surfaces, it is not surprising that most of the metals were associated with Fe.

Zinc, like Pb, had no significant correlation with Cr. Zinc and Cr, thus, must have been from different sources. Chromium is presumed to be most probably of lithogenic origin because it was generally increasing with depth and so Zn must be from anthropogenic origin especially from agrochemical applications. Cadmium and Cu must also be from same source as both

were strongly correlated. Agrochemical applications like application of Cu-containing fungicides and/or deposition from the atmosphere could be responsible for the latter observation (Wilcke and Dohler, 1995). Chromium, Mn and Ni showed no significant correlation suggesting their variable sources – both anthropogenic and/or lithogenic contributions may be the principal sources of these metals.

In all, the Haplic Ferrasol (BUA) and the Dystric Fluvisols (ENC, SAM and SEN) presented the highest heavy metal content. The high metal content could be explained by the relatively high clay and Fe contents which were the predominant controlling factors of the distribution of metals in the soils under study. This was in agreement with Oliver (1997), Alloway (1994) and Kabata-Pendias and Pendias (1992) who also found clay and Fe oxides to be among soil parameters which lead to a strong adsorption capacity for metals than sandy soils or soils with low organic matter content. Meanwhile, the lowest concentrations were found in the Haplic Luvisols (JUA, DEB and JUD) due mainly to, as explained earlier, their low Fe content, low TOC content and relatively high sand content. The Acrisols were generally more weathered than the Luvisols and, consequently, would possess more Fe oxides (Evangelou, 1998).

Chromium was the only metal that showed no significant enrichment in surface horizons from all the studied soils. Manganese like Zn and Cu among the heavy metals studied is a plant micronutrient. Most of the compound fertilizers distributed by chemical companies in Ghana notably, Wienco, Chemico and Agrimat, have been fortified by these micronutrients. Analysis of these fertilizers and information on the labels of these fertilizers indicate that Mn is next to Fe in concentration. Manganese accumulation in the surface horizons of the soils could therefore be as a result of fertilizer application.

From the enrichment factor calculations, Pb and Mn anthropogenic contributions were the most important compared to the other heavy metals. The Pb enrichment study indicated that the enrichment in the surface horizons of the Haplic Luvisols (JUA and DEB) was from an anthropogenic origin. The Ferric Acrisols (ASH and BOG) also showed contents of anthropogenic Pb in their surface horizons. Perhaps the opening up of the place by construction of more feeder roads has led to the increase in heavy duty trucks to cart cocoa. These trucks use diesel which has high levels of Pb which may have contaminated the soils.

The incorporation of anthropogenic Pb has been non-progressive, as shown by the bar charts of Pb concentration versus depth of soils (Fig. 4.11a). Soil Pb contamination is thus rather the result of recent local or regional industrial sources like from the diesel fueled galamsey trucks that, recently, constantly ply farm roads to the mining sites which are in proximity with many farming communities, than many years of deposition. This was in agreement with the findings of Veron *et al.*, (1999) in the northern part of France: Veron attributed Pb from airborne particles to local industrial activities rather than to gasoline.

Chromium accumulations, though quite insignificant, showed some enrichment in the Ferric Acrisols (ASA, ASH and BOG) and the Dystric Fluvisols (ENC and SAM). Anthropogenic Cr incorporation, like Pb, showed a non-progressive pattern except for the Dystric Fluvisol at Enchi (ENC). Chromium eluviations from the sandy clay loam surface soils into the high clay fraction of the 30 – 50 cm depth of the ENC profile greatly explain this departure.

The principal component analysis further made clear the sources of the metals. Iron, Cr and Cd appeared to be of both anthropogenic and lithogenic origins. However, Ni has been indicated to be of a lithogenic source and this is because it is relatively uniform throughout the profile of all the soils. Copper, Zn and Mn were of anthropogenic origin. The anthropogenic inputs could be from the application of inorganic fertilizers and Cu-containing

fungicides and/or from the continual use of steel-made farm tools such as cutlasses, axes and hoes.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

Assessment of the depth distribution of heavy metals in soils of cocoa farms in the Western region of Ghana was the primary objective of this work. Several statistical methods (Discriminant analysis, ANOVA, correlation analysis, accumulation-depletion ratios, enrichment factors and principal component analysis) for determining the environmental quality of the studied soils in terms of heavy metal accumulation and soil properties were used. All objectives were met and the conclusions drawn are summarized in this chapter. Recommendations to this study are also submitted here.

6.1 CONCLUSION

The study showed that most of the soils were highly weathered due to their high clay content, low sand content, and high Fe content and low organic carbon content. Their generally acidic nature indicates that P availability will be low in the soils. The soils also had low CEC and exchangeable bases, and, generally had net negative charges on their colloidal surfaces. For all soils, clay content and pH generally increased with depth, total organic carbon content decreased with depth and cation exchange capacity did not show any clear pattern with depth in most soils.

The abundance order of the heavy metals in the soils was Fe > Mn > Cr > Zn > Cu > Cd > Pb > Ni. Generally, the concentration of Fe, Cd, Cr, Cu, and Ni increased with depth but Mn content decreased with depth. However, Pb and Zn contents showed no general trends: they increased, decreased or were erratic with depth in the different soils.

Depth function, ANOVA and correlation analyses indicated that clay content influenced the distribution of all the metals except Pb due to the strong relationship between the heavy metals and clay.

High metal loadings were identified with Haplic Ferrasols and Dystric Fluvisols while the least metal loadings were observed for the Haplic Luvisols. Though the soils had low metal contents, less than or within the range of concentration for non-polluted soils and for European norms, standards for atmospheric fallout concentrations in the top soil revealed that Cd, Cu, Cr and Pb contents were of anthropogenic origin whereas Zn and Ni contents were of lithogenic origin.

Correlation analysis, accumulation-depletion ratios, enrichment factors and principal component analysis indicated that the distribution of Cd, Cu, Mn, and Pb in the soils highlighted an anthropogenic contribution. Iron and Ni distributions were associated with lithogenic origin whereas Zn and Cr distribution were related to both anthropogenic and lithogenic contributions.

In conclusion, the null hypothesis of the study was rejected and the alternative hypothesis accepted. Thus, soils in cocoa farms in the Western region of Ghana are not contaminated with heavy metals. However, there is evidence of gradual accumulation of heavy metals, particularly Cd, Cu and Pb, from anthropogenic sources. The main anthropogenic sources of these metals are from use of agrochemicals such as P fertilizers, Cu-containing fungicides (like fungarin, champion, nordox, ridomil gold plus and fungikil) and/or diesel fuel from haulage trucks that cart cocoa as a result of the construction of feeder roads in the area. Clay content had a pronounced effect on the distribution of metals in the soils. The latter observation indicates that determination of clay content and predication of its relationship

with heavy metals' concentrations in soil by means of statistical methods can be a strong tool for monitoring metal contamination in the cocoa farm soils studied.

6.2 RECOMMENDATIONS

Although metal loadings from the respective defined sources are presently low, build-up of heavy metals associated with changes in soil properties should be monitored in the study area to ascertain when the soils are likely to be polluted.

Also, studies on the heavy metal accumulation in the cocoa pod would help ascertain risk factor for consumption of cocoa products.

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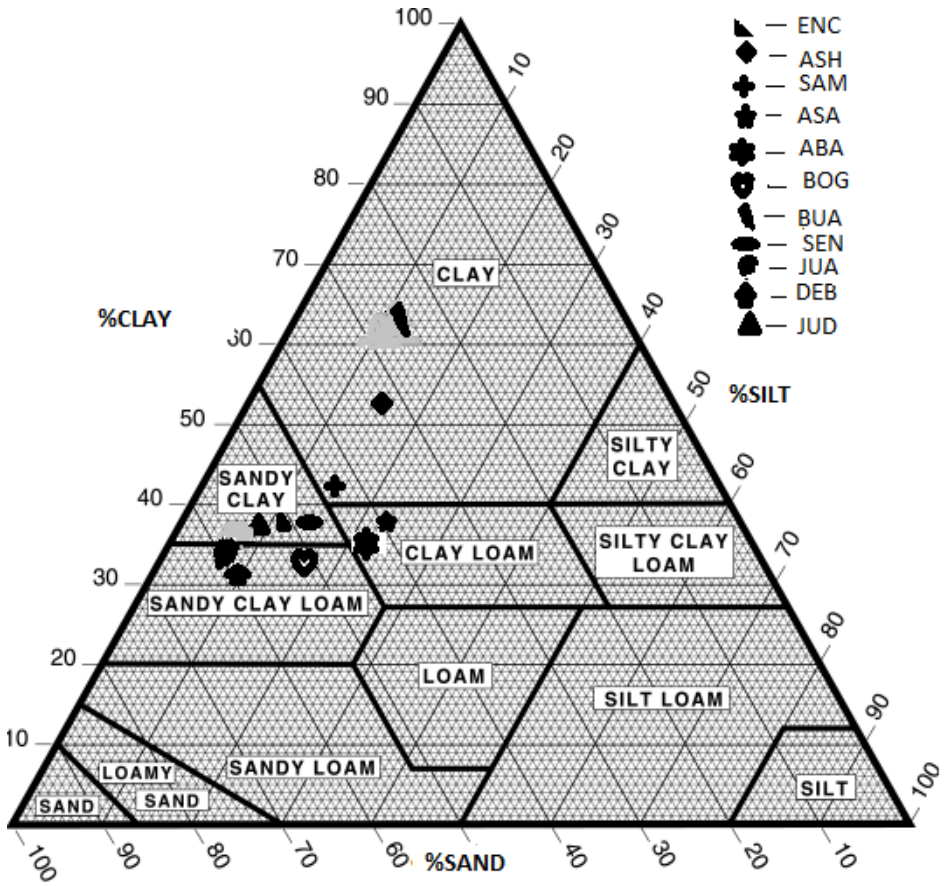
APPENDICES

APPENDIX A



Ternary diagram of soil texture showing the general texture of each site. Each point is as a result of the mean proportions of sand, silt and clay for the various depths for the respective site (fine sample < 2 mm).

APPENDIX B

Qualitative test for the presence of calcium carbonate ($CaCO_3$) in Dystric Fluvisol at Enchi (ENC)

Depth (cm)	Test	Observation	Inference
0 – 10 cm	1. 10 g of sample + 10 % HCl (dropwise) 2. Gas directed to pass through lime water	1. There is effervescence of a colourless gas 2. Lime water turns milky	1. CO_2 may be released 2. CO_2 is released and hence $CaCO_3$ is present
10 – 30 cm		1. No effervescence observed.	1. CO_2 is not released and hence $CaCO_3$ is absent
30 – 50 cm		1. No effervescence observed.	1. CO_2 is not released and hence $CaCO_3$ is absent
50 – 80 cm		1. No effervescence observed.	1. CO_2 is not released and hence $CaCO_3$ is absent
80 – 100 cm		1. There is effervescence of a colourless gas 2. Lime water turns milky	1. CO_2 may be released 2. CO_2 is released and hence $CaCO_3$ is present

APPENDIX C

C1: Paired Samples Test for standard reference ISE 918

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Certified_values - Measured_values	18.846	50.312	17.788	-23.22	60.91	1.06	7	0.325

C2: Paired Samples Test for standard reference ISE 998

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Certified_values - Measured_values	5.864	10.764	4.068	-4.09	15.82	1.44	6	0.200

APPENDIX D

D1: Exchangeable metal concentrations for the Ferric Acrisols (ASA, ASH and BOG) and Haplic Ferrasol (BUA)

Soil type	Depth (cm)	Exchangeable metal concentrations (mg/kg)							
		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ACf (ASA)	0 – 10	0.00	ND	1.35	1.80	50.09	0.98	0.47	0.87
	10 – 30	ND	ND	1.41	2.46	10.56	0.39	0.27	0.52
ACf (ASH)	0 – 10	ND	ND	1.38	1.91	10.92	ND	0.42	ND
	10 – 30	0.00	ND	1.96	2.45	1.65	ND	0.36	0.44
	30 – 50	0.01	ND	ND	1.75	3.42	ND	0.49	0.28
	50 – 80	ND	1.71	1.52	4.35	4.42	ND	0.10	0.35
	80 – 100	0.01	ND	1.40	3.11	4.72	ND	0.28	0.17
ACf (BOG)	0 – 10	0.04	0.08	1.68	2.80	127.09	0.29	0.68	2.25
	10 – 30	ND	ND	1.28	2.20	75.13	ND	0.16	0.97
	30 – 50	0.00	0.05	ND	ND	ND	0.10	0.19	ND
	50 – 80	0.00	ND	ND	ND	ND	ND	0.34	ND
	80 – 100	ND	ND	ND	ND	ND	0.09	ND	ND
FRh (BUA)	0 – 10	0.00	ND	1.14	2.49	9.24	ND	ND	ND
	10 – 30	0.00	ND	1.35	1.64	19.59	ND	0.30	ND
	30 – 50	ND	ND	1.35	1.37	18.75	ND	0.54	ND
	50 – 80	0.00	ND	1.32	1.70	13.78	ND	ND	ND
	80 – 100	ND	ND	1.34	2.26	15.06	ND	0.39	ND

ACf = Ferric Acrisol; FRh = Haplic Ferrasol; ND = not detected.

D2: Exchangeable metal concentrations for the Haplic Luvisols (DEB and JUA) and the Dystric Fluvisols (ENC and SAM)

Soil type	Depth (cm)	Exchangeable metal concentrations (mg/kg)							
		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LVh (DEB)	0 – 10	0.01	ND	1.27	2.56	58.26	ND	0.05	ND
	10 – 30	ND	ND	1.62	5.02	33.83	0.43	0.23	ND
	30 – 50	0.02	ND	1.37	1.79	23.32	ND	0.59	ND
	50 – 80	0.00	ND	1.52	1.49	16.55	ND	ND	ND
	80 – 100	0.00	ND	1.37	2.44	9.16	ND	0.38	ND
FLd (ENC)	0 – 10	ND	ND	1.38	1.38	10.34	0.20	0.18	ND
	10 – 30	0.01	ND	1.36	1.91	19.93	ND	0.18	ND
	30 – 50	ND	0.09	1.41	2.97	30.08	0.15	0.14	ND
	50 – 80	0.01	0.10	1.37	2.31	20.14	ND	0.15	ND
	80 – 100	0.01	ND	1.27	2.15	0.73	ND	0.69	ND
LVh (JUA)	0 – 10	0.01	0.18	1.33	1.74	67.66	0.10	ND	0.17
	10 – 30	0.00	ND	1.33	1.55	1.36	ND	0.35	ND
	30 – 50	0.00	0.00	1.62	1.52	6.72	ND	0.34	1.11
	50 – 80	0.00	ND	1.49	1.76	8.56	0.05	0.01	0.36
	80 – 100	0.01	ND	1.41	2.49	10.91	ND	ND	0.62
FLd (SAM)	0 – 10	ND	ND	1.41	3.32	45.93	ND	0.18	ND
	10 – 30	ND	ND	1.43	1.38	19.94	ND	0.62	ND
	30 – 50	ND	ND	1.39	1.46	16.90	ND	0.55	ND
	50 – 80	0.01	ND	1.20	1.63	14.86	0.10	0.16	ND
	80 – 100	0.01	ND	1.36	1.51	9.55	0.21	0.32	ND

LVh = Haplic Luvisol: FLd = Dystric Fluvisol; ND = not detected.

D3: Exchangeable metal concentrations for the pristine reference soils (ABA, JUD and SEN)

Soil type	Depth (cm)	Exchangeable metal concentrations (mg/kg)							
		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ACf (ABA)	0 – 10	ND	ND	1.39	11.01	8.28	0.41	ND	2.52
	10 – 30	ND	ND	1.38	9.07	8.52	0.28	0.30	1.57
LVh (JUD)	0 – 10	ND	ND	1.30	2.39	9.49	ND	0.36	ND
	10 – 30	0.00	ND	1.32	1.65	2.48	0.10	0.62	ND
	30 – 50	0.00	ND	1.14	1.99	3.13	ND	0.49	ND
	50 – 80	ND	0.04	1.15	4.22	11.25	ND	0.69	ND
	80 – 100	ND	ND	1.26	1.67	13.65	1.09	ND	ND
FLd (SEN)	0 – 10	ND	ND	1.45	3.53	24.74	ND	0.15	ND
	10 – 30	ND	ND	1.48	2.32	2.96	ND	0.37	ND
	30 – 50	ND	ND	1.60	2.45	6.76	ND	0.57	ND
	50 – 80	0.02	ND	1.51	2.05	6.79	ND	0.83	ND

ACf = Ferric Acrisol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; ND = not detected.

D4: Mean exchangeable metal concentrations for the soils

Soil type	Exchangeable metal concentrations (mg/kg)							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ACf (ASA)	0.00	ND	1.38	2.13	30.33	0.69	0.37	0.70
ACf (ASH)	0.01	1.71	1.57	2.71	5.02	ND	0.33	0.31
ACf (BOG)	0.01	0.04	0.99	1.67	67.41	0.12	0.27	1.07
FRh (BUA)	0.00	ND	1.30	1.89	15.29	ND	0.41	ND
LVh (DEB)	0.01	ND	1.43	2.66	28.23	0.43	0.31	ND
FLd (ENC)	0.01	0.09	1.36	2.14	16.25	0.18	0.27	ND
LVh (JUA)	0.01	0.09	1.44	1.81	19.04	0.08	0.23	0.57
FLd (SAM)	0.01	ND	1.36	1.86	21.44	0.16	0.37	ND
ACf (ABA)	ND	ND	1.38	10.04	8.40	0.34	0.30	2.05
LVh (JUD)	0.00	0.04	1.24	2.38	8.00	0.59	0.54	ND
FLd (SEN)	0.02	ND	1.51	2.59	10.32	ND	0.48	ND

Acf = Ferric Acrisol; FRh = Haplic Ferrasol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol; ND = not detected

The average concentration of a metal for a site was obtained by finding the mean of the various concentrations of the metal in the different depths of that site.

APPENDIX E

E1: Two-way ANOVA results (test of between subjects) for site and Clay as grouping variables

Source of Variation	Dependent Variables	SS	df	MS	F	*P*
Site	ln Cd	1.344	11	0.122	1.920	0.106
	ln Cr	9.123	11	0.829	8.063	0.000
	ln Cu	3.620	11	0.329	2.497	0.041
	ln Fe	97.326	11	8.848	148.459	0.000
	ln Mn	49.344	11	4.486	35.331	0.000
	ln Ni	8.140	11	0.740	9.399	0.000
	ln Pb	7.699	11	0.700	0.783	0.653
	ln Zn	9.356	11	0.851	14.290	0.000
CLAY	ln Cd	0.304	1	0.304	4.768	0.042
	ln Cr	0.023	1	0.023	0.219	0.645
	ln Cu	0.001	1	0.001	0.005	0.945
	ln Fe	0.287	1	0.287	4.809	0.042
	ln Mn	0.187	1	0.187	1.470	0.241
	ln Ni	0.004	1	0.004	0.050	0.825
	ln Pb	0.583	1	0.583	0.653	0.430
	ln Zn	0.026	1	0.026	0.441	0.515
Site * CLAY	ln Cd	1.190	10	0.119	1.869	0.119
	ln Cr	3.174	10	0.317	3.086	0.018
	ln Cu	0.741	10	0.074	0.562	0.823
	ln Fe	1.467	10	0.147	2.462	0.046
	ln Mn	0.986	10	0.099	0.777	0.650
	ln Ni	3.399	10	0.340	4.317	0.003
	ln Pb	5.275	10	0.528	0.591	0.801
	ln Zn	1.099	10	0.110	1.846	0.124
Corrected Model	ln Cd	141.331	22	6.424	100.905	0.000
	ln Cr	579.622	22	26.346	256.156	0.000
	ln Cu	318.793	22	14.491	109.958	0.000
	ln Fe	4285.141	22	194.779	3.268E3	0.000
	ln Mn	1125.251	22	51.148	402.848	0.000
	ln Ni	21.523	22	0.978	12.426	0.000
	ln Pb	106.766	22	4.853	5.432	0.000
	ln Zn	529.142	22	24.052	404.120	0.000

MS = Mean Square; SS = Type III sum of squares; *P* = significance threshold.

E2: Two-way ANOVA results (test of between subjects) for site and pH as grouping variables

Source of Variation	Dependent Variables	SS	df	MS	F	*P*
Site	ln Cd	2.965	11	0.270	1.950	0.101
	ln Cr	4.414	11	0.401	1.124	0.399
	ln Cu	3.088	11	0.281	1.898	0.110
	ln Fe	22.335	11	2.030	8.542	0.000
	ln Mn	7.777	11	0.707	9.078	0.000
	ln Ni	4.321	11	0.393	1.309	0.295
	ln Pb	9.508	11	0.864	1.297	0.302
	ln Zn	4.178	11	0.380	4.529	0.002
pH	ln Cd	0.025	1	0.025	0.182	0.675
	ln Cr	4.033E-8	1	4.033E-8	0	1.000
	ln Cu	0.132	1	0.132	0.892	0.357
	ln Fe	0.030	1	0.030	0.124	0.728
	ln Mn	0.067	1	0.067	0.866	0.364
	ln Ni	0.110	1	0.110	0.366	0.553
	ln Pb	0.090	1	0.090	0.135	0.718
	ln Zn	0.183	1	0.183	2.177	0.157
Site * pH	ln Cd	2.552	10	0.255	1.846	0.124
	ln Cr	1.882	10	0.188	0.527	0.849
	ln Cu	1.919	10	0.192	1.298	0.302
	ln Fe	2.229	10	0.223	0.938	0.524
	ln Mn	2.664	10	0.266	3.421	0.011
	ln Ni	3.798	10	0.380	1.266	0.318
	ln Pb	9.345	10	0.935	1.402	0.256
	ln Zn	1.801	10	0.180	2.148	0.076
Corrected Model	ln Cd	139.989	22	6.363	46.032	0.000
	ln Cr	575.046	22	26.138	73.202	0.000
	ln Cu	318.503	22	14.477	97.911	0.000
	ln Fe	4281.934	22	194.633	818.773	0.000
	ln Mn	1126.135	22	51.188	657.289	0.000
	ln Ni	17.540	22	0.797	2.657	0.020
	ln Pb	110.848	22	5.039	7.558	0.000
	ln Zn	528.703	22	24.032	286.587	0.000

MS = Mean Square; SS = Type III sum of squares; *P* = significance threshold.

E3: Two-way ANOVA results (test of between subjects) for site and total organic carbon (TOC) as grouping variables

Source of Variation	Dependent Variables	SS	df	MS	F	*P*
Site	ln Cd	42.299	11	3.845	69.653	0.000
	ln Cr	146.715	11	13.338	216.921	0.000
	ln Cu	71.218	11	6.474	46.406	0.000
	ln Fe	905.391	11	82.308	2.251E3	0.000
	ln Mn	210.374	11	19.125	139.029	0.000
	ln Ni	7.643	11	0.695	14.339	0.000
	ln Pb	34.202	11	3.109	3.683	0.007
	ln Zn	115.562	11	10.506	191.384	0.000
TOC	ln Cd	1.797	1	1.797	32.557	0.000
	ln Cr	1.459	1	1.459	23.723	0.000
	ln Cu	0.368	1	0.368	2.641	0.122
	ln Fe	2.239	1	2.239	61.229	0.000
	ln Mn	0.431	1	0.431	3.132	0.094
	ln Ni	0.610	1	0.610	12.592	0.002
	ln Pb	0.199	1	0.199	.236	0.633
	ln Zn	0.088	1	0.088	1.609	0.221
Site * TOC	ln Cd	1.380	10	0.138	2.500	0.044
	ln Cr	2.335	10	0.234	3.798	0.007
	ln Cu	1.264	10	0.126	.906	0.547
	ln Fe	1.456	10	0.146	3.981	0.005
	ln Mn	1.315	10	0.132	.956	0.510
	ln Ni	4.318	10	0.432	8.911	0.000
	ln Pb	5.844	10	0.584	.692	0.720
	ln Zn	1.639	10	0.164	2.986	0.021
Corrected Model	ln Cd	141.483	22	6.431	116.489	0.000
	ln Cr	580.366	22	26.380	429.042	0.000
	ln Cu	318.653	22	14.484	103.819	0.000
	ln Fe	4285.555	22	194.798	5.328E3	0.000
	ln Mn	1125.060	22	51.139	371.757	0.000
	ln Ni	22.068	22	1.003	20.700	0.000
	ln Pb	107.649	22	4.893	5.795	0.000
	ln Zn	529.225	22	24.056	438.227	0.000

MS = Mean Square; SS = Type III sum of squares; *P* = significance threshold.

E4: Two-way ANOVA results (test of between subjects) for site and cation exchange capacity (CEC) as grouping variables

Source of Variation	Dependent Variables	SS	df	MS	F	*P*
Site	ln Cd	33.435	11	3.040	14.029	0.000
	ln Cr	133.343	11	12.122	32.624	0.000
	ln Cu	71.553	11	6.505	33.613	0.000
	ln Fe	1034.490	11	94.045	342.494	0.000
	ln Mn	306.724	11	27.884	174.143	0.000
	ln Ni	5.615	11	0.510	1.437	0.239
	ln Pb	26.206	11	2.382	2.410	0.047
	ln Zn	122.945	11	11.177	92.441	0.000
CEC	ln Cd	0.031	1	0.031	0.142	0.710
	ln Cr	0.005	1	0.005	0.012	0.914
	ln Cu	0.012	1	0.012	0.063	0.804
	ln Fe	0.060	1	0.060	0.217	0.647
	ln Mn	0.113	1	0.113	0.707	0.411
	ln Ni	0.968	1	0.968	2.724	0.116
	ln Pb	0.070	1	0.070	0.071	0.793
	ln Zn	0.276	1	0.276	2.286	0.148
Site * CEC	ln Cd	1.136	10	0.114	0.524	0.851
	ln Cr	1.576	10	0.158	0.424	0.916
	ln Cu	0.958	10	0.096	0.495	0.872
	ln Fe	1.462	10	0.146	0.532	0.845
	ln Mn	1.014	10	0.101	0.633	0.767
	ln Ni	2.789	10	0.279	0.785	0.643
	ln Pb	3.553	10	0.355	0.359	0.949
	ln Zn	1.075	10	0.108	0.889	0.560
Corrected Model	ln Cd	138.577	22	6.299	29.072	0.000
	ln Cr	574.785	22	26.127	70.313	0.000
	ln Cu	317.681	22	14.440	74.618	0.000
	ln Fe	4281.271	22	194.603	708.710	0.000
	ln Mn	1124.654	22	51.121	319.261	0.000
	ln Ni	16.547	22	0.752	2.118	0.055
	ln Pb	105.053	22	4.775	4.830	0.001
	ln Zn	528.037	22	24.002	198.513	0.000

MS = Mean Square; SS = Type III sum of squares; *P* = significance threshold.

APPENDIX F

F1: Pearson correlation among selected physicochemical properties and heavy metals in soils

		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	CLAY	pH	TOC	CEC
Cd	*Pearson Correlation*	1	0.504**	0.652**	0.972**	0.356*	0.614**	0.198	0.564**	0.659**	0.043	-0.053	0.161
	Sig. (2-tailed)		0	0	0	0.013	0	0.177	0	0	0.769	0.722	0.276
	N	48	48	48	48	48	48	48	48	48	48	48	48
Cr	*Pearson Correlation*	0.504**	1	0.434**	0.485**	0.225	0.204	0.027	0.257	0.638**	0.119	0.125	0.487**
	Sig. (2-tailed)	0		0.002	0	0.124	0.165	0.854	0.078	0.000	0.422	0.397	0.000
	N	48	48	48	48	48	48	48	48	48	48	48	48
Cu	*Pearson Correlation*	0.652**	0.434**	1	0.636**	0.731**	0.468**	0.072	0.803**	0.460**	0.126	-0.023	0.179
	Sig. (2-tailed)	0	0.002		0	0	0.001	0.626	0	0.001	0.393	0.877	0.224
	N	48	48	48	48	48	48	48	48	48	48	48	48
Fe	*Pearson Correlation*	0.972**	0.485**	0.636**	1	0.319*	0.641**	0.223	0.524**	0.651**	0.033	-0.090	0.281
	Sig. (2-tailed)	0	0	0		0.027	0	0.128	0	0	0.822	0.543	0.053
	N	48	48	48	48	48	48	48	48	48	48	48	48
Mn	*Pearson Correlation*	0.356*	0.225	0.731**	0.319*	1	0.143	0.241	0.637**	0.012	0.305*	0.042	-0.083
	Sig. (2-tailed)	0.013	0.124	0	0.027		0.334	0.100	0	0.938	0.035	0.779	0.576
	N	48	48	48	48	48	48	48	48	48	48	48	48
Ni	*Pearson Correlation*	0.614**	0.204	0.468**	0.641**	0.143	1	0.128	0.549**	0.516**	-0.177	0.071	0.239
	Sig. (2-tailed)	0	0.165	0.001	0	0.334		0.387	0	0	0.228	0.634	0.102
	N	48	48	48	48	48	48	48	48	48	48	48	48

**. Correlation is significant at the 0.01 level (2-tailed) i.e. significance threshold, $P \leq 0.01$;

*. Correlation is significant at the 0.05 level (2-tailed) i.e. significance threshold, $P \leq 0.05$.

F2: Pearson correlation among selected physicochemical properties and heavy metals in soils

		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	CLAY	pH	TOC	CEC
Pb	*Pearson Correlation*	0.198	0.027	0.072	0.223	0.241	0.128	1	0.099	-0.002	0.263	-0.145	-0.041
	Sig. (2-tailed)	0.177	0.854	0.626	0.128	0.100	0.387		0.504	0.987	0.070	0.326	0.782
	N	48	48	48	48	48	48	48	48	48	48	48	48
Zn	*Pearson Correlation*	0.564**	0.257	0.803**	0.524**	0.637**	0.549**	0.099	1	0.268	-0.098	-0.029	-0.024
	Sig. (2-tailed)	0	0.078	0	0	0	0	0.504		0.066	0.508	0.847	0.870
	N	48	48	48	48	48	48	48	48	48	48	48	48
CLAY	*Pearson Correlation*	0.659**	0.638**	0.460**	0.651**	0.012	0.516**	-0.002	0.268	1	-0.095	-0.032	0.422**
	Sig. (2-tailed)	0	0	0.001	0	0.938	0	0.987	0.066		0.519	0.827	0.003
	N	48	48	48	48	48	48	48	48	48	48	48	48
pH	*Pearson Correlation*	0.043	0.119	0.126	0.033	0.305*	-0.177	0.263	-0.098	-0.095	1	-0.157	0.031
	Sig. (2-tailed)	0.769	0.422	0.393	0.822	0.035	0.228	0.070	0.508	0.519		0.286	0.834
	N	48	48	48	48	48	48	48	48	48	48	48	48
TOC	*Pearson Correlation*	-0.053	0.125	-0.023	-0.090	0.042	0.071	-0.145	-0.029	-0.032	-0.157	1	-0.035
	Sig. (2-tailed)	0.722	0.397	0.877	0.543	0.779	0.634	0.326	0.847	0.827	0.286		0.811
	N	48	48	48	48	48	48	48	48	48	48	48	48
CEC	*Pearson Correlation*	0.161	0.487**	0.179	0.281	-0.083	0.239	-0.041	-0.024	0.422**	0.031	-0.035	1
	Sig. (2-tailed)	0.276	0	0.224	0.053	0.576	0.102	0.782	0.870	0.003	0.834	0.811	
	N	48	48	48	48	48	48	48	48	48	48	48	48

**. Correlation is significant at the 0.01 level (2-tailed) i.e. significance threshold, $P \leq 0.01$;

*. Correlation is significant at the 0.05 level (2-tailed) i.e. significance threshold, $P \leq 0.05$.

APPENDIX G

GI: Accumulation-depletion ratios of heavy metals for the Ferric Acrisols (ASA, ASH and BOG) and Haplic Ferrasol (BUA)

Soil type	Depth (cm)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ACf (ASA)	0 – 10	0.5	0.9	1.1	0.5	1.8	1.1	0.4	1.2
	10 – 30	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ACf (ASH)	0 – 10	0.4	0.4	0.9	0.4	1.2	0.4	1.9	0.7
	10 – 30	0.4	0.3	0.5	0.5	0.7	0.4	2.0	0.4
	30 – 50	0.5	0.4	0.7	0.6	0.9	0.5	5.4	0.7
	50 – 80	0.6	0.5	0.8	0.5	0.8	0.5	0.3	0.8
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ACf (BOG)	0 – 10	0.6	0.7	0.6	0.6	1.5	0.6	4.2	0.7
	10 – 30	1.0	0.7	0.4	1.0	0.5	0.9	3.9	0.6
	30 – 50	1.0	0.9	0.8	0.9	1.2	0.9	1.0	0.9
	50 – 80	1.1	1.2	1.0	1.0	0.9	1.0	1.0	1.0
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	-	1.0
FRh (BUA)	0 – 10	0.9	0.9	0.8	0.8	1.8	0.9	-	0.9
	10 – 30	1.0	1.4	1.5	0.9	1.2	1.0	0.1	1.3
	30 – 50	1.0	0.9	1.2	1.1	1.3	1.0	1.1	1.1
	50 – 80	0.7	1.2	1.3	0.7	4.7	1.1	-	1.1
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

ACf = Ferric Acrisol; FRh = Haplic Ferrasol.

Accumulation-depletion ratio was calculated against the deepest soil horizon sampled (80 – 100 cm) for each representative core.

G2: Accumulation-depletion ratios of heavy metals for the Haplic Luvisols (DEB and JUA) and the Dystric Fluvisols (ENC and SAM)

Soil type	Depth (cm)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LV h (DEB)	0 – 10	0.2	0.3	0.3	0.2	2.4	0.2	4.0	0.3
	10 – 30	0.4	0.6	0.8	0.5	1.1	0.4	0.4	0.9
	30 – 50	0.3	0.6	0.9	0.6	1.0	0.6	1.6	0.8
	50 – 80	0.6	0.7	0.8	0.6	2.3	0.7	-	0.8
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
FLd (ENC)	0 – 10	4.5	0.6	12.0	26.3	3.8	0.4	0.2	10.8
	10 – 30	4.1	0.7	15.4	31.2	3.9	0.7	1.1	11.1
	30 – 50	6.4	1.2	24.8	48.6	0.4	1.1	0.4	16.6
	50 – 80	5.7	1.0	20.6	47.4	0.5	1.0	1.4	15.3
	80 – 100	1.0	-	-	1.0	1.0	-	1.0	1.0
LVh (JUA)	0 – 10	0.3	0.1	0.6	0.2	0.6	0.2	1.4	0.4
	10 – 30	0.7	0.5	0.7	0.9	0.8	1.0	1.5	0.5
	30 – 50	0.9	0.7	0.9	1.0	0.8	1.2	0.5	0.7
	50 – 80	0.9	0.9	0.6	1.0	0.7	1.2	1.0	0.7
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	-	1.0
FLd (SAM)	0 – 10	0.2	0.5	0.8	0.2	2.7	0.2	0.1	0.6
	10 – 30	0.3	0.7	0.9	0.3	4.2	0.3	0.2	0.6
	30 – 50	0.7	0.7	0.3	0.6	1.1	0.6	0.7	0.6
	50 – 80	0.9	1.2	1.0	0.8	1.2	0.9	0.1	1.0
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

LVh = Haplic Luvisol; FLd = Dystric Fluvisol.

Accumulation-depletion ratio was calculated against the deepest soil horizon sampled (80 – 100 cm) for each representative core.

G3: Accumulation-depletion ratios of heavy metals for the pristine reference soils (ABA, JUA and SEN)

Soil type	Depth (cm)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ACf (ABA)	0 – 10	0.7	0.6	1.1	0.6	1.0	5.8	0.5	3.0
	10 – 30	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
LVh (JUD)	0 – 10	0.7	0.4	0.3	0.5	1.9	0.2	0.5	0.5
	10 – 30	0.8	0.6	0.9	0.5	1.1	0.2	0.9	1.1
	30 – 50	0.8	0.8	0.9	0.6	1.0	-	1.1	1.1
	50 – 80	0.8	1.0	0.9	0.8	1.0	0.3	1.0	1.1
	80 – 100	1.0	1.0	1.0	1.0	1.0	1.0	-	1.0
FLd (SEN)	0 – 10	0.7	0.6	1.2	0.5	1.5	0.5	0.3	1.3
	10 – 30	0.9	0.8	1.4	0.9	1.5	0.8	0.6	1.2
	30 – 50	1.3	1.1	2.6	1.2	2.2	1.3	0.7	1.6
	50 – 80	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

ACf = Ferric Acrisol; LVh = Haplic Luvisol; FLd = Dystric Fluvisol.

Accumulation-depletion ratio was calculated against the deepest soil horizon sampled for each representative core

G4: Average accumulation-depletion ratios of heavy metals in the surface soils (0 – 10 cm) grouped according to soil types

Soil type	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ferric Acrisols, n = 4	0.54	0.63	0.90	0.54	1.37	1.94	1.73	1.40
Haplic Ferrasol, n = 1	0.88	0.86	0.80	0.84	1.85	0.86	0.00	0.85
Haplic Luvisols, n = 3	0.40	0.26	0.42	0.30	1.64	0.21	1.95	0.40
Dystric Fluvisols, n = 3	1.78	0.56	4.69	9.02	2.71	0.34	0.22	4.24

n = number of sampling sites that had that soil type.

The average accumulation-depletion ratio of a metal for a soil type was obtained by finding the mean of the accumulation-depletion ratios of the metal in the surface soils of sampling sites with that soil type.

APPENDIX H

H1: Anthropogenic contribution of heavy metals (%) for the Ferric Acrisols (ASA, ASH and BOG) and Haplic Luvisol (BUA)

Soil type	Depth (cm)	Cd		Cr		Cu		Mn		Ni		Pb		Zn	
		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.	
		PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH
ACf (ASA)	0 – 10	-	-	44.3	42.6	-	52.6	74.5	72.6	-	53.4	-	-	-	59.0
	10 – 30	-	-	-	-	-	-	38.0	-	1.8	-	-	-	-	-
ACf (ASH)	0 – 10	-	-	69.7	4.0	-	54.5	-	65.3	-	-	-	78.7	-	43.6
	10 – 30	-	-	41.1	-	-	-	-	29.4	3.1	-	-	75.5	-	-
	30 – 50	-	-	-	-	-	20.2	-	33.5	-	-	-	89.2	-	10.5
	50 – 80	-	3.1	-	-	-	29.0	-	31.3	-	-	-	-	-	27.7
	80 – 100	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ACf (BOG)	0 – 10	-	1.1	56.3	4.9	-	-	91.0	59.6	-	1.9	-	85.4	-	9.7
	10 – 30	1.7	3.8	29.9	-	-	-	69.2	-	1.9	2.3	-	76.0	27.1	-
	30 – 50	-	6.0	-	0.5	-	-	-	22.6	-	2.4	-	9.4	-	2.1
	50 – 80	-	7.8	-	12.6	-	2.9	-	-	-	5.3	-	-	-	-
	80 – 100	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FRh (BUA)	0 – 10	-	4.4	-	2.4	-	-	-	54.7	-	1.2	-	-	-	1.6
	10 – 30	-	9.3	-	33.7	-	38.1	-	26.4	-	3.9	-	-	-	28.0
	30 – 50	-	-	-	-	-	12.0	-	15.2	-	-	-	-	-	4.5
	50 – 80	-	5.9	-	44.1	-	46.1	-	85.5	-	37.9	-	-	-	40.2
	80 – 100	-	-	-	-	-	-	-	-	-	-	-	-	-	-

ACf = Ferric Acrisol; FRh = Haplic Ferrasol

%Anthropogenic was calculated against the value of the pristine reference (PR) and against the value of the deepest soil horizon sampled, 80 – 100 (DSH).

H2: Anthropogenic contribution of heavy metals (%) for the Haplic Luvisol (DEB and JUA) and Dystric Fluvisols (ENC and SAM)

Soil type	Depth (cm)	Cd		Cr		Cu		Mn		Ni		Pb		Zn	
		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.		%Anthrop.	
		PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH	PR	DSH
LVh (DEB)	0 – 10	-	3.6	-	18.2	-	24.7	24.0	90.8	-	-	83.5	94.4	-	33.7
	10 – 30	-	-	-	21.4	-	41.5	-	57.8	-	-	-	-	-	48.5
	30 – 50	-	-	-	0.4	-	31.5	-	42.3	-	-	-	62.2	-	28.9
	50 – 80	6.9	2.7	-	9.4	-	24.2	38.0	73.1	14.1	3.6	-	-	-	22.6
	80 – 100	2.3	-	-	-	-	-	-	-	-	-	-	-	-	-
FLd (ENC)	0 – 10	9.4	-	29.4	10.8	-	-	-	31.3	-	-	-	-	-	-
	10 – 30	3.4	-	39.8	11.3	25.1	-	26.1	19.3	6.8	6.6	-	-	13.7	-
	30 – 50	4.1	-	41.9	16.6	1.0	-	-	-	-	7.0	-	-	11.7	-
	50 – 80	-	-	23.8	-	46.2	-	48.0	3.0	-	-	-	-	29.5	-
	80 – 100	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LVh (JUA)	0 – 10	30.9	33.3	-	-	67.9	65.4	-	64.0	-	4.8	95.3	84.9	72.1	38.3
	10 – 30	-	-	-	-	-	-	-	-	-	6.2	71.0	42.5	-	-
	30 – 50	-	-	-	-	-	-	-	-	-	4.3	-	-	-	-
	50 – 80	21.2	-	7.9	-	-	-	-	-	8.2	10.0	65.1	-	23.2	-
	80 – 100	26.5	-	30.7	0.0	-	-	-	0.0	-	-	-	-	58.3	-
FLd (SAM)	0 – 10	-	14.7	24.9	62.7	3.1	76.5	-	93.0	0.3	-	-	-	10.3	70.2
	10 – 30	-	2.1	15.3	50.9	-	63.1	-	92.0	1.2	-	-	-	3.8	42.9
	30 – 50	4.6	9.1	-	13.9	-	-	-	40.6	-	-	17.5	10.9	-	1.7
	50 – 80	4.0	6.7	-	32.5	-	21.1	-	29.2	3.0	5.3	-	-	-	18.7
	80 – 100	-	-	-	-	-	-	-	-	-	-	-	-	-	-

LVh = Haplic Luvisol; FLd = Dystric Fluvisol

%anthropogenic was calculated against the value of the pristine reference (PR) and against the value of the deepest soil horizon sampled, 80 – 100 cm (DSH).

APPENDIX I

I1: Enrichment Factors of heavy metals for the Ferric Acrisols (ASA, ASH and BOG) and Haplic Ferrasol (BUA)

Soil type	Depth (cm)	Cd		Cr		Cu		Mn		Ni		Pb		Zn	
		EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2
ACf (ASA)	0 – 10	0.8	1.0	1.8	1.7	0.7	2.1	3.9	3.6	0.2	2.1	0.2	0.7	0.4	2.4
	10 – 30	0.8	1.0	1.0	1.0	0.6	1.0	1.6	1.0	1.0	1.0	0.2	1.0	0.7	1.0
ACf (ASH)	0 – 10	0.9	1.0	3.3	1.0	0.7	2.2	0.9	2.9	0.1	0.9	0.4	4.7	0.3	1.8
	10 – 30	0.9	0.9	1.7	0.6	0.5	1.0	0.7	1.4	1.0	0.9	0.3	4.1	0.5	0.8
	30 – 50	-	0.9	-	0.6	-	1.3	-	1.5	-	0.8	-	9.2	-	1.1
	50 – 80	-	1.0	-	0.9	-	1.4	-	1.5	-	0.9	-	0.6	-	1.4
	80 – 100	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0
ACf (BOG)	0 – 10	0.9	1.0	2.3	1.1	1.0	1.0	11.1	2.5	0.1	1.0	0.9	6.9	0.5	1.1
	10 – 30	1.0	1.0	1.4	0.7	0.7	0.4	3.2	0.5	1.0	1.0	0.4	4.2	1.4	0.6
	30 – 50	-	1.1	-	1.0	-	0.9	-	1.3	-	1.0	-	1.1	-	1.0
	50 – 80	-	1.1	-	1.1	-	1.0	-	0.9	-	1.1	-	1.0	-	1.0
	80 – 100	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	-	-	1.0
FRh (BUA)	0 – 10	-	1.0	-	1.0	-	1.0	-	2.2	-	1.0	-	-	-	1.0
	10 – 30	-	1.1	-	1.5	-	1.6	-	1.4	-	1.0	-	0.1	-	1.4
	30 – 50	-	1.0	-	0.9	-	1.1	-	1.2	-	1.0	-	1.0	-	1.0
	50 – 80	-	1.1	-	1.8	-	1.9	-	6.9	-	1.6	-	-	-	1.7
	80 – 100	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0

ACf = Ferric Acrisol; FRh = Haplic Ferrasol.

EF_1 was calculated against the value of the pristine reference (PR); EF_2 was calculated against the value of the deepest soil horizon sampled, 80 – 100 cm (DSH)

I2: Enrichment factors of heavy metals for the Haplic Luvisols (DEB and JUA) and the Dystric Fluvisols (ENC and SAM)

Soil type	Depth (cm)	Cd		Cr		Cu		Mn		Ni		Pb		Zn	
		EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2
LVh (DEB)	0 – 10	0.8	1.0	0.7	1.2	0.7	1.3	1.3	10.8	1.0	0.9	6.0	18.0	0.6	1.5
	10 – 30	0.6	0.9	0.5	1.3	0.4	1.7	0.5	2.4	1.0	0.9	0.2	0.8	0.4	1.9
	30 – 50	0.4	0.5	0.4	1.0	0.4	1.5	0.6	1.7	-	1.0	0.5	2.6	0.4	1.4
	50 – 80	1.1	1.0	0.5	1.1	0.4	1.3	1.6	3.7	1.2	1.0	-	-	0.5	1.3
	80 – 100	1.0	1.0	0.5	1.0	0.4	1.0	0.5	1.0	0.5	1.0	-	1.0	0.4	1.0
FLd (ENC)	0 – 10	1.1	0.2	1.4	1.1	0.8	0.5	0.9	1.5	0.7	0.7	0.2	0.0	0.7	0.4
	10 – 30	1.0	0.1	1.7	1.1	1.3	0.5	1.4	1.2	1.1	1.1	0.9	0.0	1.2	0.4
	30 – 50	1.0	0.1	1.7	1.2	1.0	0.5	1.0	0.9	1.0	1.1	0.2	0.0	1.1	0.3
	50 – 80	1.0	0.1	1.3	1.0	1.9	0.4	1.9	1.0	0.9	1.0	0.5	0.0	1.4	0.3
	80 – 100	-	1.0	-	-	-	1.0	-	1.0	-	-	-	1.0	-	1.0
LVh (JUA)	0 – 10	1.4	1.5	0.4	0.3	3.1	2.9	0.6	2.8	1.0	1.1	21.3	6.6	3.6	1.6
	10 – 30	0.7	0.8	0.7	0.6	0.3	0.8	0.4	0.9	1.0	1.1	3.4	1.7	0.7	0.6
	30 – 50	0.9	0.9	0.8	0.7	0.5	0.9	0.5	0.8	-	1.0	1.0	0.5	1.0	0.7
	50 – 80	1.3	0.9	1.1	0.9	0.4	0.6	0.5	0.7	1.1	1.1	2.9	1.0	1.3	0.7
	80 – 100	1.4	1.0	1.4	1.0	0.8	1.0	0.9	1.0	0.4	1.0	-	-	2.4	1.0
FLd (SAM)	0 – 10	0.9	1.2	1.3	2.7	1.0	4.3	0.6	14.4	1.0	1.0	0.6	1.3	1.1	3.4
	10 – 30	1.0	1.0	1.2	2.0	1.0	2.7	0.9	12.4	1.0	1.0	0.5	0.8	1.0	1.8
	30 – 50	1.0	1.1	0.7	1.2	0.1	0.4	0.1	1.7	0.9	1.0	1.2	1.4	0.6	1.0
	50 – 80	1.0	1.1	0.8	1.5	0.7	1.3	0.2	1.4	1.0	1.1	0.1	0.2	1.0	1.2
	80 – 100	-	1.0	-	1.0	-	1.0	-	1.0	-	1.0	-	-	-	1.0

LVh = Haplic Luvisol; FLd = Dystric Fluvisol

EF_1 was calculated against the value of the pristine reference (PR); EF_2 was calculated against the value of the deepest horizon sampled, 80 – 100 cm (DSH)