HEAVY METAL LEVELS IN NAKURU TOWN AND THE SURROUNDING FARMLAND SOILS

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A Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Master of Science Degree in Chemistry of Egerton University

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DECLARATION AND RECOMMENDATION

Declaration

I hereby declare that this research thesis is my original work and has not been submitted wholly or in part for any award in any other institution.

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Recommendation

We confirm that this thesis was prepared under our supervision and has our approval to be presented for examination as per the Egerton University regulations.

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DEDICATION

To my wife Sibia, our children Edgar, Sammy and Jebet, for their love and unconditional support, and to my father Kimisoi Kositany and my mother the late Rosalliah.

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ABSTRACT

Heavy metals input in soils has been found to present a serious agro-environmental concerns in areas of intensive industrial and agricultural activities and Nakuru town and its surrounding farmland soil is not an exception. High input of heavy metals beyond the threshold limit values is a potential health hazard to plants, and even to animals and human beings through the food chain. The source of heavy metals in soil is primarily the parent rock material, however significant increases may occur through anthropogenic activities. The main objective of this study was to investigate the presence and levels of total and extractable selected heavy metals such as cadmium, chromium, copper, nickel, lead, and zinc in soils of Nakuru town and the surrounding farmlands busing the flame atomic absorption spectrometric technique. The status of some soil chemical properties such as pH, percentage organic carbon and cation exchange capacity were also investigated using stipulated standard methods. The sampling was done randomly in triplicate from 8 sites within Nakuru town and 8 sites in the surrounding farmlands. The data obtained from the experimental analysis were subjected to both descriptive and inferential statistics. The study revealed the presence of heavy metals in Nakuru town and its surrounding farmland soils but they were in very low levels as compared to world health organization maximum permissible levels. The heavy metal concentrations levels were found to correlate($P \leq 0.05$) with the chemical properties either positively or negatively. The levels of heavy metals in Nakuru town soils were observed to be generally higher compared to the levels in the surrounding farmland soils, industrial and domestic emissions being the main contributing factor. The levels of extractable metals in Nakuru town soils had an effect on the levels of extractable metals in the surrounding farmland. It can be concluded from this study that there is no risk of heavy metal toxicity in the study area but accumulation of these heavy metals over time in soil can exceed the stipulated levels hence posing a potential hazard.

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LIST OF ABBREVIATIONS AND ACRONYMS

ATSRD	-	Agency for Toxic Substances and Disease Registry
CEC	-	Cation Exchange Capacity
DEFRA	-	Department for Environment, Food & Rural Affairs
DEPA	-	The Danish Environmental Protection Agency
FAO	-	Food and Agriculture Organization
GoK	-	Government of Kenya
mg/Kg	-	milligram per kilogram
NATO	-	North Atlantic Treaty Organization
OC	-	Organic Carbon
PPM	-	Parts per million
SAS	-	Statistical Analysis System
WHO	-	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background information

Heavy metals are natural constituents of the Earth's crust and therefore their natural occurrence in soil is derived from parent rock material but in trace amounts(Orhue & Frank, 2011; Kabata-Pendias& Mukherjee, 2007; Cheng, 2003).However, change in environmental conditions such as weathering of rocks and pedogenesis, and human activities such as rapid industrialization, urbanization and agricultural activities have drastically altered the balance and the biogeochemical cycles of some heavy metals (Zeng *et al*., 2011;Dharani*et al.,*2010;Facchinelli *et al*., 2001; Bilos *et al*., 2001;McLaughlin *et al*., 2000).Studies have revealed that such activities as mentioned above have led to the accumulation of heavy metals in soils and therefore increasing concern and great interest in the past few years not only to ecologists, biologists and farmers but also to environmentalists (Ding *et al.,*2017;Bilos *et al*., 2001). An assessment of the potential environmental risk due to increased level of heavy metal in soil is of particular importance for agricultural and non-agricultural areas (Huang *et al*., 2018; WHO, 2007).

Public attention on environmental contamination has increased significantly in recent years and a major area of concern is the accumulation and persistence of heavy metals in soils (Huang *et al*., 2018; Singh *et al*., 2010). Of the different land use types in the study area, towns and the surrounding farmlands uses have the highest human health risk because ingestion is the dominant exposure pathway for heavy metals(Yang *et al*., 2018;WHO, 2007). The increased awareness and concern have been accompanied by regulations regarding waste disposal and establishing levels of soil contamination (Huang *et al*., 2018; Ozcan & Altundag, 2013; Morton *et al.,* 2009; WHO, 2007; Wong *et al*., 2003). Heavy metals receiving attention relevant to accumulation in soils, uptake by plants and contamination of ground water include cadmium, chromium, copper, nickel, lead and zinc. Much of the concern with heavy metals has arisen from the use of soils for disposal of sewage sludge and industrial waste, accumulation in landfills, and the application of fertilizers and pesticides (Kim *et al.,*2015; Suruchi & Pankaj, 2011; Yusuf & Oluwole, 2009).

According to numerous studies, the anthropogenic sources of heavy metals in urban soils include traffic emissions (vehicle exhaust particles, tire wear particles, weathered street surface particles, brake lining wear particles), industrial emissions (power plants, coal combustion, metallurgical industry, auto repair shop, chemical plant, etc.), domestic emissions, weathering of buildings and pavement surfaces, atmospheric deposition and so on (Qin *et al.,*2014;Oliva &Espinosa, 2007;Bilos *et al.,* 2001; Koch & Rotard, 2001). However, the anthropogenic sources of heavy metals in agricultural soils include mining, smelting, waste disposal, urban effluent, vehicle exhausts, sewage sludge, pesticides, fertilizers application and so on (Yang *et al.,* 2009; Li *et al.,* 2008;Montagne *et al.,* 2007;McLaughlin *et al.,* 2000). Apart from the sources of the heavy metals, the physicochemical properties of soil also affect the concentration of heavy metals in soil. Soil organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in the soil environment (Hagan *et al*., 2012)

The properties of heavy metals in urban soils and agricultural soils are still of great interest to scientists and this fact is seen in the number of articles in the recent years(Ashrafzadeh *et al.,* 2018; Taghipour *et al.,* 2013; Babula *et al*., 2008). The interest is probably attributed to the potential public health risk associated with intake of heavy metals. In urban area soils, heavy metals can be accumulated in human body via direct inhalation, ingestion and dermal contact absorption (Duzgoren-Aydin *et al*., 2006; Madrid *et al*., 2002).However, intake of heavy metals via the soil-crop system has been considered as the predominant pathway of human exposure to environmental heavy metals in agricultural area (Asta *et al.,*2014; Li *et al.,* 2008).

In many parts of the world like China, it is reported that the geological or naturally occurring heavy metals are low but anthropogenic activities in recent decades have immensely contributed to the increased levels (Huang *et al.,* 2018; Chao *et al.,* 2014; Cheng, 2003). In Kenya, the issue of heavy metal levels in urban and agricultural soils has become a concern especially with the rapid industrialization and urbanization observed in the last two decades (Koskei *et al.,* 2017). Though there is a concern, quite a few studies associated with heavy metal contamination in town and agricultural soils in a number of cities and their surroundings have been carried out (Nguta *et al.,* 2008; Nguta, & Guma, 2004).Another issue is that the quantitative data on heavy metal background concentrations and their contamination levels have not been systematically gathered and documented. Thus this study was focused on determining the presence and the levels of heavy metals in Nakuru town soils and the surrounding agricultural farmlands.

1.2 Statement of the problem

Town and surrounding farmland soils have some specific characteristics such as unpredictable layering, poor structure, and high concentrations of trace elements. Although town soils are not mostly used for farming, pollutants in town and farmland soils can be easily transferred into humans through ingestion, inhalation, or dermal routes, hence they pose a myriad of health risks to residents in this areas. Due to rapid urbanization, the high population density and intensive anthropogenic activities, many towns and surrounding farmland soils have been severely disturbed and Nakuru is not an exception. Consequently, a great number of environmental problems have emerged, among which the heavy metal pollution remains as a major issue. The pollutants can be released in many ways such as vehicle emission, chemical industry, municipal solid waste, the sedimentation of dust and suspended substances in the atmosphere. These emissions have continuously added heavy metals to soils and they will remain present for many years even after the pollution sources have been removed. Heavy metals are toxic and when they accumulate in soil beyond the threshold limits, they become a potential environmental hazard. Increased levels of heavy metals in soil directly affects the soil and water quality, and eventually the animals and human beings through the food chain.

1.3 Objectives of the study

1.3.1 Main objective

To enhance understanding of heavy metal levels in the prevention of possible public health risks in Nakuru town and the surrounding farmland soils.

1.3.2 Specific objectives

This research work was undertaken with the following specific objectives, namely:

i. To determine the presence and concentration levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils.

ii. To assess the status of chemical properties such as pH, organic carbon and cation exchange capacity, and their effect on the levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils.

iii. To compare the levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and those in the surrounding farmland soils.

iv. To determine the relationship of extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town on those of the surrounding farmland soils.

1.4 Hypotheses

H_o The presence and levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils are not significant.

H_o The status of chemical properties such as pH, percentage organic carbon and cation exchange capacity, have no significant influence on the levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils.

H_o The levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils are not significantly different.

H_o The levels of extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town soil have no significant influence on the extractable levels in the surrounding farmland soils.

1.5 Justification

In the past recent years, Nakuru town and the surrounding farmland has been heavily populated, extensively cultivated, urbanized and industrialized. Soil anthropogenic activities, vehicle emission, chemical industry, municipal solid waste, the sedimentation of dust and suspended substances in the atmosphere are believed to be the main source of increased heavy metal loading or inputs in the soils of Nakuru town and its surrounding farmlands, and hence a potential environmental problem. Like most industrial centers, Nakuru town is a prodigious producer of waste, but waste-handling facilities for both domestic and industrial waste have not kept pace with the rate of 250 tones generated per day and population growth rate of 13% per year, thereby posing the threat of pollutant accumulation in the environment.

Recent analyses of storm water, sewage, lake sediment, dead birds and fish from the studied site have revealed the presence of heavy metals and pesticide residues which could possibly be from urban sites, industries and farmlands due to run-offs and other sources of deposition. Studies have also shown that high heavy metal levels in soils, plants and water are toxic, and is considerably associated with closeness to some urban centers. Although previous studies have documented heavy metal pollution in soils and plants in Lake Nakuru national park, limited research depicting on the presence and levels of heavy metals in Nakuru town and its surrounding farmlands has been done. Therefore, in this study aimed at the determination of the presence and concentration levels of heavy metals was necessary so as to set baselines for heavy metal pollution policies by the local authorities in order to provide appropriate monitoring actions that can effectively target reduction of these inputs to the soils and the environment as a whole.

CHAPTER TWO
LITERATURE REVIEW

2.1 Heavy metals

The term heavy metal has often been used to mean metals and semimetals (metalloids) found in the earth crust and have been associated with soil contamination and potential toxicity. It is also a term referring to the group of metals and metalloids with an atomic density of more than 6 gcm^{-3}. Such metals include cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn).Many studies have revealed that these are the metals commonly associated with pollution and toxicity problems when they accumulate in soil(Lu *et al*., 2017; Jar up, 2003;Duffus, 2002).

Most sources of heavy metals such as zinc, cadmium, copper, lead, nickel, and chromium in all soils is from natural occurrence derived from parent rock materials which is usually found at low concentrations. Baseline concentrations vary depending on soil type, soil parent rock material, and type of heavy metal but are usually in the range of 0.1–200 mg/Kg (Tian *et al*., 2017; Lu *et al*., 2014; Duran *et al.,* 2012; Bilos 2001; McLaughlin *et al*., 2000). It was expected that the levels of heavy metals in these soils would be within the acceptable maximum limits stipulated by World Health Organization (WHO) and Food and Agriculture Organization (FAO) which are Cd-0.10 mg/Kg, Cr-0.01 mg/Kg, Cu-0.20 mg/Kg, Ni-0.20 mg/Kg, Pb-5.0 mg/Kg and Zn-2.0 mg/Kg (DEFRA, 2002). Enhanced concentrations (above 0.1-200 mg/Kg range) of heavy metals have been reported in soils from naturally mineralized areas (Bilos *et al*., 2001). Studies have shown that much of it have been either dispersed as a result of atmospheric deposition, waste disposal and incineration or urban effluents, traffic emissions, fertilizer application and long-term applications of wastewater in farmlands (Bilos *et al*., 2001; McLaughlin *et al*., 2000). Furthermore, as a result of their dispersion into the environment, top soils tend to be the most heavily contaminated (Koskei *et al.,* 2017; Chen, 2012; Oliva & Espinosa, 2007).

Chemical properties of soil such as organic matter, cation exchange capacity and pH among others have been reported to be the most important parameters controlling the accumulation, mobility and availability of heavy metals in soil environment (Sauvé *et al.,* 2000). It is necessary then to evaluate the relationship among these parameters and heavy metal accumulation in soil in addition to their sources (Pandey & Pandey,2008).

Heavy metal extractability, in contaminated soils and their mobility have been found to depend also not only on total concentration but also on the metal speciation in the soil solution which is critical in assessing both their bioavailability and their potential threat to the environment (Bednářová, 2016; McLaughlin *et al.,* 2000). This could have long-term implications for the quality of agricultural soils, including phytotoxicity at high concentrations, to the microbial processes, and the transfer of the elements to the human and animal diet from increased crop uptake or soil ingestion by grazing livestock (DEFRA, 2002). Therefore the protection of soils from heavy metal contamination is an essential aspect of maintaining soil and food quality and many countries now have legislation to control the contamination of these elements in soils and the wider environment (Bednářová, 2016; Kaasalainen & Yli-Halla, 2003).

The soil has been known to be a long-term sink for heavy metals, and any heavy metals reaching it can remain in the pedosphere for many years even after the removal of the contamination source (Imperato *et al*., 2003). Whilst these elements display a range of properties in soils including difference in mobility and bioavailability, leaching losses and plant uptake are usually relatively small compared to the total quantities remaining in soil after entering the soil from different diffuse and agricultural sources. As a consequence, these potential toxic elements slowly accumulate in the soil profile over long periods of time (Bunzl *et al.,* 2001).

Accumulation of most of the heavy metals in the soil is known to exert toxicological effects by inhibiting or over activating enzymes in microorganisms and plants. This may block essential biological groups, modify their active conformation or displace the essential ions in the biomolecules of soil microorganisms, plants, or in animals and human beings through the food chain(Bednářová, 2016; Henk *et al.,* 2002). Studies have shown that heavy metals tend to accumulate in the liver and kidney, the principle sites of tissue damage in human beings and animals when they are ingested in contaminated food (Khan *et al.,* 2008; Parker & Hamr, 2001).

He *et al.,* (2015) study on soil samples from arable and urban areas states that arable soils are contaminated with heavy metals at a low percentage, but greater soil contamination may be present in heavily industrialized regions and in large city agglomerations. The city environment forms a mosaic of soils with different levels of mechanical surface transformations which causes it to be even more complex (He *et al.,*2015). Majority of studies on the contamination of soils with heavy metals involves to a large extent the determination of their content in a few soil samples without considering the specificity of their random and systematic variations (Chang, 2014;Jarup, 2003).

2.2 Occurrence and distribution of heavy metals in soil

Heavy metals are known to be present in the environment in diverse amounts as natural constituents of rocks and sediments with a range of normal background concentration in soils, sediments, waters and living organisms (Fosu-Mensah *et al.,* 2017; Green-Ruiz *et al.,* 2006). However, studies have shown that anthropogenic sources, including industrial emissions and effluents, bio solids, fertilizers, soil ameliorants and pesticides have contributed to increased levels of heavy metals in soils although it is very difficult to distinguish between the natural sources and that of anthropogenic origin (Arenas-Lago *et al.*, 2014; Siegel, 2002). Heavy metals derived from anthropogenic inputs have been found to be present in soils in reactive forms and lead to a higher risk of toxicity compared to heavy metals derived from parent materials which are generally immobilized in relatively inert forms (Kabata-Pendias, 2001). However, contamination of soils by heavy metals and other toxic compounds arising from parent rock materials or point sources are known to occur on a limited area and can be identified easily (He *et al.,* 2015; Mavura & Wangila, 2003).

2.2.1 Cadmium (Cd)

Cadmium occurs in the earth's crust and is commonly associated with zinc, lead, and copper ores. Cadmium concentrations in soil, not contaminated by anthropogenic sources, range from 0.06 to 1.1 mg/kg (ATSDR, 2012). Topsoil concentrations are often twice as high as subsoil levels and average concentration in agricultural soils is 0.27 mg/kg (Lin *et al.*2014; Kabata-Pendias, 2001).The principal species of Cd reported in the soil solution is Cd^{+2} but the metal can also form complex ions such as $CdCl^{+}$, $CdOH^{+}$, $CdHCO_3^{+}$, $CdCl_3^{+}$, $CdCl_4^{2-}$, $Cd(OH)_3^{-}$ and $Cd(OH)_4^{2-}$ with organic complexes (Kabata-Pendias, 2001).

Studies have shown that amounts of indigenous cadmium in cultivated and non-cultivated soils as determined by the quantities of Cd in the parent rock materials together with amounts added through atmospheric deposition, phosphatic fertilizers, pesticides, and irrigation water. Some amounts are removed by leaching, erosion, and in harvested crops. Under acidic conditions cadmium solubility increases and very little adsorption by soil colloids, hydrous oxides and organic matter takes place. At a pH value above 6, cadmium is adsorbed by soil solid phase or is precipitated and therefore reducing its solubility and increasing accumulation in soil (Mohajer *et al.,* 2013; N'guessan *et al.,* 2009).

2.2.2 Chromium (Cr)

Chromium is a naturally occurring element found in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds. The mean concentration of chromium in soil is 37.0 mg/kg(ATSDR, 2012).The main forms of chromium are: chromium (0), chromium (III), and chromium (VI). In most soils, chromium will be present predominantly in the chromium (III) oxidation state which is mostly present as insoluble carbonate and oxide of chromium (III); therefore, it will not be mobile in soil. The solubility of chromium (III) in soil and its mobility may increase due to the formation of soluble complexes with organic matter in soil, with a lower soil pH potentially facilitating complexation (Lin *et al.*2014; Chattopadhyay *et al.,* 2010).

The mobility of chromium in soil is also dependent upon the speciation of chromium, which is a function of redox potential and the pH of the soil. This form has very low solubility and low reactivity, resulting in low mobility in the environment (Chattopadhyay *et al.,* 2010). Under oxidizing conditions, chromium (VI) may be present in soil as CrO_4^{-2} and $HCrO_4$andin this form, chromium is relatively soluble and mobile. A leachability study comparing the mobility of several metals, including chromium, in soil demonstrated that chromium had the least mobility of all of the metals studied (Sherene, 2010). These results support previous data finding that chromium is not very mobile in soil, especially in the trivalent oxidation state (Chattopadhyay *et al.,* 2010). A smaller percentage of total chromium in soil exists as soluble chromium (VI) and chromium (III) complexes, which are more mobile in soil. Chromium that is irreversibly sorbed onto soil will not be bioavailable to plants and animals under any condition. Organic matter in soil is expected to convert soluble chromate, chromium (VI), to insoluble chromium (III) oxide, Cr_2O_3. Surface runoff from soil can transport both soluble and bulk precipitate of chromium to surface water. Soluble and unadsorbed chromium (VI) and chromium (III) complexes in soil may leach into groundwater. The leachability of chromium (VI) in the soil increases as the pH of the soil increases. On the other hand, lower pH present in acid rain may facilitate leaching of acid-soluble chromium (III) complexes and chromium (VI) compounds in soil.

2.2.3 Copper (Cu)

Copper is found as native copper in mineral form though not abundantly in nature. It rangesfrom20-50 mg/kg in soils and occurs in several forms that are partitioned between the soil solution and the solid phases (ATSDR, 2012). Distribution of copper between different soil constituents is mostly influenced by the presence of soil organic matter, and manganese and iron oxides. Its retention in the soil is due to exchange and specific adsorption mechanism. Copper shows a strong affinity for soluble organic ligands and these complexes increases copper mobility in the soil. Soil reaction affects copper speciation, its solubility and adsorption; however, a weak correlation has been known to exist between soil reaction and copper concentration in soil solution since dissolved copper has high affinity for organic matter (Lin*et al.*2014; Cornu *et al.,* 2007; Wang *et al.,* 2002). Studies have shown that copper complexes with dissolved organic matter, the most dominant species, averaging 97.1%, in the neutral and mildly acidic soils (Gummuluru *et al.,* 2002).

2.2.4 Nickel (Ni)

Nickel is generally uniformly distributed in the soil profile and typical soil nickel contents vary widely based on the parent rock, with elevated levels at surface soils been associated with soil- forming processes and anthropogenic contamination principally ascribed to agricultural and industrial activities (Cempel & Nikel, 2006; DEPA, 2005). Studies have shown that the underlying geology and soil-forming processes strongly influence the amounts of nickel in soils with higher median concentrations reported in clays, silts, and fine grained loams relative to coarser grained loams, sandy and peaty soils (Kabata-Pendias & Mukherjee, 2007). Nickel (Ni) in soil is as low as 0.2 mg/kg or as high as 450 mg/kg with an average concentration of 20mg/kg (Lin*et al.,*2014; Ahmed, 2011).

Industrial waste materials, lime, fertilizer and sewage sludge constitute the major sources of nickel into soils (Lin*et al.,* 2014; Tye *et al*., 2004). Moreover, nickel is apparently a heavy metal of environmental concern only in urban cities, but could become a problem resulting from decreased soil pH, due to reduced use of soil liming in agricultural soils and mobilization arising from increased acid rain in industrialized areas (Cempel & Nikel, 2006). With decreasing pH, the solubility and mobility of nickel increases, hence, soil pH is the major factor controlling nickel solubility, mobility and sorption, while clay content, iron-manganese mineral and soil organic matter being of secondary importance (Lin*et al.,* 2014; Ge *et al*., 2000; Sauvé *et al*., 2000). In the presence of fulvic and humic acids, the complexes are much more mobile, and may be prominent than the hydrated divalent cation in soil solution (ATSDR, 2005).

2.2.5 Lead (Pb)

Lead in the earth's crust has been estimated to be between 13 and 20 mg/kg(Shen *et al.*2017; Lin*et al.*2014; Kabata-Pendias & Mukherjee, 2007).Lead rarely occurs as a pure element in the earth, but is common in ores such as galena and the other ores like anglesite and cerussite. Lead has strong affinity for organic ligands and competing cations. At pH values above 6 lead is adsorbed on clay surfaces or forms lead carbonate increasing its retention in soils(ATSDR, 2012). Lead is present in uncontaminated soils at concentrations < 20mg/kg, but much higher concentrations have been reported in many areas as a consequence of anthropogenic emissions, often over the years.

2.2.6 Zinc (Zn)

Zinc makes up about 0.0075%of the Earth's crust; and the soil contains 5–770ppm zinc with an average of 64ppm (Shen *et al.,*2017; Lin*et al.,*2014; Emsley, 2001). The element is normally found in association with other base metals such as copper and lead in ores. Sphalerite, a form of zinc sulfide, is the most heavily mined zinc-containing ore because its concentrate contains 60–62% zinc. The most common species of zinc in soil is Zn^{2+}. Zinc is readily adsorbed by clay minerals, carbonates or hydrous oxides. Zinc compounds have relatively high solubility and as the pH increases Zn adsorption increases (Liu *et al.,* 2016; Reichman, 2002).

2.3 Factors influencing levels of heavy metals in soils

Heavy metals are very low in abundance and particularly sensitive to surrounding environmental conditions, which influence their physicochemical speciation and their behavior in the ecosystems (Alamgir, 2016; Akan *et al.,* 2013; N'guessan *et al.,* 2009). Soil has the ability to mobilize or immobilize chemicals like heavy metal ions through sorption properties. Metal stability in soils is determined predominantly by physicochemical properties of soil such as amount of clay and organic carbon content, pH, water content, amount of metal cations exchange capacity, temperature of the soil, oxidation state of the system and properties of the particular metal ion (Olayinka *et al.,* 2017; Hati *et al.,* 2007; Ghosh & Singh, 2005).Physicochemical properties have different influence on the mobility and bioavailability of heavy metals in the soil. These factors will affect the heavy metal potential hazard to the environment and they are discussed below (Elrashidi *et al.,* 2016; Violante *et al.,* 2010).

2.3.1 Soil pH

Soil pH is the most important parameter influencing metal-soil solution and soil surface chemistry. Soil pH can be classified as very strongly acidic (4.5-5.0), strongly acidic (5.1-5.5), moderately acidic (5.6-6-0), slightly acidic (6.1-6.5), neutral (6.6-7.3), and slightly alkaline (7.4-7.8) using the pH scale (Liu *et al.,*2016; Charman & Murphy, 2000). The increase of hydrogen ion concentration affects the mobilization intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. Mobility of metals in soils with low pH decreases in the order: Cd > Ni > Zn > Mn > Cu > Pb(Marrugo-Negrete *et al.*, 2017; Hagan *et al.*, 2012). However, note that the effect of pH on the mobility of metallic elements in the soil is highly variable.

In general, heavy metal adsorption in soil is small at low pH values, and then it increases at intermediate pH from near zero to near complete adsorption over a relatively small pH range, referred to as pH-adsorption range (McCauley *et al.*,2009; Ming, 2008; Apace, 2002). At high pH values (above 7), there is greater retention of metal ions in the soil due to increased number of negatively charged surface sites from organic matter rendering them immobile in the soil (Finzgar *et al.*, 2007).Natural environments often contain low metal concentrations, and at intermediate pH levels (pH 4-7), the sorption by carboxylic groups is more important than the sorption by phenolic groups due to the wide difference between their acidity constants. Liu *et al.,* (2005) study states that toxic elements can become stabilized in the soil due to high soil pH which may result in decreased leaching effects and less element concentration in the soil solution.

Several studies have demonstrated that pH is the most influential factor controlling sorption-desorption of heavy metals in soils (Olalekan *et al.,* 2016; Kazlauskaite *et al.,* 2014; Finzgar *et al.*, 2007).Sauvé *et al.* (2000) reported a multiple linear regression analysis that approximately 50% of the overall variation in the distribution coefficient for metals such as cadmium and lead could be explained by variations in pH. For a metal such as copper, 30% of the total variation could be ascribed to pH, probably due to the influence of copper complexation by dissolved organic matter (Sauvé *et al.,* 2000). The steep increase in heavy metal sorption with rising pH is usually illustrated by means of sorption edges (Mohammadi *et al., 2018*; McCauley *et al.*,2009; Kabata-Pendias & Mukherjee, 2007).

2.3.2 Metal ions

Metal-metal interactions (antagonistic and synergetic effects) can affect heavy metal accumulation and this will depend on the number of factors including the chemical nature of the reactive surface groups, the level of adsorption (i.e. adsorbate/adsorbent ratio), the pH at which adsorption is measured, and the ionic strength of the solution (Ali *et al.*, 2013; Finzgar *et al.*, 2007).However, all these determine the intensity of competition by other cations for bonding sites, and the presence of soluble ligands that could complex the free metal ion in the soil (Arao *et al.*, 2013; Apak, 2002). The above variables are likely to change the metal adsorption isotherms and its bioavailability in the soil.

Competition from monovalent metals in background electrolytes has relatively little effect on adsorption of heavy metals, although the presence of metal ions such as calcium does suppress adsorption on iron oxide (Batista *et al.*, 2012; Apak, 2002).Affinity measured by a selectivity distribution coefficient and the reduction of this selectivity with increased adsorption is observed for metal adsorption on both clay of soil component and pure minerals (Finzgar *et al.*, 2007).This factor plays a role in the mobility of heavy metals in soil and hence soil pollution.

2.3.3 Soil type

The soil type and composition plays an important role for heavy metal accumulation in soil. In general, coarse-grained soils exhibit lower tendency for heavy metal adsorption than fine-grained soils(Dutta *et al.*, 2018; Arenas-Lago *et al.*, 2014; Heike, 2004). The fine-grained soil particles with large surface reactivity and large surface areas such as clay minerals, iron and manganese oxyhydroxides, humic acids and others can display enhanced adsorption properties.

Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides (Ahmed *et al.*, 2016; Heike, 2004; Gasco & Lobo, 2007).Soil colloidal particles of natural soils and sediments provide large interfaces and specific surface areas, which play an important role in regulating the concentrations of many trace elements and heavy metals. Aging of soils may play an important role for heavy metal retention by forming stable surface coatings with time and heavy metal retention onto aged soils acquires a more irreversible character (Dutta *et al.*,2018; Apak, 2002).

2.3.4 Organic matter

Soil organic matter content is one of the most important factors that control the accumulation, mobility and availability of heavy metals in soil. Studies suggest that an increase in soil organic matter content can lead to elevated soil adsorption capacity by which accumulation of heavy metal will be enhanced (Alamgir, 2016; McCauley *et al*.,2009; Rattan *et al*., 2005; Friedel *et al*., 2000). The presence of organic matter in soil affects the biogeochemical processes and it exhibits a large number and variety of functional groups. High cation exchange capacity values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange, and surface precipitation are dependent on organic matter. Humic substances as a component of organic matter are considered as the major adsorbents for heavy metals in oxic sediments (Dutta *et al*.,2018; Alamgir, 2016;McCauley*et al*.,2009; Impellitteri *et al.,* 2002). The sorption ability of organic matter for heavy metals is predominantly through its cation exchange capacity by ion-exchange mechanism rather than by its chelating ability. In addition to cation exchange capacity, soil humus has also chelating ability and some metals have the tendency to combine with certain chelating groups leading to accumulation (Novara *et al.,* 2015;Heike, 2004).

Organic acids from the decomposition of organic matter have been found to play an important role on the solubility of micronutrients in plant rhizosphere (Dutta *et al*.,2018; Heike, 2004). Impellitteri *et al.*(2002)reported that low-molecular weight organic acids such as oxalic and citric acid have some ability to desorb metal ions from the soils with malate, fumarate and succinate being more effective than the others.

2.3.5 Cation exchange capacity

Cation exchange capacity refers to the ability of soil to exchange cations between the counter-ions balancing the surface charge on the colloids and the ions in the soil solution. It is the key factor determining heavy metal concentration in soil. Cation exchange capacity depends on pH, organic matter content in soil and the soil clay content (Dutta *et al.,* 2018; Aydinalp & Manirova, 2003).It also depends on the ionic strength of the surface of soil colloids and relative charges of metal species in soil solution (Finzgar *et al.,* 2007). Studies by Mansur and Gabra, (2010)found that cation exchange capacity can be high where organic matter content in soil is high.

Thus the cation exchange capacity can play an important role in the sorption of heavy metals in soils. The cation exchange capacity is more important than organic matter in the sorption of heavy metals because the pH buffering capacity of soils increases with cation exchange capacity. Also the potential for increased heavy metal availability in acidic soils is less in soils with high cation exchange capacity (Mansur & Gabra, 2010).

2.3.6 Metal-soil macronutrient interactions

In general, an interaction of metals with macronutrients such as nitrogen and phosphorus in the soil induces metal deficiency resulting in low solubility of metal ion (Alkorta *et al.*, 2004). Some of these metal-macronutrient interactions are the nitrogen-copper and phosphorus-copper couples which have been shown to occur for several crops (Alkorta *et al.*, 2004). Increased protein concentration in roots as a result of increased nitrogen application have shown increased retention of Cu by increasing formation of protein-Cu complexes. Thus over time with these conditions prevailing, heavy metals will accumulate in soil and therefore posing a potential hazard.

2.4 Soil contamination in urban and surrounding areas

Soils in urban and surrounding areas apart from their nature have been transformed by human activities. They have been found to be characterized by a strong spatial heterogeneity resulting from the various inputs of exogenous materials and the mixing of original soil materials (Giuffr'e *et al.*, 2012). Such soils often will hold pollutants such as heavy metals that may be a potential hazard to the environment. Work carried out in China and other parts of the world have shown that heavy metal accumulation and finally pollution in urban and the surrounding farmland soils has become serious with the rapidly increasing industrialization and urbanization (Binggan & Linsheng, 2010).

2.4.1 Urban areas

Research carried out in most of urban area soils have shown that different land use (commercial, industrial, residential, recreational) have an impact on the soil, thus disturbing it in some manner ending up modifying its properties such as pH, organic matter and soil texture(Yin *et al.*, 2015;Ghosh*et al.*, 2012; Giuffr'e *et al.*, 2012).As a consequence of high population density and intensive anthropogenic activities in urban areas, it is reported that urban surfaces receive deposits issued from more or less remote sources which include vehicle emissions, industrial discharges, energy production, waste disposal and other human anthropogenic activities (Ozcan & Altundag, 2013; Maas *et al.*, 2010; Biasioli *et al.*, 2006). Because urban soil is an important component of the urban ecosystem, it is considered both as a sink of pollutants and a source of pollution with the capacity to transfer pollutants to ground water, the food chain and the human body (Islam *et al.*,2015; Li *et al*., 2008; Wong *et al*., 2003; NATO, 2002;Adriano, 2001). Therefore, it is indubitable that heavy metal accumulation in urban soils is a significant environmental issue (Ngure *et al.,* 2015). The interest in the characteristics of urban soils has increased greatly in the last two decades and investigations of urban soils in many cities around the world have reported elevated concentration of heavy metal in general (Li, 2014; Zhang *et al.,* 2012; Lu *et al*., 2003).

Giuffr'e *et al*.(2012) reported that the ground making up urban environments or soils represents a complex mixture of natural parent rock materials and residues from the continued use and reuse of sites for human activity. Some work have also shown that urban soils have received little attention as a functional medium in the urban ecosystem, beyond the identification of contaminated sites and specific programmes to mitigate the risks posed by the contaminants (Maas *et al*., 2010; Kachenko & Singh, 2006; Hursthouse, 2001; Pollard *et al*., 2001).

Further, Giuffr'e *et al*.(2012) stated that the dynamic nature of human interactions with soil such as the redevelopment and reuse of urban space have often resulted in the addition of heavy metals from a wide variety of sources with correspondingly diverse physical and chemical properties. The most common is the addition of building rubble which includes cement, concrete, brick, structural metallic components, wood and a variety of other wastes (Rosenbaum *et al*., 2003).Contamination of urban soils by heavy metals is widely recognized at point source locations, and increasingly from diffuse inputs (Zuo *et al.,* 2018; Hursthouse *et al*., 2004; Madrid *et al*., 2002).Surveys on the distribution and concentration of heavy metals in the urban soils are important for planning management strategies to achieve urban environmental quality and to control the risk associated with the excessive increase of heavy metal in the environment (Salah *et al.,* 2013; Pouyat *et al*., 2007).

There is a wealth of information available on metal ions demonstrating a wide range of uptake capacities and interaction mechanisms. The literature recognizing heavy metal persistence in urban soils is available, but little data exist in the literature for metal contaminant interaction with urban soil containing significant anthropogenic debris. Clearly there is a gap in knowledge, related to urban soils and empirical data is needed as the basis for wider modeling and assessment (Moller *et al.,* 2018;Ozturk *et al.,* 2017; Bable & Kurniawan, 2003; Plassard *et al*., 2000).

2.4.2 Suburban areas

Soils of farmland area surrounding the urban areas have been reported to face major problems due to heavy metal and other pollutants transfer into its soils and subsequently into the food chain through atmospheric deposition and utilization of wastewater and sewage sludge from town area in farms (Liu *et al.,* 2016; Nguta & Guma, 2004). Apart from influence of town activities, it has been found that intensive agricultural activities that utilize phosphatic fertilizers, pesticides and herbicides also contribute to heavy metal loading in soils of surrounding farmlands (Sulaiman *et al.,* 2016; Cui *et al.,* 2015; Evaristo, 2013; Taghipour *et al.,*2013;Chen *et al.,* 2007). Adriano (2001)has shown that sites with low or medium contamination levels, metal concentration in crops is mostly not as high to cause acute toxicity, but in the long run it may cause chronic damage to human health and soil quality.

Due to the heavy metal burden in human nutrition, there is a need for measures to reduce the metal transfer into agricultural soil (Sulaiman & Hamzah, 2018; Nabulo, 2006). In areas, where conventional or other remediation technologies are not feasible or too expensive, other simple but effective approaches may help to reduce the accumulation of heavy metals in the edible parts of crops and this is only feasible when the levels are known.

Work carried out by Binggan and Linsheng (2010) on suburban soils of China have shown that anthropogenic activities such as industrial effluents and traffic emissions have dominant influence on the level of contamination of soils in that area. Some work has also shown that natural and to some extent anthropogenic activities have strong influence on suburban soils (Wang *et al.,* 2018; Zou *et al.,* 2015; Maas *et al*., 2010; Chen *et al.,* 2007; Celine *et al.,* 2006). Thus there is need to determine the level of heavy metals and find out if there is an relationship between the two areas (town and the surrounding farmlands) in terms of soil contamination.

CHAPTER THREE
MATERIALS AND METHODS

3.1Description of the study area

Nakuru town and its surrounding farmlands which is located between longitudes 35° 0′ East and 37° 0′ East, and latitudes 0° 0′ South and 1° 0′ South were chosen as the study area(GoK, 2010). The area is within a closed drainage system of $1800Km^2$ (Figure 3-1). To the North lies the Menengai crater, Bahati highlands to the Northeast, Mau escarpment to the West, Eburu crater to the South and gentle grasslands between Lake Nakuru and Lake Elementaita basin lie to the East. Lake Nakuru national park lies in the depression of this catchment basin acting as a buffer zone between human activities and the Lake. The geology of the study area is made up of igneous rocks (volcanic) and the soil having high porosity, permeability and loose structure(Mavura & Wangila, 2003). The study area occupies $290Km^2$, 70% being dominated by housing, 18% industry and commerce and the rest is intensive farming (Raini, 2009).

The study area was divided into two sections as shown in Figure 3-1 for sampling; the town area being within 2 Km from the town center and the surrounding farmlands being those beyond 2 Km from the town center.

Table 3.1: Sampling sites and their activities in Nakuru town soils

Site	Activity
ST_1	Battery factory, Saw milling, Residential and Commercial buildings, Moderate Traffic activity, Open playground
ST_2	Saw milling, residential and Commercial buildings, Moderate traffic activity, Open playground
ST_3	Commercial buildings, Heavy traffic
ST_4	Sparingly populated, Residential buildings, Forested
ST_5	Many residential, Small parks
ST_6	Garages, engineering works, Metal works ,Commercial buildings
ST_7	Commercial buildings, less traffic and Manufacturing enterprises
ST_8	Residential buildings, Dusty roads, Small parks, Soap making factory

Table 3.2: Sampling sites and their activities in the surrounding farmland soils

Sampling site	**Activity**
SF_1	Cultivated farms and partly forested.
SF_2	Cultivated farms and grazing fields.
SF_3	Small farms, small pasture areas, housing and trees.
SF_4	Large pasture fields and large cultivated farms.
SF_5	Both small and large cultivated farms and residential buildings,
SF_6	Both small and large cultivated farms and residential buildings.
SF_7	Small cultivated farms, many trees and quite a distance from town.
SF_8	Both small and large farms and just adjacent to town area.

ST-Sample site in town, SF-Sample site in the surrounding farmland

3.2 Instrumentation and Reagents

3.2.1 pH meter

The pH meter used in this study was a Fisher Accumet 610A model. This is a digital bench top meter fitted with a combined electrode. The pH meter was calibrated using loba chemie buffer tablet solution of pH 4.0 and 7.0.

3.2.2 Flame atomic absorption spectrophotometer

A Buck model 210VGP flame atomic absorption spectrophotometer with digital display was used in this study. The settings used were as shown in Table 3-1.

Table 3.3: Atomic absorption spectrophotometer settings

Metal	**Band pass(nm)**	**Lamp current(A)**	**Wavelength(nm)**	**Flame**
Cd	1.0	3.0	228.8	Air-acetylene
Cr	0.5	6.0	357.9	Fuel rich air-acetylene
Cu	1.0	5.0	324.7	Air-acetylene
Ni	0.3	8.0	232.0	Air-acetylene
Pb	1.0	5.0	217.0	Air-acetylene
Zn	1.0	3.0	213.9	Air-acetylene

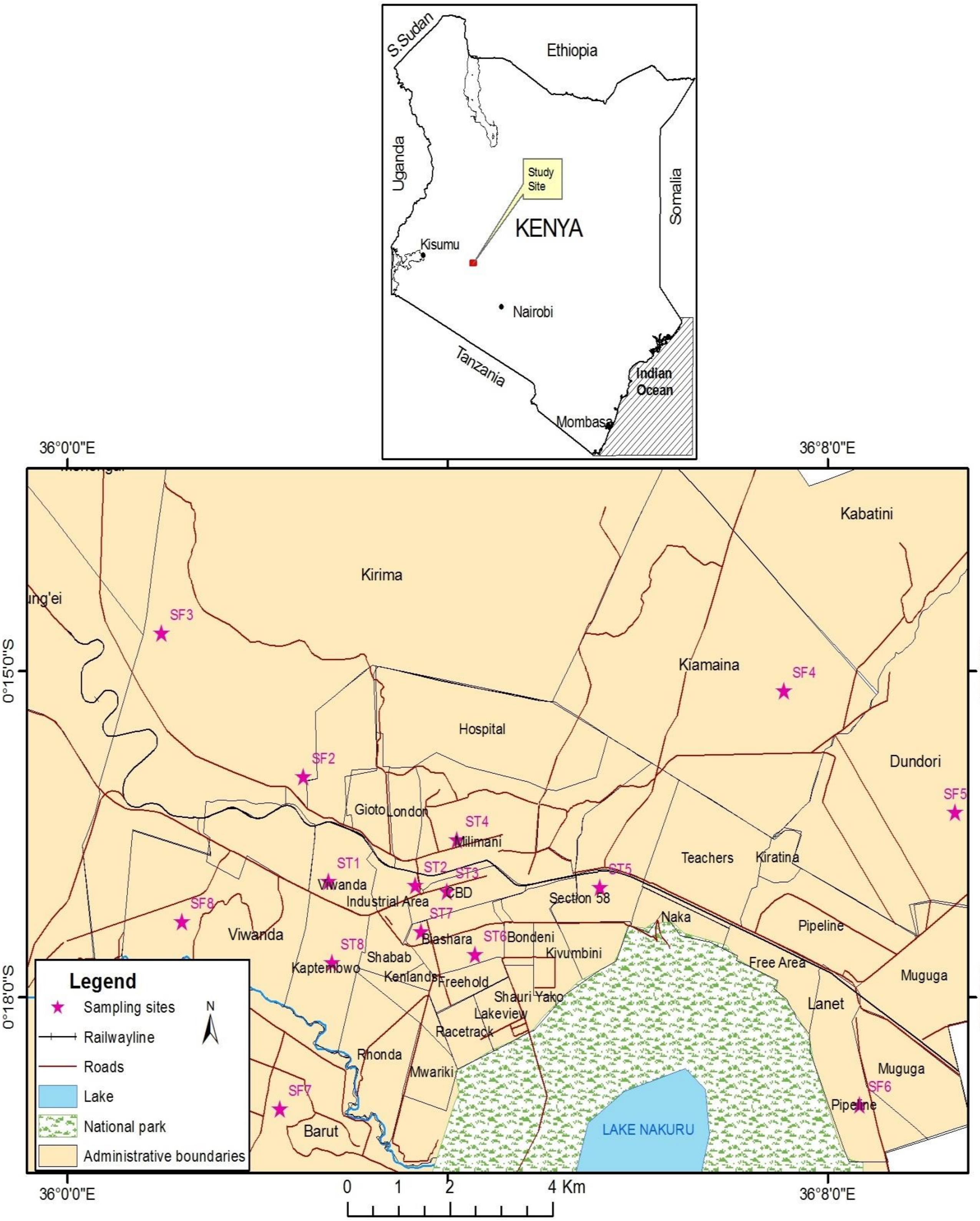

Figure 3.1: Map of the study area and sampling points(GoK, 2010)

3.2.3 Auto distillation apparatus

A Foss Tecator 2200 Kjeltec Auto Distillation apparatus was used to steam distillate samples for cation exchange capacity analysis in this study.

3.2.4 Electric shaker

A Heidolph Unimax 2010 electric shaker was used to shake the samples for effective extraction and solubility of ions.

3.2.5 Reagents

All reagents used were analytical grade.

3.3 Sampling and sample preparation

3.3.1 Sampling

The sampling for the study was done randomly and undertaken at the onset of a rainy season (March –April) when the soils were soft and easy to auger. A sampling site in Nakuru town and the surrounding farmlands involved an area of 20 m^2.The samples were collected randomly (zigzag method) with the aid of a 30mm diameter stainless steel hand auger to a uniform depth of 30 cm(the potentially affected part of the soil). From each site 3 composite (well mixed) soil samples were taken as a representative of that site. The samples were put in well-labeled khaki bags and transported to a soil laboratory at Crops, Horticulture and Soil Science Department of Egerton University.

3.3.2Sample preparation

The soil samples were sorted out first by removing any plant materials and stones present before air drying for one week in shallow trays in a well-ventilated area. The dry soil samples were then crushed using a mortar and pestle and sieved using a 2 mm sieve.

3.3.3 Standards preparation

The working standard solutions for cadmium, chromium, copper, nickel, lead and zinc were prepared from the analytical grade commercial standard stock solution of 1000 ppm accordingto the operation manual of the spectrophotometer. The working standard solutions were then used to calibrare the atomic absorption spectrophotmeter and calibration curves developed for each metal.

3.4 Chemical properties analysis

Standard methods as modified by Van Reeuwijk, 1995; Nelson and Sommers, 1996; Summer and Miller, 1996; Mathieu and Pieltain, 2003; and Burt, 2004 were used to measure physicochemical properties of the soil such as pH, organic carbon content and cation exchange capacity.

3.4.1 Soil pH

Soil pH was measured in a 1:2.5 (w/v) ratio of soil and water suspension (Van Reeuwijk, 1995). Twenty grams of each of the soil samples was weighed in duplicate into plastic bottles, and 50 cm^3 of distilled water were added, and then shaken for 30 minutes. The soil pH values were then measured in duplicate using a pH meter in the laboratory.

3.4.2 Organic carbon

The total organic carbon content in the soil samples was determined by the oxidation method of Walkley and Black method as modified by Nelson and Sommers, (1996).One gram of each of the soil sample in duplicate were weighed into a 500 cm^3 flasks, Each sample was separately oxidized with 10cm^3 of 1MPotassium dichromate and 20 cm^3 of concentrated sulphuric acid for 30 minutes. The samples were then diluted by adding 200 $cm^3$of distilled water, acidified with 10cm^3 of 80 % orthophosphoric acid and a few drops of diphenylamine indicator were added before titrating with 0.5M Ferrous ammonium sulphate. The titre obtained was then used to calculate the percentage of organic carbon in each of the soil samples.

$$\%\ \text{Organic Carbon} = \frac{10\ (A - B)}{A} \times \frac{0.003}{S.W} \times 100$$ ………………………....***Equation 1***

A= Blank titre, B= Sample titre, and S.W= Sample weight

A blank (without soil sample) was treated in the same manner and the results recorded.

3.4.3 Cation exchange capacity (CEC)

The cation exchange capacity (CEC) was determined as a sum of basic cations extracted by leaching 10 g of duplicate soil samples into a 250 cm^3 conical flasks with 50 $cm^3$of 1M neutral ammonium acetate solution(Van Reeuwijk, 1995). The suspensions were stirred occasionally for an hour and then left overnight before filtering the contents through Whatman No. 42 filter. The soil residues left on the filter paper were washed with 200 cm^3 of 60% ethanol (in portions of 25 cm^3) to remove excess ammonium acetate before washing with 300 cm^3 of 10% KCl (in 5-6 portions) and a clean filtrate collected into a conical flask. An aliquot of 20ml of the filtrate was then transferred into auto distillation tube, 3 g of

Magnesium oxide and 10 cm^3 of 45% NaOH were added before steam distilling using an Auto distillation apparatus. The evolved ammonia was absorbed into10 $cm^3$of 2% H_3BO_3in a 250cm^3 conical flask to which a few drops of methyl red indicator had been added. About 150 cm^3 distillate was collected, and titrated with standardized 0.1M H_2SO_4

CEC(cmol/Kg)= VMT/20x100/SW…………………………..…***Equation 2***

Where V= Vol. of acid used, M= Molarity of the acid, T= Total final vol. of NH_4^+ filtrate and SW= Sample weight.

3.5 Heavy metal analysis

Heavy metal analysis involved the determination of the total and the extractable metal contents in the soil samples. The total heavy metal content was determined from the acid-digested samples and the extractable metal content was determined from the EDTA extract samples as stipulated by standard methods (Sabrina & Luis, 2013).

3.5.1 Total metal content analysis

The total metal content in the soil samples (Sabrina & Luis, 2013) were prepared by wet ashing or digesting one gram of the air-dried sieved sample in 30 cm^3 of aqua regia (1:3 Nitric acid; Hydrochloric acid). This was done by heating the samples under reflux, cooling it before filtration using Whatman filter paper no.42 and dilution with100 cm^3 of 2M Nitric acid in a 100 cm^3 volumetric flask. The blank was prepared the same way the samples were prepared. Standard working solutions were run to calibrate the atomic absorption spectrophotometer for each metal at a time according to the operation manual of the spectrophotometer. The absorbencies of the sample solutions for cadmium, chromium, copper, nickel, lead and zinc and the blank were then obtained from the atomic absorption spectrophotometer respectively. The concentrations of cadmium, chromium, copper, nickel, lead and zinc in the sample solutions were then obtained by using plotted standard calibration curves developed earlier from the working standards.

3.5.2 Extractable metal content analysis

Samples for extractable metal content analysis were prepared by extracting them with 0.05M Ethylenediamine tetraacetic acid (EDTA). Five grams of each soil sample were weighed into separate plastic bottles and 125cm^3 of the extracting solution was added to each of them and then shaken for 1 hour on an electric shaker before filtering. The filtrates were used to determine the extractable content of cadmium, chromium, copper, nickel, lead and zinc in soil in the same manner as the total content above using the atomic absorption spectrophotometer.

3.6 Data analysis

The data obtained from the experimental analysis was analyzed statistically using STATA version 14 programme (Tokalioglu & Kartal, 2003). Descriptive analysis was done to determine the mean concentration levels of heavy metals and the chemical properties levels of the soil. Pearson correlation analysis was also done to determine the strength of relationship between the heavy metal and chemical properties levels, the direction of relationship whether positive or negative, and the significance of the relationship. A student t-test was done to compare both the heavy metal and chemical properties levels in town and the surrounding farmland, and to determine if there are any significant differences. Lastly, regression analysis was performed to determine the percentage of variation of heavy metals caused by the chemical properties, their significance and the rate of change, and the relationship between heavy metal concentration levels in town and the surrounding farmland.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discussed the results of the study. The first section discusses the levels of cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils. The second section discusses the status of the chemical properties of the soil and their relationship with the levels of total and extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils. Further, the third section discusses the comparison between levels of cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils, and lastly, the fourth section discusses the effect of extractable cadmium, chromium, copper, nickel, lead and zinc levels in Nakuru town on those of the surrounding farmland.

4.2Levels of heavy metals

4.2.1Levels of total heavy metals

The mean values of total cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils are presented and expressed as milligrams per kilogram (mg/Kg) in table 4.1.The mean concentration levels of cadmium in Nakuru town soils ranged from 0.42 to 1.03 mg/kg. The observed results from the study area in relation to other works were above the naturally (0.1-0.3 mg/kg)occurring levels (ATSDR, 2012). The levels of Cd in the study area varied from residential areas, busy central business center to industrial areas hence making the variation in heavy metal distribution to be in agreement with observations from other urban areas in the world that range from 0.06 to 1.1 mg/kg (ATSDR, 2005). Research work in other parts of the world have shown that in addition to soil make up and the parent rock material of a particular area, paint peels and pigments from many buildings, and atmospheric deposition from industrial activities can contribute to total Cd content and the study area is not exceptional (Campbell, 2006).Anthropogenic activities as suggested by other studies from Nakuru town soils and Lake Nakuru sediments could also be another source but very insignificant(Raini & Kulich, 2008;Nguta & Guma, 2004). Although atmospheric deposition due to vehicular emissions and burning of garbage in urban areas is known to be a contributor of Cd in urban soil, the results of the study suggest that the levels obtained could be related to the naturally occurring content. The mean concentration levels of total Cadmium (Cd) content in the farmland soils surrounding the town ranged from 0.26 to

Table 4.4: Mean values (mg/Kg) of total heavy metals in Nakuru town and the surrounding farmland soils

Nakuru town								Surrounding farmlands						
Site/Metal		**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Site/Metal**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
ST_1	Mean	0.70	2.24	2.67	2.00	1.49	0.27	SF_1	0.42	0.61	1.61	0.67	0.61	0.18
	SD	0.07	0.06	0.19	0.25	0.02	0.01		0.03	0.09	0.09	0.14	0.10	0.02
ST_2	Mean	1.03	1.06	1.61	1.50	0.61	0.32	SF_2	0.58	1.00	2.42	0.83	0.56	0.31
	SD	0.06	0.06	0.14	0.25	0.10	0.00		0.02	0.06	0.19	0.14	0.10	0.00
ST_3	Mean	0.72	1.59	1.79	1.75	0.72	0.27	SF_3	0.73	0.84	1.73	0.58	0.61	0.15
	SD	0.06	0.06	0.23	0.25	0.10	0.01		0.03	0.07	0.09	0.14	0.10	0.00
ST_4	Mean	0.76	1.06	1.73	0.92	0.89	0.23	SF_4	0.92	1.08	1.67	0.58	0.56	0.13
	SD	0.05	0.06	0.09	0.14	0.10	0.01		0.02	0.03	0.11	0.14	0.01	0.01
ST_5	Mean	0.72	0.88	1.61	1.17	1.17	0.26	SF_5	0.84	0.88	0.91	0.58	0.83	0.17
	SD	0.04	0.06	0.11	0.14	0.00	0.02		0.03	0.06	0.09	0.14	0.00	0.01
ST_6	Mean	0.48	1.65	2.73	1.08	1.00	0.46	SF_6	0.91	1.65	2.58	0.75	0.50	0.12
	SD	0.03	0.06	0.18	0.14	0.17	0.01		0.03	0.06	0.10	0.25	0.01	0.00
ST_7	Mean	0.42	1.73	1.73	0.83	0.72	0.21	SF_7	1.39	0.59	2.61	0.67	0.50	0.11
	SD	0.03	0.12	0.09	0.14	0.10	0.01		0.04	0.06	0.05	0.14	0.00	0.01
ST_8	Mean	0.63	1.12	2.52	1.08	1.11	0.32	SF_8	0.26	1.10	4.39	0.83	0.67	0.16
	SD	0.11	0.10	0.19	0.14	0.11	0.01		0.03	0.09	0.11	0.14	0.00	0.01

SD- standard deviation; ST- site in Nakuru town; SF-site in surrounding farmland

1.39 mg/kg which is slightly above the background range (0.06-1.1 mg/kg) as is in most uncontaminated soils of the world(DEFRA 2002). The amounts of Cd in soils from farmlands surrounding the town varied slightly from one site to the other suggesting the distribution pattern in the soil of the area under study (ATSDR, 2005). The use of phosphate fertilizers, pesticides and other farming activities that are a source of Cd input in the soil could contribute to the total content (ATSDR, 2012).

The chromium levels in Nakuru town soils ranged from 0.88 to 2.24 mg/kg as compared to the average (37.0 mg/kg) distribution of Cr in soil of many parts in the world (ATSDR, 2012). The sites in the study area showed a slight variation in the amount of Cr which could be attributed to the naturally occurring levels since it is very low compared to what is normally found in soils on average(ATSDR,2012). Work done on sediments of Lake Nakuru can attest that soils of Nakuru town contain chromium probably originating from anthropogenic activities in town but in small quantities (Raini & Kulecho, 2008).This observation compares well with other works done in many urban areas of the world with similar activities as those of Nakuru town. The chromium (Cr) in farmland soils surrounding the town ranged from 0.59 to 1.65 mg/kg. The total content observed here was way below the average (37.0 mg/kg)for uncontaminated soils (ATSDR, 2012). The results observed from the study suggest that Cr in these soils could be the naturally occurring content and any variation could be due to distribution in the soil.

The levels of total copper ranged from 1.61 to 2.73 mg/kg in Nakuru town sites. The results indicated that copper in town soils was below the average range (20-50 mg/kg)according to the world copper distribution in urban area soils (ATSDR, 2012). Although the amount of Cu varied from one site to the other, the mean values were below the maximum permissible levels or limits of 100.00mg/kg(DEFRA, 2002). The concentration levels of copper in Nakuru town was very low as compared to those of other urban (120 mg/kg for Naples city in Italy) areas in the world (Imperato *et al*., 2003). The results suggest that apart from the naturally occurring levels, activities that contribute to Cu input such as dumping or accumulation of solid waste in town soil are minimal in relation to other urban areas of the world(Binggan & Linsheng, 2010).The copper (Cu) levels in the farmland soils surrounding the town ranged from 0.91 to 4.39 mg/kg. The observed range in the study area is way below 20-30 mg/kg reported in uncontaminated soils(ATSDR, 2012). The observation made from the results indicated that copper was low compared to levels from other parts of the world (a mean of 31.71 mg/kg in all agricultural soils in cities from China) meaning its distribution is low in this area or the inputs of cooper here are minimal (Everisto, 2013; Binggan &Linsheng, 2009).

The mean concentration levels of nickel in Nakuru town soils ranged from 0.83 to 2.00 mg/kg. The average nickel content in soils is 20 mg/kg especially in soils derived from igneous rocks and therefore the results are within the observed range (Yahaya, 2011). Apart from nickel coming from the parent rock material, domestic cleaning products that contain nickel as part of their composition e.g. soaps and powdered detergents are known to add nickel in town soils as observed from the results (Kabata-Pendias & Pendias, 2001). The total nickel (Ni) content in the farmland soils surrounding the town ranged from 0.58 to 0.83 mg/kg. Though the total content of nickel as observed from the study is within the average of uncontaminated soil (20 mg/kg), its presence in the soil is influenced by the underlying geology and soil forming processes(Kabata-Pendias&Mukherjee, 2007).

The mean concentration levels of lead (Pb) in Nakuru town soils ranged from 0.61 to 1.49 mg/kg. The average amount of lead in uncontaminated soil range from 13 to 20mg/kg and therefore what was observed in Nakuru town sites was low (Kabata-Pendias & Mukherjee, 2007).The investigated sites gave a variation in the mean values of lead which can be supported by the distribution pattern of activities in the area of study The observations from the work done on soils of Nakuru town within 0-15 km radius (45 mg/kg), are in agreement with the values observed in this study(Nguta & Guma, 2004). These variations are reflective of many other urban areas where use of lead formulated paints, pipes and other related products are a major source of Pb into soil(ATSDR, 2005; DEFRA, 2002).The lead in the farmland soils surrounding the town ranged from 0.50 to 0.83 mg/kg. The results suggest that these are naturally occurring levels because it has been observed that uncontaminated soil has an average of 20 mg/kg (Kabata-Pendias & Mukherjee, 2007). In comparison with other work in the study area, levels of lead (Pb)in the farmland soils surrounding the town meant that the contents observed could be originating from the naturally occurring content(Nguta & Guma, 2004).

The mean levels of zinc in Nakuru town soils ranged from 0.21 to 0.46 mg/kg. Naturally occurring zinc on average is 64 mg/kg and the results obtained in this work indicate that the content of zinc is very low in this area (Emsley, 2001). Though there was variation in the observed mean values of zinc among the sites, still it was low as compared to the average distribution in most soils. Unlike in most developed towns where the observed zinc levels are high due to its industrial use, what was found in the study area was low meaning low input of zinc here(Opaluwa *et al*., 2012).Zinc (Zn) farmland soils surrounding the town ranged from 0.11 to 0.31 mg/kg. Most uncontaminated soils in farmlands have an average of 64 mg/kg zinc, and from the results obtained it indicates that these are naturally occurring content(Emsley, 2001). Observations done in most soils of suburban areas in the world indicate that zinc levels averaging 64 mg/kg or less are mostly the natural content values(Cheng, 2003).

In summary, the results observed from Nakuru town and the farmland sites surrounding the town indicate the presence of heavy metals in the soils but in small amounts and therefore not significant (Cheng, 2003; Nguta & Guma, 2004). The low levels suggest natural content that originate from the parent rock material, but it is also possible that anthropogenic activities both in town and the farmland surrounding it such as industrial and automobile emissions, peeling of paints and building debris, and the use of phosphate fertilizers, pesticides, herbicides and other soil ameliorants could be an attributing factor to the total content levels observed(Kabata-Pendias & Mukherjee, 2007; He *et al*., 2005). The variation in mean values observed across the sites is dependent on the activities therein(Nguta *et al*., 2005).

4.2.2 Levels of extractable heavy metals

The mean values of extractable cadmium, chromium, copper, nickel, lead and zinc in Nakuru town and the surrounding farmland soils are presented and expressed in milligrams per kilogram (mg/Kg) in table 4.2. It was observed that extractable cadmium in Nakuru town sites ranged from 0.12 to 0.74 mg/kg. The variation across the investigated sites though not much could be attributed to activities therein. The observed amounts of cadmium in the town soil in this work are within the range of 0.06 to 1.1 mg/kg (ATSDR, 2012). The cadmium concentrations in this soil suggest that the soil is not contaminated by anthropogenic sources. Extractable cadmium in the farmland surrounding the town ranged from a mean value of 0.07 to 0.59 mg/kg. The results indicated that cadmium is easily extractable in farmland soil surrounding the town though in small quantities. The observation suggests that the soil is not contaminated by anthropogenic sources as it is within the stipulated range of 0.06 to 1.1 mg/kg which is for uncontaminated soil (ATSDR, 2012).

The extractable chromium content in Nakuru town soils ranged from 0.06 to 1.10mg/kg. The observed variation from site to site though small suggests the distribution pattern of chromium in soil. The mobility of chromium in soil is dependent upon the speciation of chromium. These results support previous data finding that chromium is not very mobile in soil, especially in the trivalent oxidation state (Chattopadhyay *et al.,* 2010). The mean values for easily extractable chromium in the farmland soils also ranged from 0.30 to 0.59 mg/kg. The extractable chromium in farmland soil is suggested to be low which could be the background extractable value as suggested by work carried out in other parts of the world (Kabata-Pendias & Mukherjee, 2007; Balasoiu *et al.,* 2001).

The mean values for extractable copper ranged from 0.76 to 1.55 mg/kg in town soils. The observed results were low in comparison to those of uncontaminated soil (20-50 mg/kg) and above maximum permissible levels (0.2 mg/kg) in city soil solution (ATSDR, 2005; DEFRA, 2002). The variation observed from one site to another suggests the distribution pattern of copper in the study area. Though the source of copper in town soil is diverse, the variation observed could also be due to partitioning between the soil solution and the soil solid phase (Cornu *et al.,*2007). The extractable copper in the farmland soils surrounding the town ranged from a mean value of 0.61 to 1.55 mg/kg. The observed results were low in comparison to maximum permissible levels (0.2 mg/kg) in suburban area soil solution (ATSDR, 2005; DEFRA, 2002). While the interaction of copper with the environment is complex, research shows that most copper introduced into the environment rapidly becomes stable and results in a form which does not pose a risk in the environment. Soil reaction will affect copper speciation and its solubility and adsorption in the soil (Wang *et al*., 2002).An example is where copper is known to complex strongly with organic matter, implying that only a small fraction of copper will be found in soil solution (Martinez & Motto, 2000) and this work supports the nature of results observed in this study.

The extractable levels of nickel in Nakuru town soils ranged from 0.25 to 0.83 mg/kg. The maximum permissible level of nickel in soil solution is 0.2 mg/kg (ATSDR, 2005; DEFRA, 2002). The observed amount of Ni is low meaning that much of it is retained by the soil colloid hence resulting in accumulation. As indicated by many studies, the type of the soil and amount of organic matter affects Ni solubility (Kabata-Pendias & Mukherjee, 2007).The mean values for easily extractable nickel in the farmland soils ranged from 0.25 to 0.42 mg/kg. The observed results were low in comparison to maximum permissible levels (0.2 mg/kg) in soil solution (ATSDR, 2005). Nickel is known to occur in the environment only at very low levels and the results in this study are not an exception (Wuana & Okieimen, 2011; Kabata-Pendias & Mukherjee, 2007). The levels of extractable lead in the town soils ranged from 0.17 to 0.61 mg/kg. The observed results were low in comparison to maximum permissible levels of 5.0 mg/kg in soil solution (ATSDR, 2005; DEFRA, 2002).Studies have shown that chemical properties have an effect on availability (Cornu *et al.,* 2007). The amount of lead observed suggests that much of it is held by the soil colloids and over time it will accumulate and therefore pose a hazard. The lead levels in the farmland soils ranged from a mean value of 0.17 to 0.33 mg/kg. The observed results were low compared to what is tabulated as the maximum permissible level (5 mg/kg) that can be extracted from the soil (ATSDR, 2005; DEFRA, 2002). Most of the lead does not accumulate in soil but rather in the leafy parts of the plants and this suggests that the low results observed in this study are due to the accumulation in the leafy parts of the plants(Rosen, 2002).

The levels of extractable zinc in Nakuru town soils ranged from 0.07 to 0.18 mg/kg. The maximum permissible levels of zinc (2.0 mg/kg) that can be in soil solution is higher than what was observed in this study (ATSDR, 2005; DEFRA, 2002).Observation from many workers have shown that zinc is one of the most abundant metals in everyday use as well as in urban waste (Nguta *et al*., 2005), but from these results there is a suggestion that zinc is bound tightly and very little goes into the soil solution. This trend allows the accumulation of the metal in the soil which is a potential hazard. Extractable zinc in the surrounding farmland soils ranged from 0.04 to 0.12 mg/kg. The mean concentration of Zn in this investigation was low as compared to maximum permissible levels of 2mg/kg Zn (ATSDR, 2005; DEFRA, 2002).

In summary, the results obtained indicate that the heavy metals under study are found in soil solution though in small quantities and therefore the greater portion is held tightly by the soil colloids. Though the observed amounts are low and insignificant, they can be hazardous over time when taken up by plants easily, washed away easily by runoff water into rivers endangering the aquatic life or leaching into aquifers thus contaminating drinking water (Nabulo, 2006).

Table 4.5: Mean values (mg/Kg) of Extractable heavy metals in Nakuru town and the surrounding farmland soils

Nakuru town								Surrounding farmlands						
Site/Metal		**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Site/Metal**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
ST_1	Mean	0.20	1.10	0.76	0.42	0.61	0.07	SF_1	0.24	0.30	0.79	0.25	0.17	0.07
	SD	0.02	0.09	0.05	0.14	0.10	0.00		0.03	0.01	0.05	0.00	0.00	0.00
ST_2	Mean	0.74	0.75	1.55	0.83	0.17	0.09	SF_2	0.17	0.45	0.88	0.33	0.33	0.09
	SD	0.03	0.03	0.64	0.144	0.00	0.00		0.02	0.03	0.10	0.14	0.00	0.00
ST_3	Mean	0.22	0.65	0.88	0.50	0.39	0.07	SF_3	0.34	0.59	0.73	0.25	0.17	0.12
	SD	0.02	0.06	0.14	0.25	0.10	0.00		0.021	0.06	0.09	0.00	0.00	0.00
ST_4	Mean	0.33	0.51	0.82	0.42	0.39	0.13	SF_4	0.40	0.59	0.73	0.25	0.17	0.05
	SD	0.02	0.03	0.09	0.14	0.10	0.00		0.02	0.06	0.09	0.00	0.00	0.00
ST_5	Mean	0.30	0.41	0.82	0.58	0.49	0.15	SF_5	0.42	0.47	0.61	0.25	0.33	0.05
	SD	0.02	0.06	0.09	0.14	0.02	0.01		0.03	0.06	0.05	0.00	0.00	0.00
ST_6	Mean	0.22	0.06	0.76	0.58	0.49	0.18	SF_6	0.43	0.57	1.55	0.25	0.17	0.04
	SD	0.02	0.00	0.05	0.14	0.01	0.00		0.12	0.07	0.09	0.00	0.00	0.00
ST_7	Mean	0.12	0.47	0.91	0.42	0.17	0.08	SF_7	0.59	0.37	1.00	0.25	0.33	0.08
	SD	0.02	0.06	0.09	0.14	0.00	0.01		0.02	0.03	0.09	0.00	0.00	0.01
ST_8	Mean	0.26	0.59	1.36	0.25	0.33	0.13	SF_8	0.07	0.59	1.36	0.42	0.17	0.06
	SD	0.03	0.06	0.09	0.00	0.00	0.00		0.02	0.06	0.09	0.14	0.00	0.01

SD- standard deviation; ST- site in town; SF-site in farmland

4.3Soil chemical properties

4.3.1 Levels of soil chemical properties

In this section, the mean values of soil chemical properties are presented in table 4.3. The mean values of chemical properties such as pH were expressed as per the pH scale range of 1-14, organic carbon (OC) as a percentage (%) of oven dry soil and the cation exchange capacity (CEC) in centimoles per kilogram of soil (cmol/kg).The observations from the table of results indicated that the mean soil pH level in Nakuru town soils generally ranged from 6.02 to 6.92. Though there was a slight variation of pH levels from one site to another it was observed that the soils of Nakuru town ranged from slightly acidic (6.1-6.5), to neutral (6.6-7.3) based on pH grading(Charman& Murphy, 2000).

Table 4.6: Mean values of Chemical Properties in Nakuru Town and the surrounding Farmland soils

Nakuru town					**Surrounding farmland**			
Site		**pH**	**% OC**	**CEC (cmol/Kg)**	**Site**	**pH**	**% OC**	**CEC (cmol/Kg)**
ST_1	Mean	6.87	1.42	12.02	SF_1	5.41	2.07	8.02
	SD	0.02	0.01	0.02		0.02	0.07	0.03
ST_2	Mean	6.92	1.26	22.08	SF_2	5.32	2.13	12.02
	SD	0.05	0.02	0.03		0.03	0.02	0.04
ST_3	Mean	6.56	1.85	26.02	SF_3	5.41	2.32	12.03
	SD	0.02	0.02	0.03		0.03	0.03	0.02
ST_4	Mean	6.50	2.27	18.03	SF_4	5.73	1.27	9.96
	SD	0.02	0.02	0.01		0.02	0.02	0.02
ST_5	Mean	6.21	2.26	8.13	SF_5	5.77	0.99	3.94
	SD	0.02	0.02	0.02		0.02	0.03	0.06
ST_6	Mean	6.72	0.84	14.6	SF_6	6.02	0.82	14.02
	SD	0.04	0.02	0.02		0.04	0.03	0.02
ST_7	Mean	6.02	2.32	12.05	SF_7	5.64	1.59	5.97
	SD	0.03	0.02	0.01		0.02	0.02	0.02
ST_8	Mean	6.53	2.02	13.02	SF_8	6.65	0.96	8.01
	SD	0.04	0.03	0.03		0.02	0.01	0.03

% OC- Organic carbon, CEC-Cation exchange capacity, ST- site in Nakuru town, SF- site in Surrounding farmland, and SD- standard deviation

The observation from the study results are in agreement with soil acidity grading made from most research work in other town soils all over the world (Hagan *et al*., 2012). This condition might have risen from increasing human modification of soils whereby the soils become more compacted and less acidic due to the liming effect of concrete, which is more prevalent here as in heavily developed town soils (Hagan *et al*., 2012).

The mean soil pH in the farmland soils surrounding the town ranged from 5.32 to 6.65. Although there were variations observed in pH values from one site to the other, the farmland soils were moderately acidic (Charman& Murphy, 2000). The activities such as farming in terms of soil ameliorants (fertilizers) that acidify the soil could be one of the factors that affect the soil pH here. The use of acidified fertilizers in soil has been known to raise the relative amounts of H^+ ions on the surface charges of the soils and their associations with soil exchangeable colloids hence making the soils acidic which could be the case in this area (Hagan *et al*., 2012; Apak, 2002).

The mean percentage of organic carbon level in town ranged from 0.84% to 2.32%. The observation from the analyzed results showed a slight variation of about one unit in the amount of organic carbon from one site to another, a fact that is based on the nature of activities in these areas. Studies have shown that the amount of organic carbon content in soil is influenced mostly by the amount of organic matter (Rattan *et al*., 2005). The complexity of town soil due to organic material occurring in layers buried by fill, or additions to the soil surface and topsoil from elsewhere could be contributing to variation in the amount of organic carbon, hence easy accumulation of heavy metals in town soil will depend on the amount of organic matter present (Friedel *et al*., 2000).The mean percentage of organic carbon content of the farmland soils surrounding the town as in Table 4-1ranged from 0.82% to 2.32%. Some of the sites had higher values in relation to the other sites which are depend on the activities and the nature of the site soils. The results of the study suggest that organic carbon content may be due to agricultural activities, such as addition of compost manure into the soil as observed in research work from other parts of the world in relation to farmland soils surrounding the town (Hagan *et al*., 2012; Rattan *et al*., 2005; Impellitteri *et al*., 2002).

The mean cation exchange capacity levels for the soils in the Nakuru town as presented in table 6rangedfrom8.13 to 26.02(cmol/ Kg). There was a variation in CEC observed across the sites. Studies worldwide indicate that the range of CEC in the soil is dependent on the amount of organic matter and soil pH whereby CEC will be high where the pH and organic carbon is high (Gasco & Lobo, 2007). High CEC levels are an indication of greater capacity for the soil to hold on to the cations. The relatively high CEC values in town soils suggest that there is less availability of heavy metals in the soil solution since they are adsorbed by soil colloids strongly. The mean cation exchange capacity values in the farmland soils surrounding the town ranged from 3.94 to 14.02 (cmol/ Kg). There was a variation in CEC in that some sites had a higher mean value in relation to the other sites. These variations in CEC among the sites are dependent on amount of organic matter, the soil type and soil pH (Gasco & Lobo, 2007). The CEC mean values for the surrounding farmland soils were relatively low as compared to those of Nakuru town soils which is in line with the pH and percentage organic carbon of the study areas respectively. This suggests that accumulation of heavy metals through adsorption may be low in these soils but easily available in soil solution, which is a potential hazard (Hagan *et al*., 2012).

In summary the mean values of chemical properties showed that the pH values, amounts of organic carbon contents and cation exchange capacity of town soils were generally higher than those of farmland soils surrounding it. The complex nature of town soils which affects its chemical properties could be the contributing factor to the high values observed (Charman& Murphy, 2000). The wearing off of concrete surfaces, use of cement, peeling of paints and many other factors result in the liming of soils and even affecting the organic matter content and the results observed can attest to that (Hagan *et al.,* 2012). The results obtained from this study suggest that heavy metals can accumulate in town soils over time thus resulting in soil pollution (Hagan *et al.,* 2012). In the farmland soils, the results suggest that heavy metals can easily go into soil solution which is an immediate hazard unlike in town soils (Violante *et al.,* 2010). The status of chemical properties in this study suggest that they favors the accumulation of heavy metals in the soils which over time is a potential hazard.

4.3.2Correlation between the chemical properties and total and extractable heavy metal levels in soil

In this section a correlation was done between the chemical properties of soil and total and extractable cadmium, chromium, copper, nickel, lead and zinc metals in Nakuru town and the surrounding farmland soils. The results obtained showed the strength and the direction of the relationship between the chemical properties and the heavy metals in soil.

4.3.2.1 Correlation between the chemical properties and total heavy metal levels in soil

In figure4.1 to figure 4.3,the correlation between chemical properties of the soil and the total cadmium, chromium, copper, nickel, lead and zinc metal levels in Nakuru town and the surrounding farmland soils is presented.

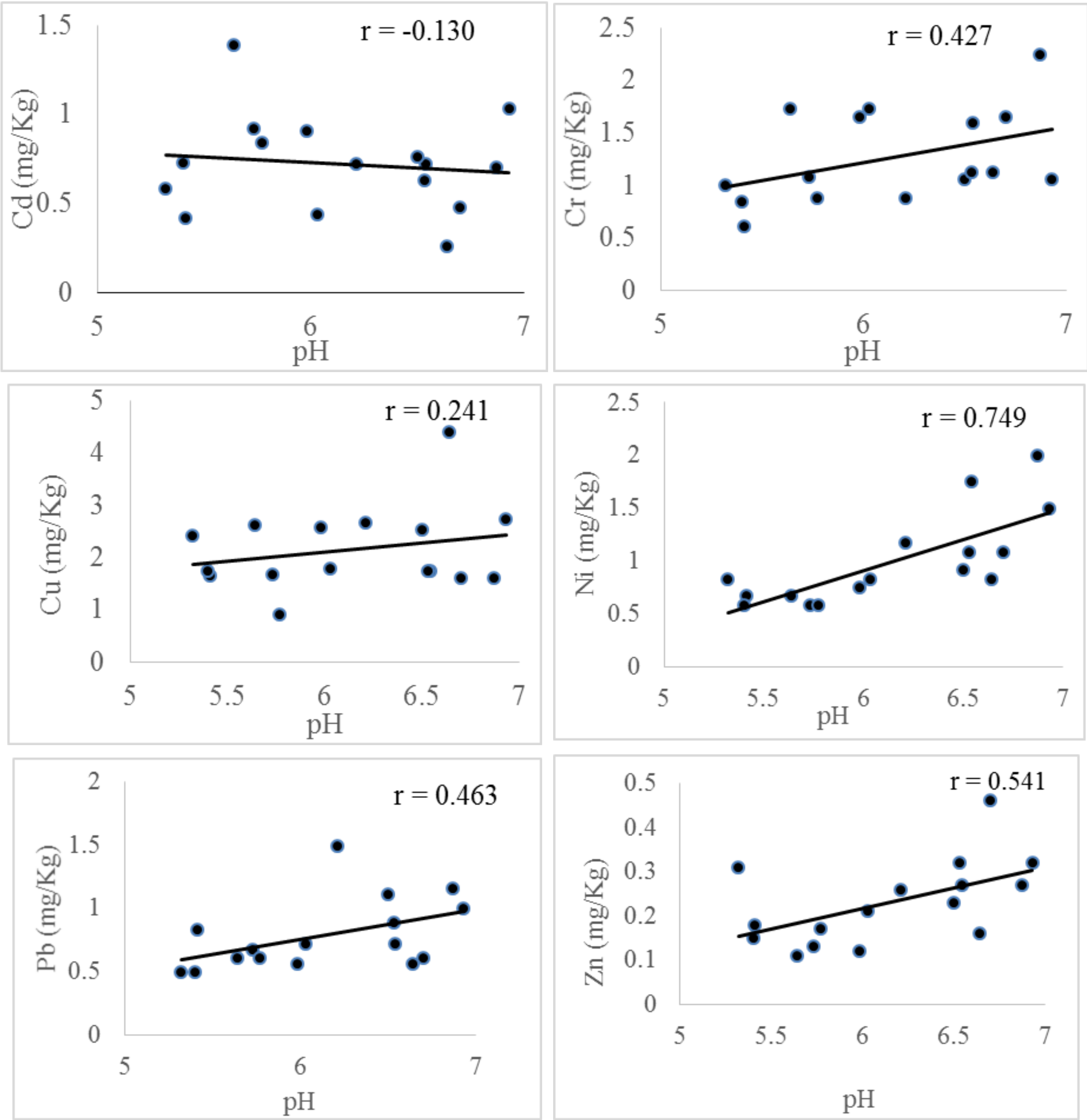

Figure 4.2: Correlation between the pH and total heavy metal levels in soil

In figure 4.1 above, it was observed that total nickel (Ni) had a significant linear positive correlation (r = 0.749) with soil pH while chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn) in Nakuru town and the surrounding farmland soil had an insignificant linear positive (r = 0.426, 0.241, 0.463 and 0.541 respectively) correlation ($P \leq 0.05$).The concentration levels of total cadmium (Cd) showed a linear negative (r = -0.130) correlation with soil pH. Therefore the results suggest that the total heavy metals in these soils is influenced by soil pH but to a small extend due to complicated mechanisms such as adsorption, solubility and mobility of heavy metals in the soil (Kazlauskaitė-Jadzevičė *et al.*, 2014; Hagan *et al.*, 2012).In either case, low or high soil pH will lead to heavy metal toxicity in the soil which is a potential health hazard.

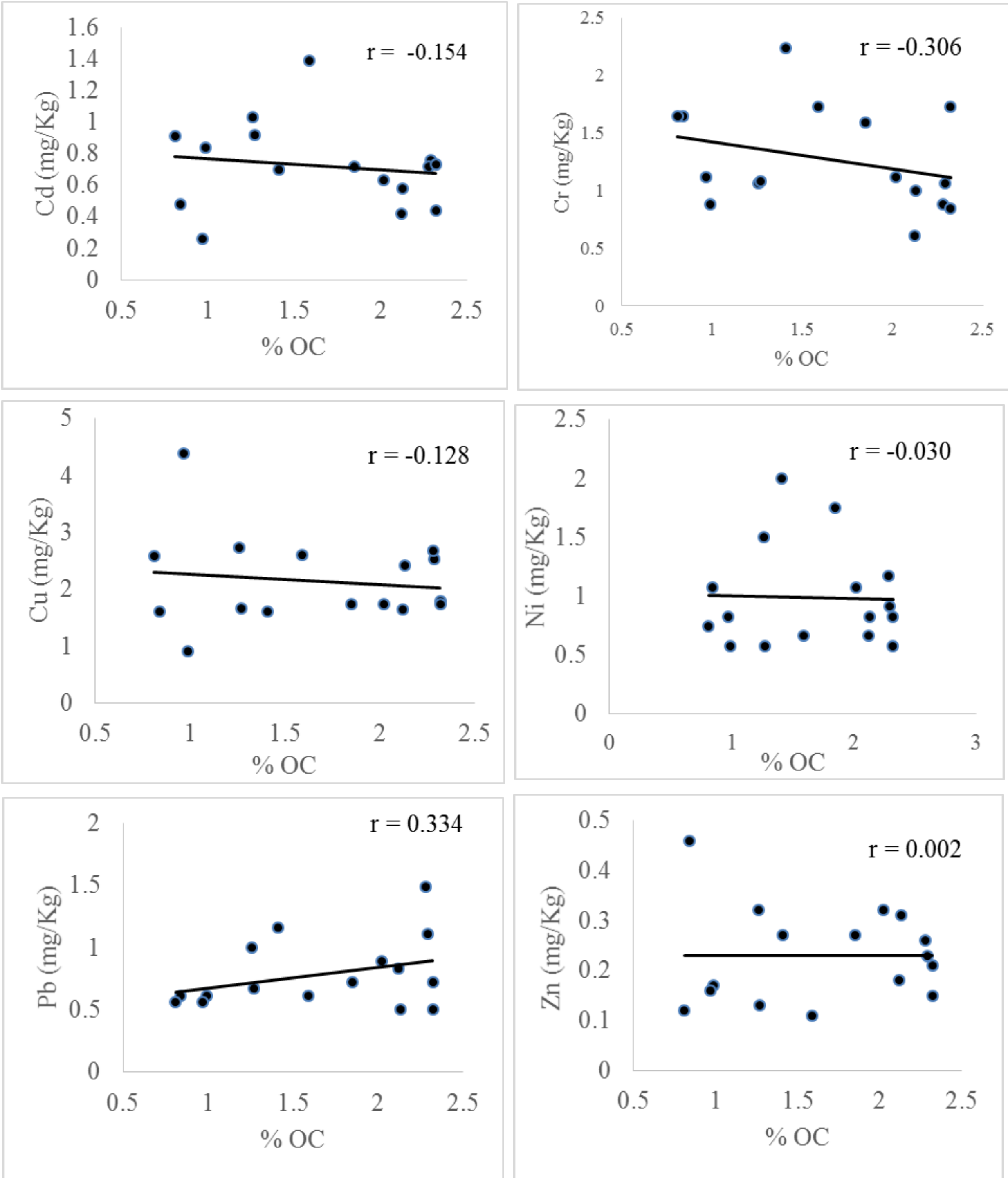

Figure 4.3: Correlation between organic carbon and total heavy metal levels in soil

The correlation observed in figure 4.2 above between total cadmium (Cd), chromium (Cr), copper (Cu) and nickel (Ni) (r = -0.154, -0.306, -0.128 and -0.031 respectively) content and percentage organic carbonin Nakuru town and the surrounding farmland soil was negative and insignificant while that for lead (Pb) and zinc (Zn) (r = 0.334 and 0.002 respectively) was positive and insignificant($P \leq 0.05$). The amount and availability of metals in soils can increase with increasing amounts of organic matter and the association of heavy metals with organic carbon depends on the affinity or complexation and complicated mechanisms due to levels of organic matter that lead to heavy metal retention or accumulation in the soil (Wang & Zhang, 2018; Novara *et al*., 2015; Arenas-Lago *et al*., 2014; Xuefen, 2010)

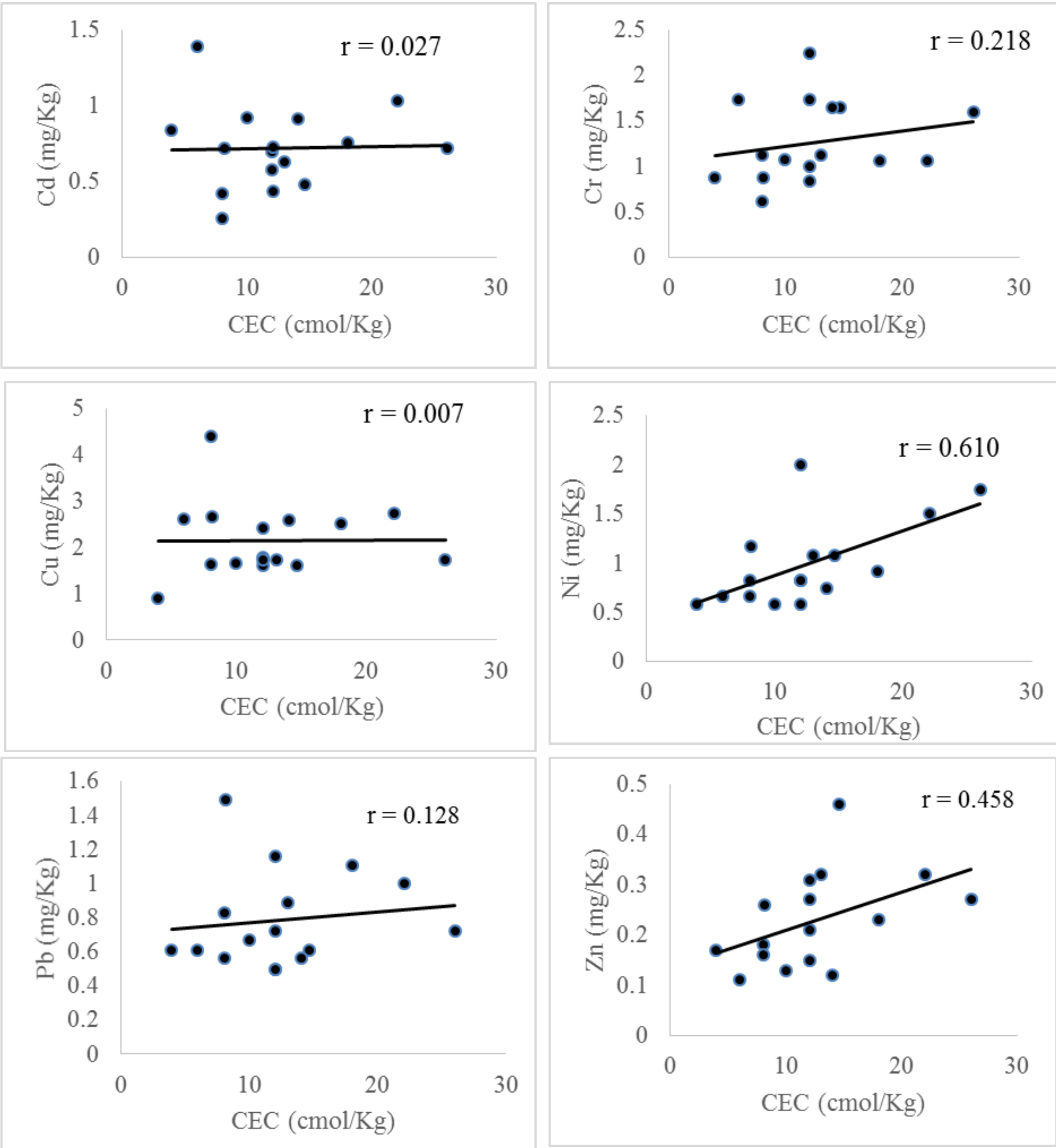

Figure 4.4: Correlation between the cation exchange capacity and total heavy metal levels in soil

In figure 4.3 above, it was observed that the correlation between cation exchange capacity and total cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) (r = 0.027, 0.218, 0.007, 0.610, 0.128 and 0.458 respectively)in Nakuru town and the surrounding farmland soils was positive and insignificant. Cation exchange capacity is dependent on the amount of organic matter in soil because it gives soil the ability to retain cationic metals and therefore as observed from the levels of organic carbon accumulation of heavy metals that leads to toxicity is possible(Chang *et al*., 2014).

In summary, the total metal content of most metals under study whether in Nakuru town or the surrounding farmland soils had a correlation though insignificant with the chemical properties. The adsorption, solubility and mobility of heavy metals in soil are dependent on the state of chemical properties of the soil and therefore due to the above observation, either there will be accumulation or easy release of heavy metals into the environment(Novara *et al*., 2015).

4.3.2.2 Correlation between the chemical properties and extractable heavy metal levels in soil

The correlation between the chemical properties of soil and extractable heavy metal concentration levels in Nakuru town and the surrounding farmland soils are shown in the figures below. In figure 4.4 below, the extractable cadmium Cd)in soils had a negative (r = -0.022) and insignificant ($P \leq 0.05$) correlation with soil pH, while chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) (r = 0.374, 0.585, 0.694, 0.415 and 0.259 respectively) had a positive and insignificant($P \leq 0.05$) correlation with soil pH. The relationship between soil pH and heavy metals was observed but it was weak which suggests that the retention or accumulation of heavy metals is high and not readily available in soil solution(Hagan *et al*., 2012).

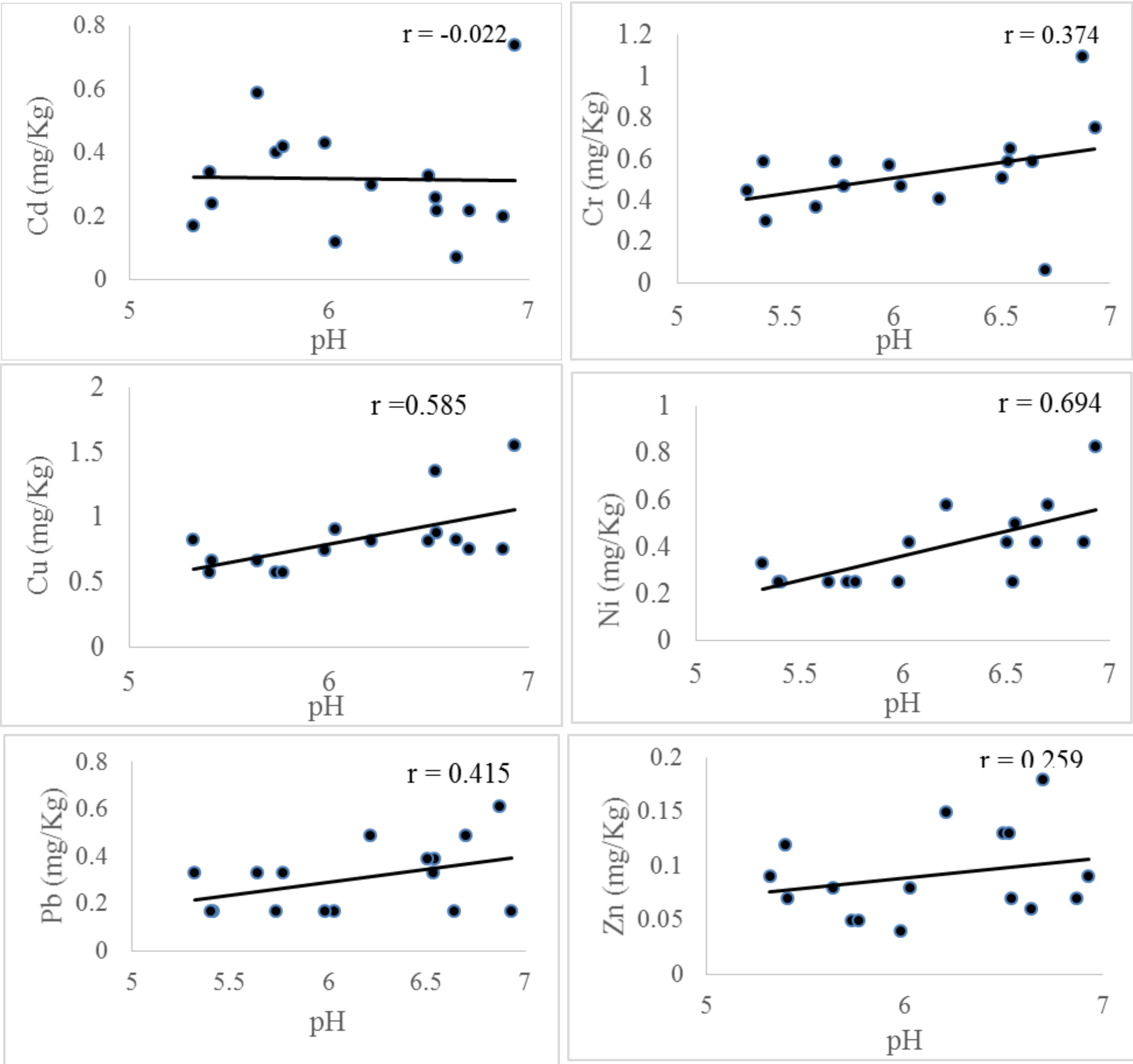

Figure 4.5: Correlation between the pH and extractable heavy metal levels in soil

In figure 4.5 below, the extractable cadmium (Cd), chromium (Cr), and nickel (Ni) in Nakuru town and the surrounding farmland soils had a negative (r = -0.247, -0.041 and -0.097 respectively) and insignificant correlation with organic carbon, while copper (Cu), lead (Pb) and zinc (Zn) had a positive (r = 0.058, 0.027 and 0.334 respectively) and insignificant ($P \leq 0.05$) with organic carbon. Availability of heavy metals depends on percentage of soil organic carbon which is one of the most important components of the soil system and the correlation between the organic carbon and heavy metals as was observed indicates accumulation of heavy metals in soil solution which is a potential health risk in the environment (Novara *et al.*, 2015).

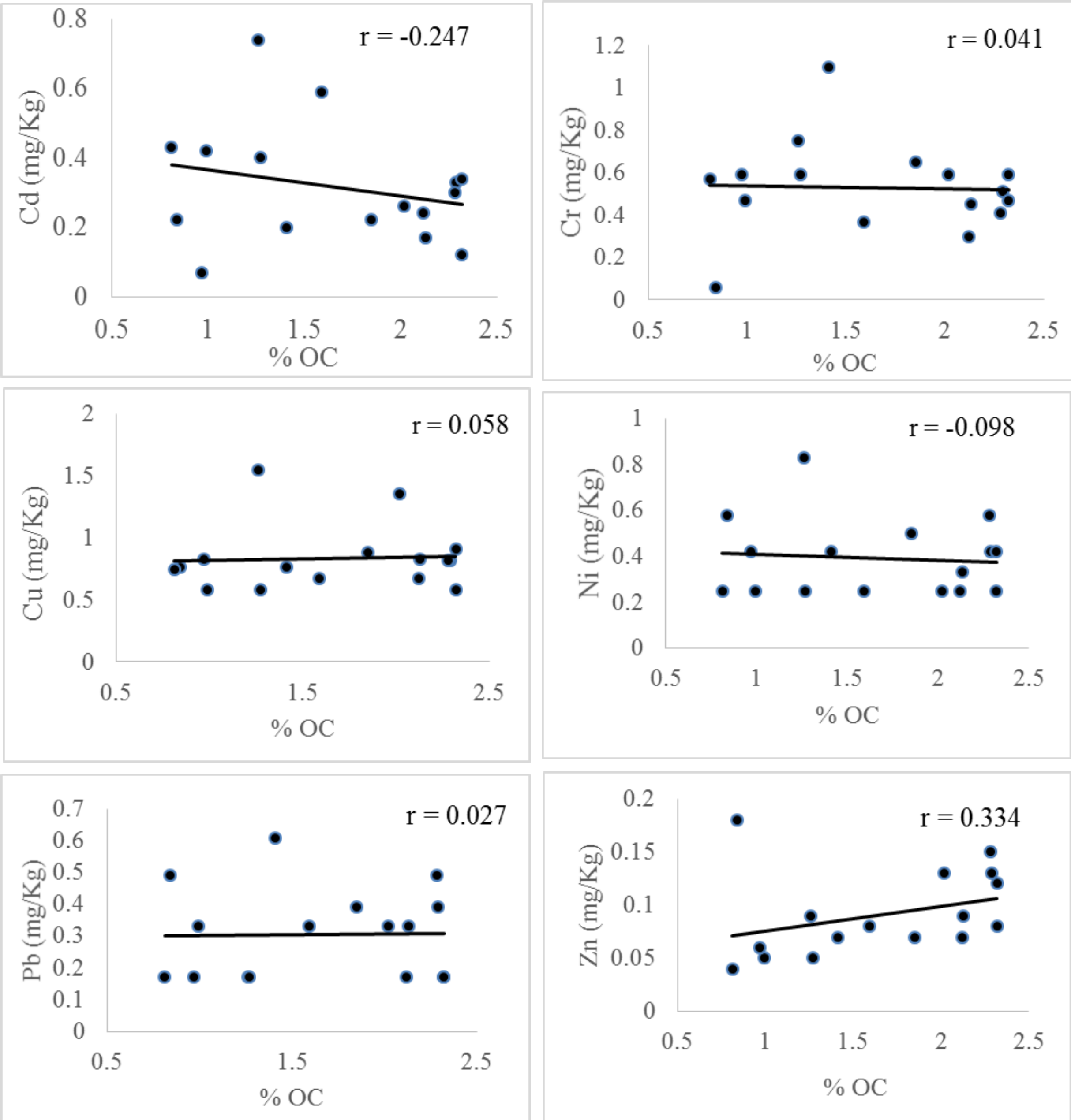

Figure 4.6: Correlation between the percentage organic carbon and extractable heavy metal levels in soil

In figure 4.6 below, it was also observed that cation exchange capacity and extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in soil had a positive ($r = 0.108$, 0.271, 0.533, 0.566, 0.070 and 0.163 respectively) and insignificant ($P \leq 0.05$) correlation. Cation exchange capacity depends on the levels of organic matter and pH in the soil and it suggests that there is a relationship with heavy metals that can lead to accumulation or availability and mobility in the soil (Eeruola, 2015; Ali *et al.*, 2014).

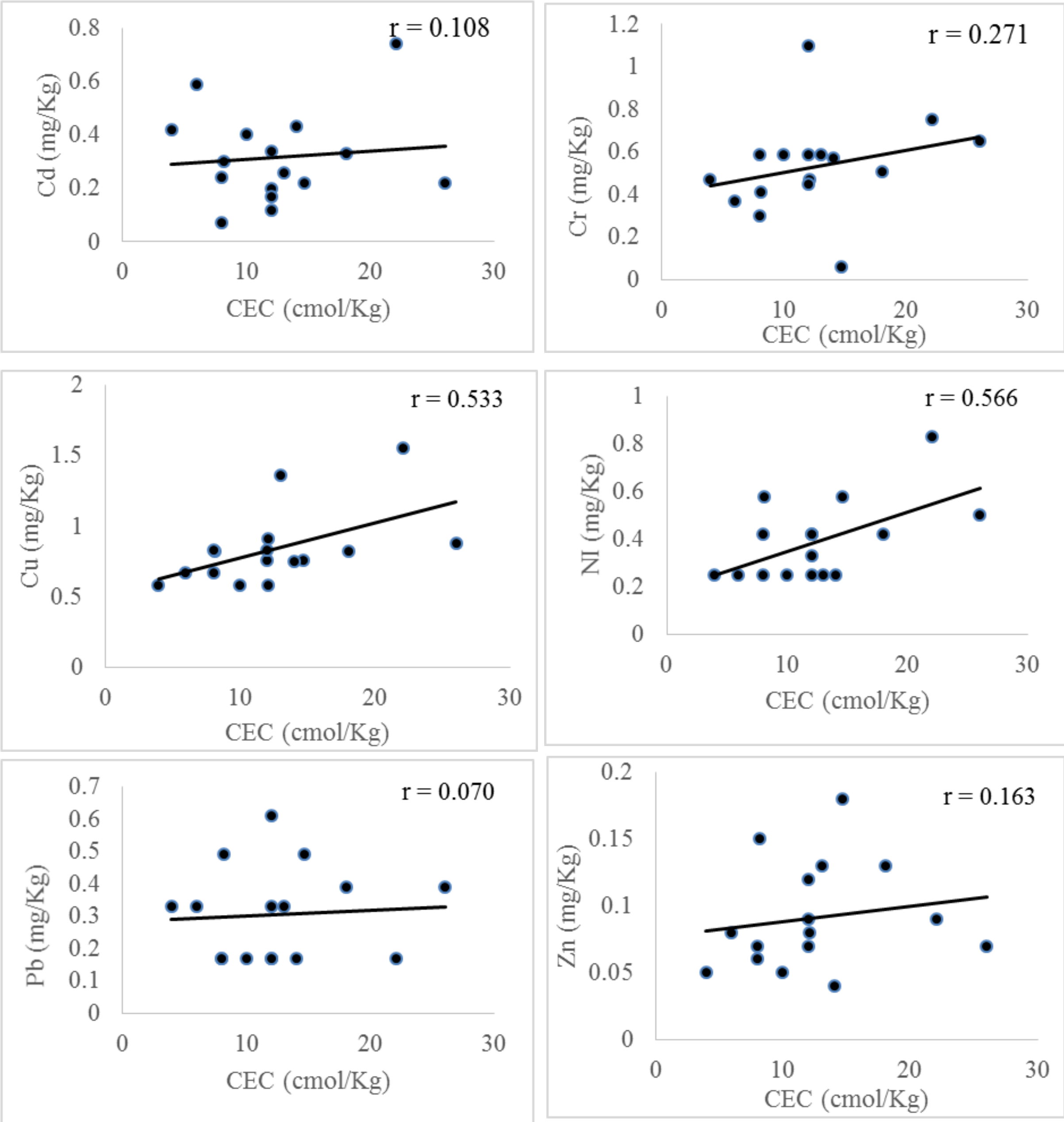

Figure 4.7: Correlation between the cation exchange capacity and extractable heavy metal levels in soil

In summary, the correlation between the chemical properties and the levels of extractable heavy metals in soil in most cases was insignificant though in other few cases it was significant. Where it was insignificant it meant the chemical properties did not influence the availability of heavy metals in soil and therefore take up by plants or leaching and contamination through food chain is low and accumulation is high because of adsorption processes. Where the relationship was significant it meant the heavy metal could go into soil solution easily and therefore potentially risky in terms of toxicity (Chang *et al*., 2014).

4.3.3 The effect of chemical properties on the total and extractable heavy metal in soils

Figure 4.7tofigure 4.12 are regression models graphs that examine the effect of chemical properties on the total and extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)levels in Nakuru town and the surrounding farmland soils.

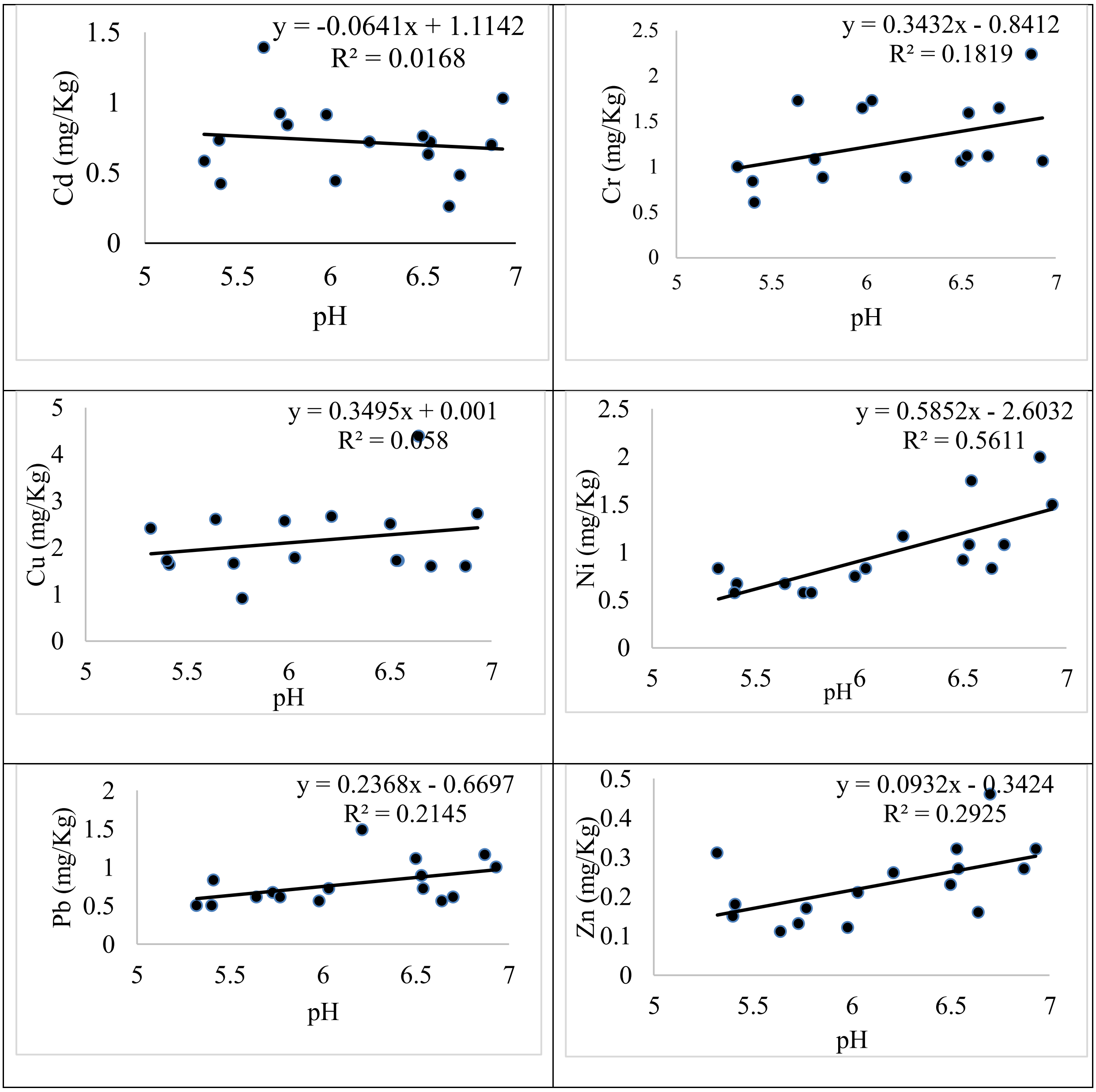

Figure 4.8: The effect of pH on total heavy metal in soils

The observation from figure 4.7 above indicated that soil pH had a positive but an insignificant ($P \leq 0.05$) effect on the total concentration levels of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), and a negative insignificant effect on total cadmium (Cd) concentration levels in Nakuru town and the surrounding farmland soils. The soil pH was shown to contribute to 1.68%, 18.19%, 5.8%, 56.11%, 21.45%, and 29.25% in the variation of total cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively. Soil pH in known to affect the solubility and speciation of heavy metals in soil and this can be observed from this study (Zeng *et al*., 2011;Zhao *et al*., 2010).

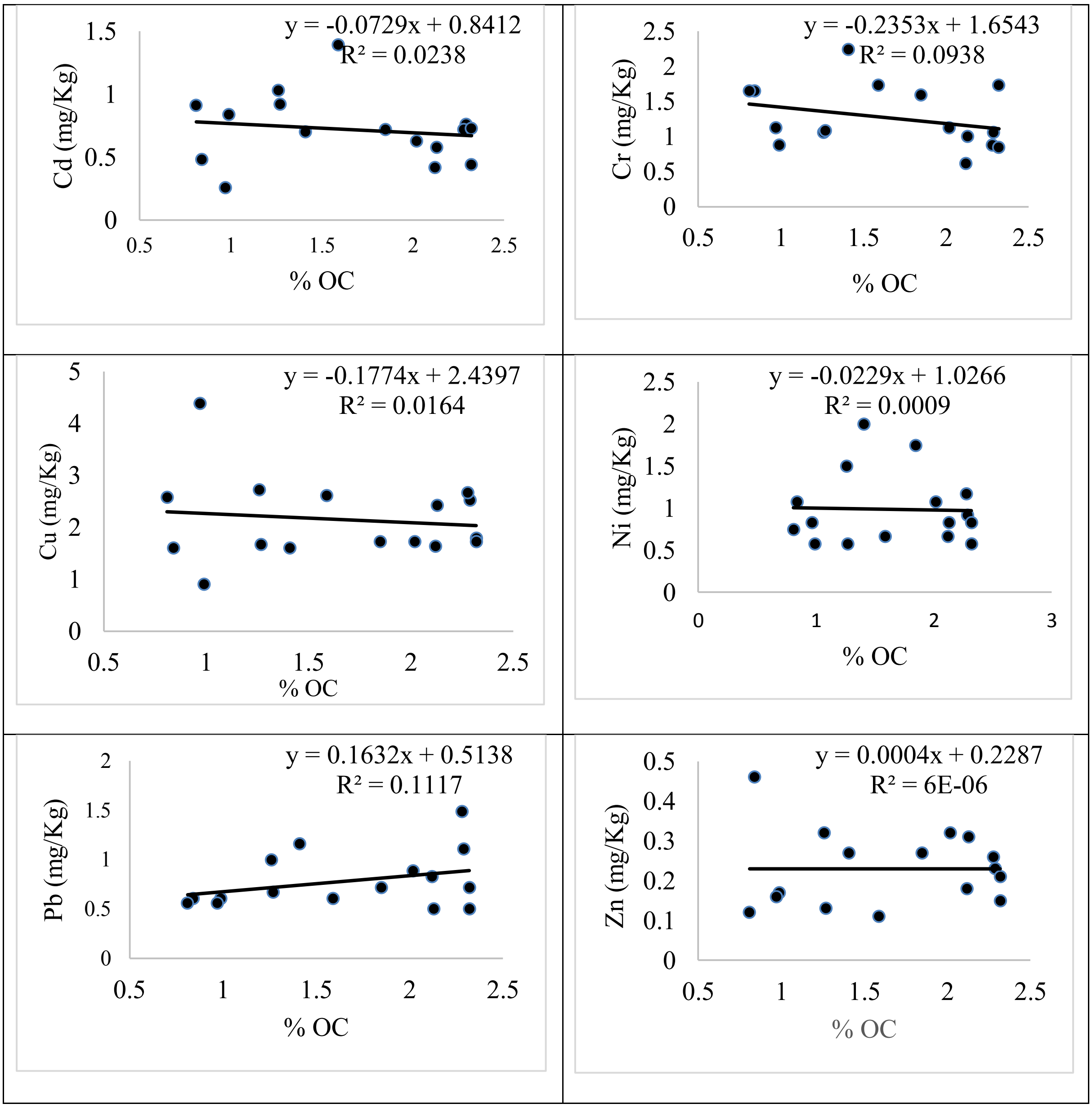

Figure 4.9: The effect of percentage organic carbon on total heavy metal in soils

The observation from figure 4.8 above indicated that organic carbon had a positive but an insignificant ($P \leq 0.05$) effect on the total concentration levels of lead (Pb), and a negative insignificant effect on total cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) concentration levels in Nakuru town and the surrounding farmland soils. The organic carbon in the soil was shown to contribute to 2.38%, 9.38%, 1.64%, 0.09%, 11.17%, and 0%

in the variation of total concentration levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively. Organic carbon affects element mobilization in soil and is known to influence the mobility and availability of soil heavy metals by supplying organic chemicals to the soil solution as synthetic chelates, increasing heavy metal availability (Antoniadis *et al.*,2017)

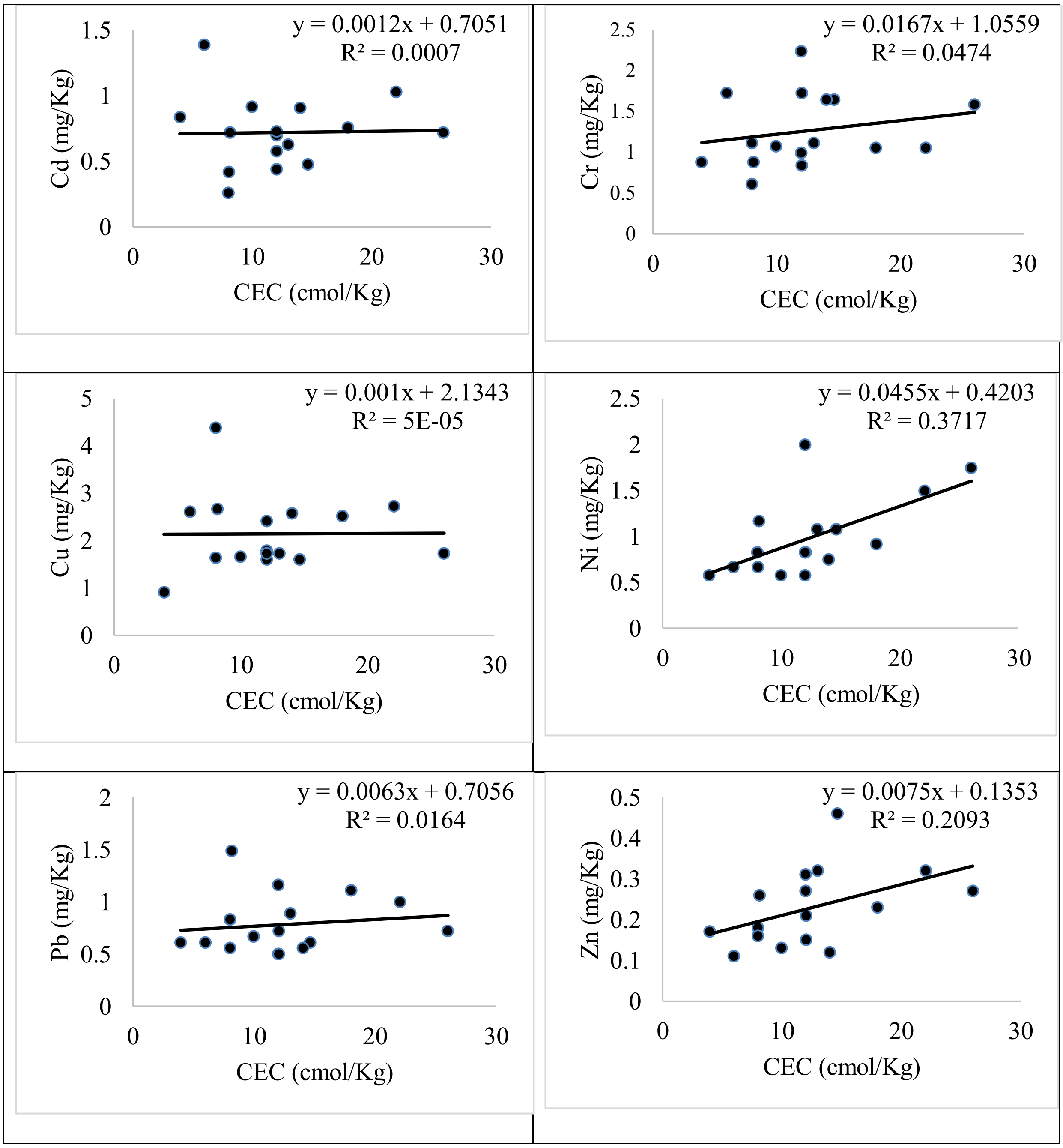

Figure 4.10: The effect of cation exchange capacity on total heavy metal in soils

The observation from figure 4.9 above indicated that cation exchange capacity had a positive but an insignificant ($P \leq 0.05$) effect on the total concentration levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town and the surrounding farmland soils. The organic carbon in the soil was shown to contribute to 0.07%, 4.74%, 0%, 37.17%, 1.64%, and 20.93% in the variation of total concentration levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively. Cation exchange capacity depends on the levels of organic matter and pH in the soil and it suggests that there is a relationship with heavy metals that can lead to accumulation or availability and mobility in the soil(Eeruola *et al*., 2015; Dutta *et al.*, 2011).

In summary, the chemical properties of Nakuru town and the surrounding farmland soils showed both positive and negative insignificant effect on the concentration levels of total selected heavy metals under study. These results suggest that chemical properties may act synergistically to determine the availability or retention of heavy metals and therefore the observation showed that an increase in chemical properties either increased or decreased the availability of heavy metals in soils and therefore increases the accumulation in the soil leading to environmental pollution(McCauley *et al*., 2009).

The observation from figure 4.10 below indicated that soil pH had a positive but an insignificant ($P \leq 0.05$) effect on the extractable concentration levels of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), and a negative insignificant effect on extractable cadmium (Cd) concentration levels in Nakuru town and the surrounding farmland soils. The soil pH was shown to contribute to 0.05%, 13.98%, 34.26%, 48.13%, 17.20%, and 6.69% in the variation of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively.

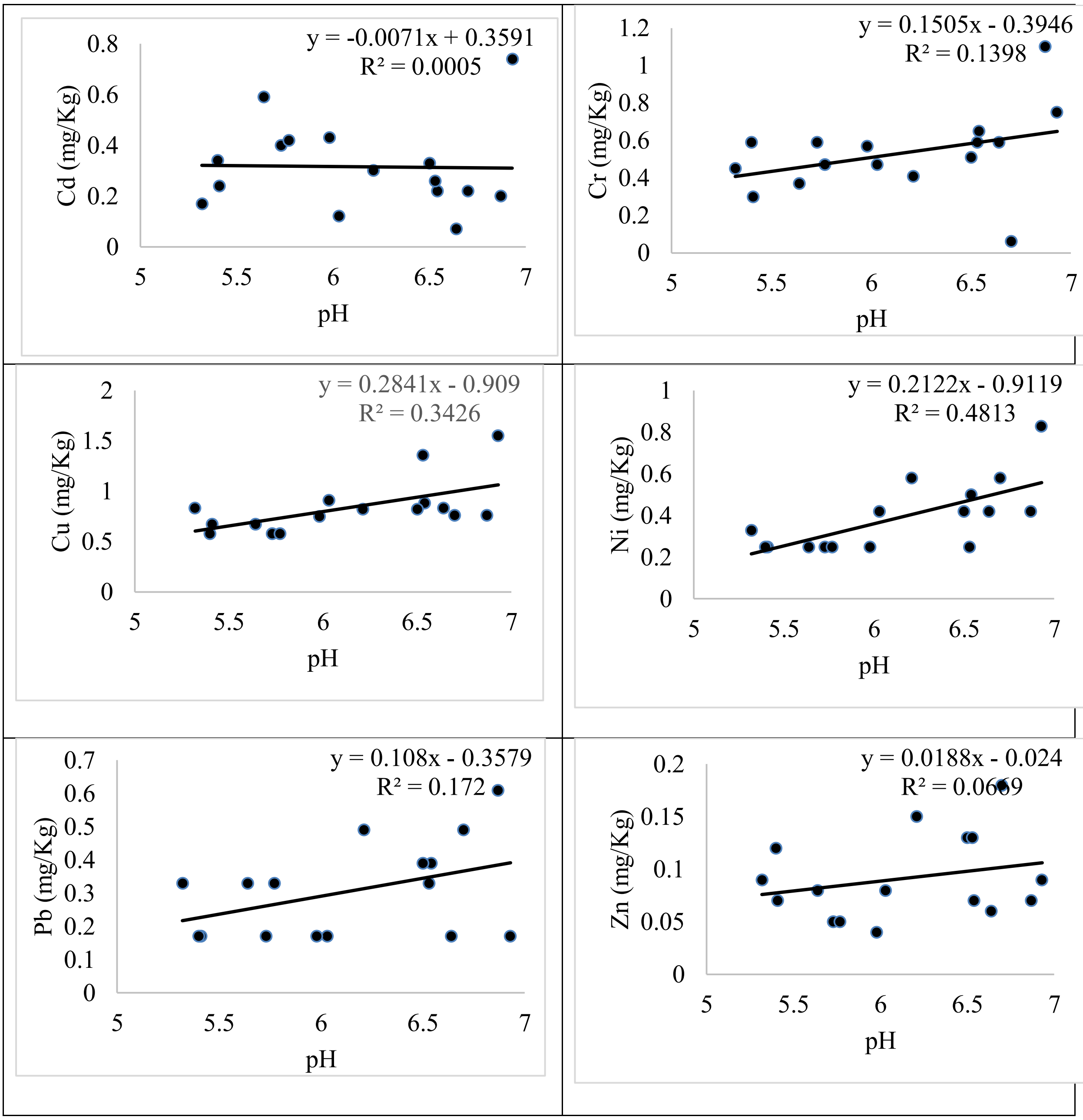

Figure 4.11: The effect of pH on extractable heavy metal in soils

In general, soil pH value has the greatest effect of any single factor on the solubility or retention of metals in soils and pH influences metal sorption through a range of mechanisms (Alloway, 2012).The effect of pH on metal bioavailability varies between different metals which is observed in the above study and this can cause toxicity in the soils at various levels.

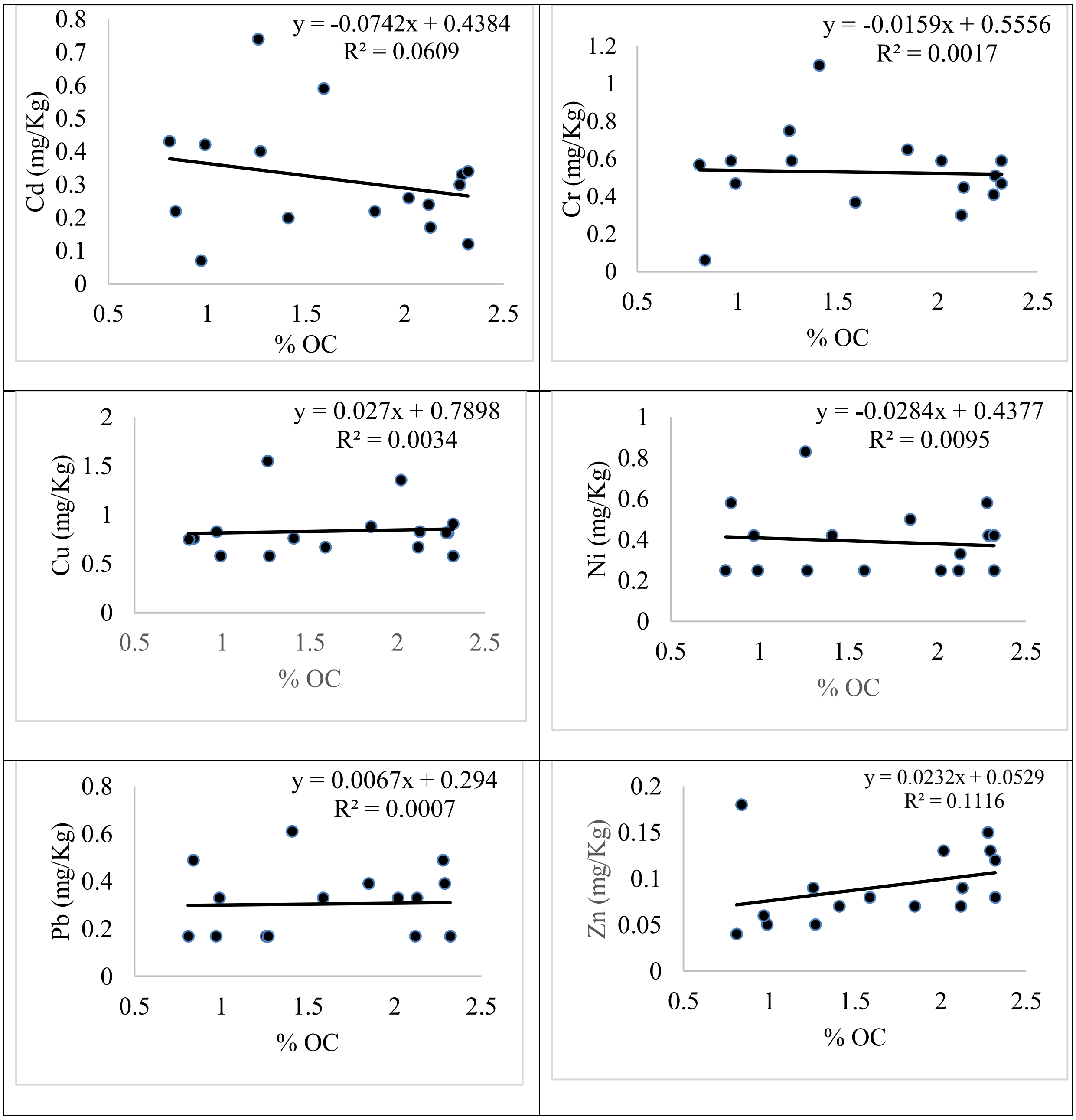

Figure 4.12: The effect of percentage organic carbon on extractable heavy metal in soils

The observation from figure 4.11 above indicated that organic carbon had a positive but an insignificant ($P \leq 0.05$) effect on the concentration levels of extractable copper (Cu) and zinc (Zn), and a negative insignificant effect on extractable cadmium (Cd), chromium (Cr),nickel (Ni), and zinc (Zn) concentration levels in Nakuru town and the surrounding farmland soils. The concentration levels of extractable lead (Pb) was insignificantly affected by organic carbon. The organic carbon in the soil was shown to contribute to 6.09%, 0.17%, 0.34%, 0.95%, 0.07%, and 11.16% in the variation of concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively. Soil organic carbon has been of particular interest in studies of heavy metal sorption by soils, because organic carbon is known to form strong complexes with heavy metals. Organic carbon can reduce or increase the bioavailability of heavy metal in soil through immobilization or mobilization by forming various insoluble or soluble heavy metal-organic complexes and this is observed in the variation effect on the heavy metals under study (ATSDR, 2012; Ghosh & Singh 2005). Therefore there is high chance of heavy metal accumulation in soil when organic carbon is high in soil.

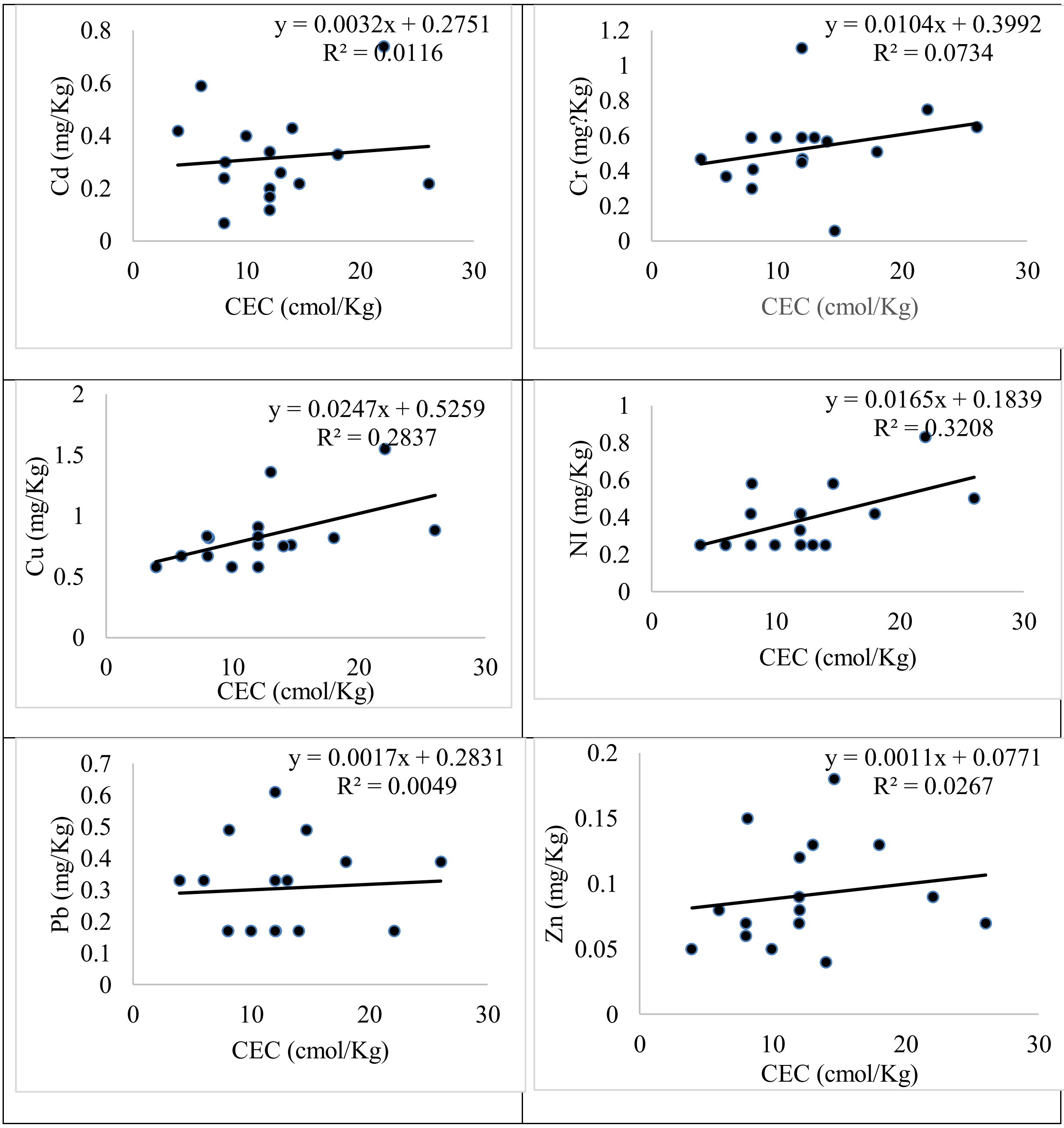

Figure 4.13: The effect of cation exchange capacity on extractable heavy metal in soils

The observation from figure 4.12 above indicated that cation exchange capacity had a positive but an insignificant ($P \leq 0.05$) effect on the concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town and the surrounding farmland soils. The cation exchange capacity in the soil was shown to contribute to 1.16%, 7.34%, 28.37%, 32.08%, 0.49%, and 2.67% in the variation of extractable concentration levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)concentration levels in Nakuru town and the surrounding farmland soils respectively. Cation exchange capacity (CEC) is a dominant factor in heavy metals retention. The capacity of the soils for adsorbing heavy metals is correlated with their cation exchange capacity (CEC) and the greater the cation exchange capacity (CEC) values, the more exchange sites on soil minerals will be available for metal retention and this observation is in agreement with the obtained results(Chen, 2012).

In summary, the chemical properties of Nakuru town and the surrounding farmland soils showed an insignificant positive or negative effect on the concentration levels of the selected extractable heavy metals under study. The observation showed that an increase in chemical properties increased the complexation of heavy metals in soils and therefore increases the accumulation of heavy metals in the soil (ATSDR, 2012).

4.4 Comparison of the town concentration levels with that of the surrounding farmland

Table 4.4examines whether there is any significant mean difference in the total and extractable heavy metal content in Nakuru town and the surrounding farmland soils.

Table 4.7: Comparison of Mean Concentration of Total and extractable Metals in Nakuru town and surrounding farmland soils

		Heavy Metal Means					
Heavy Metal		**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Total	**Town**	0.685	1.416	2.049	1.291	0.963	0.293
	Farmland	0.756	1.114	2.244	0.686	0.605	0.166
	P(T ≤ t) value	0.616	0.179	0.641	0.001*	0.006*	0.003*
Extractable	**Town**	0.299	0.568	0.983	0.500	0.380	0.113
	Farmland	0.333	0.491	0.686	0.281	0.230	0.070
	P(T ≤ t) value	0.710	0.509	0.020*	0.004*	0.030*	0.027*

T ≤ t = t-Test: Two-Sample Assuming Equal Variances, Significance levels: * $P \leq 0.05$

The mean difference values for total Cd content in Nakuru town were 0.685 and 0.756 in the farmland. However, there was no significant mean difference($P \leq 0.05$)in the total cadmium

(Cd) content between Nakuru town and the surrounding farmland soils. The mean difference in cadmium (Cd) content in the two areas could be due to the soil make-up as supported by research work showing that the ground making up urban environments or soils represents a complex mixture of natural parent rock materials and residues from the continued use and reuse of sites for human activity (Campbell *et al*., 2006).

The mean difference values for total chromium(Cr) were 1.416in Nakuru town and 1.114 in the surrounding farmland soils. There was no significant mean difference ($P \leq 0.05$) in the total chromium(Cr)content between Nakuru town and the surrounding farmland soils. The major contributor of Cr apart from the parent rock material is the tanning industry in town and this may be the source of Cr content mean difference (Raini & Kulecho, 2008).

The mean difference values observed for total copper (Cu) content were 2.049 in town and 2.244 in the surrounding farmland soils. It indicated that there was no significant mean difference ($P \leq 0.05$)in total copper (Cu) content between the Nakuru town and the surrounding farmland soils. The nature of the parent rock material from the previous results indicates low Cu content in the area resulting to the observation made (Binggan & Linsheng, 2009).

The mean difference values for total nickel (Ni) observed in Nakuru town and the surrounding farmland soils were 1.291 and 0.686 respectively. There was a significant mean difference ($P \leq 0.05$) in the total nickel(Ni) content between Nakuru town and the surrounding farmland soils. The results suggest that in addition to naturally occurring nickel (Ni), the variation in total nickel (Ni) content may be coming from the wrongly disposed used-up dry cell batteries in soil especially in town (Kabata-Pendias & Mukherjee, 2007).

The mean difference for total lead (Pb) was 0.963 in Nakuru town and 0.605 in the surrounding farmland soils. There was significant mean difference ($P \leq 0.05$) in the total lead (Pb) content between Nakuru town and the surrounding farmland soils. This observation suggests that in addition to contribution from the parent rock material, other sources such as the deposition of lead (Pb) from traffic emissions and waste disposals in Nakuru town could be adding to the total lead (Pb) content in soil (Kabata-Pendias & Mukherjee, 2007).

The mean difference for total zinc (Zn) observed was 0.293 in Nakuru town and 0.166in the surrounding farmland soils. There was a significant mean difference ($P \leq 0.05$) between Nakuru town and the surrounding farmland soils in terms of total zinc (Zn)content. The observation suggested that what was observed is a contribution both from the parent rock material and the anthropogenic activities of the study area (Kabata-Pendias & Mukherjee, 2007).

In summary, there was a mean significant difference in total heavy metal content between the town soils and its surrounding farmland except for cadmium (Cd), chromium (Cr) and copper (Cu). The soil make-up another sources such as the deposition from traffic emissions and waste disposals in town could be the reason for the mean significance difference($P \leq 0.05$) in total metal concentration levels in these two areas (Binggan & Linsheng, 2009;Campbell *et al*., 2006).

The observations in Table 4.4also shows a comparison of mean difference values and the significant mean differences in extractable heavy metals in Nakuru town and the surrounding farmlands. The mean difference values for extractable cadmium (Cd) content were 0.299 in Nakuru town and 0.333 in the surrounding farmland soils. There was no significant mean difference ($P \leq 0.05$) in extractable cadmium (Cd) content between Nakuru town and the surrounding farmland soils. The intensity of competition by other cations and complexation of free metal ion by organic matter could affect Cd availability in both cases thus the nature of observation (Apak, 2002; Martinez & Motto, 2000).

The mean difference values for extractable chromium (Cr) content in Nakuru town soils were 0.568 and 0.491 in the surrounding farmland soils. There was no significant mean difference ($P \leq 0.05$) in extractable chromium (Cr) content between Nakuru town and the surrounding farmland soils. The complexation of free metal ion by organic matter could affect chromium (Cr) availability in both cases(Martinez & Motto, 2000).

The mean difference values for extractable copper (Cu) content observed were 0.983 in Nakuru town and 0.686 in the surrounding farmland soils. There was a significant difference ($P \leq 0.05$) in extractable copper (Cu) content between Nakuru town and the surrounding farmland soils. The complex make-up of town soils and the use of copper (Cu) based products in farms is suggested to be the reason behind the difference in extractable copper (Cu) content (Giuffr'e *et al*., 2012).

The extractable nickel (Ni) mean difference values for Nakuru town and the surrounding farmland soils were 0.500 and 0.281 respectively. There was a significant mean difference($P \leq 0.05$) between the surrounding farmland and Nakuru town soils. Soil acidity and the amount of organic matter in the soil can affect the solubility and hence the availability of nickel (Ni) in soil solution (Kabata-Pendias & Mukherjee, 2007).

The extractable lead (Pb)mean difference values were found to be 0.380 in Nakuru town soils and 0.281 in surrounding farmland soils. There was a significant mean difference($P \leq 0.05$) in extractable lead (Pb) content between the Nakuru town and the surrounding farmland soils. The Nakuru town soil is susceptible to deposition of lead (Pb)from traffic emissions and waste disposals which could contribute to the amount observed (Rosen, 2002).

The extractable zinc (Zn) content mean difference in the surrounding farmland of soils was 0.070 and that of Nakuru town soils was 0.113. There was a significant mean difference($P \leq 0.05$) between the Nakuru town and the surrounding farmland soils in terms of extractable zinc (Zn) content. It is known and even many observation from many researchers, have shown that zinc (Zn) is one of the most abundant metals in everyday use (Nguta *et al*., 2005).

In summary, there was a significant mean difference ($P \leq 0.05$) in concentration levels of extractable Copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) between the Nakuru town soils and those of the surrounding farmland except for cadmium (Cd) and chromium (Cr). Studies globally have shown that the complexation of free metal ion by organic matter, complex make-up of town soils and the intensity of competition by other cations can have an effect on extractable levels of heavy metals hence the mean significance difference between the two areas(Giuff're *et al*., 2012;Martinez & Motto, 2000).

4.5 Effect of extractable heavy metal levels in Nakuru town on those of the surrounding farmlands

The table below examines the effect of extractable heavy metal levels in Nakuru town on those of the surrounding farmlands.

Table 4.8: Effect of Nakuru town extractable heavy metal levels on those of the surrounding farmlands

		Farmland Soils											
		Cd		Cr		Cu		Ni		Pb		Zn	
		Coeff	P-value	Coeff	P-value	Coeff	P-value	Coeff	P-value	Coeff	P-value	Coeff	P-value
Nakuru Town Soils	Constant	0.865	0.140	1.748	0.064	-0.241	0.831	0.031	0.069	-0.408	0.641	0.242	0.173
	Cd	-0.554	0.262	1.755	0.080	-0.789	0.607	-0.064	0.042*	-0.907	0.463	0.121	0.387
	Cr	0.389	0.285	-1.532	0.071	0.307	0.782	-0.021	0.100	0.775	0.432	-0.204	0.197
	Cu	-0.718	0.079	0.164	0.293	0.500	0.438	0.282	0.004*	-0.108	0.778	0.064	0.287
	Ni	0.597	0.193	-1.460	0.074	0.508	0.660	-0.138	0.015*	0.903	0.385	-0.073	0.462
	Pb	-1.410	0.107	1.592	0.087	-0.133	0.924	0.142	0.019*	-1.182	0.378	0.233	0.219
	Zn	3.159	0.241	-8.430	0.086	2.616	0.730	0.170	0.083	5.092	0.439	-1.845	0.149
	R-Square	0.996		0.992		0.786		0.999		0.813		0.980	

Coeff = Coefficient, Significance levels: * $P \leq 0.05$

In Table 4.5, the results indicated that the concentration levels of extractable chromium (Cr),nickel (Ni) and zinc (Zn) in the Nakuru town soils had an insignificant($P \leq 0.05$) positive effect on extractable cadmium (Cd) levels in farmland soils. The extractable levels of Nakuru town cadmium (Cd), copper (Cu) and lead (Pb) had an insignificant($P \leq 0.05$) negative effect on the levels of extractable cadmium (Cd) in the surrounding farmland soils. In overall, the concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town soils insignificantly ($P \leq 0.05$) affects the concentration levels of cadmium (Cd) in the surrounding farmland soils and contributes to 99.6 % in the variation of extractable cadmium (Cd) levels in the surrounding farmland soils.

The concentration levels of extractable chromium (Cr), nickel (Ni) and zinc (Zn)in Nakuru town soils had an insignificant ($P \leq 0.05$) negative effect on the concentration levels of extractable chromium of the surrounding farmland soil. The concentration levels of extractable cadmium (Cd), copper (Cu) and lead (Pb) in Nakuru town soils had an insignificant($P \leq 0.05$) positive effect on the concentration levels of chromium in the surrounding farmland soils. In overall, the concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town soils had an insignificant($P \leq 0.05$) effect on the concentration levels of chromium in the surrounding farmland soils and contributed to 99.2 % in the variation of extractable levels of chromium in the surrounding farmland soils.

According to the observed results the concentration levels of extractable chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) in Nakuru town soils had a positive insignificant($P \leq 0.05$) effect on extractable levels of coppering the surrounding farmland soils. The concentration levels of extractable cadmium (Cd) and lead (Pb)in Nakuru town soils had a negative insignificant($P \leq 0.05$) effect on the concentration levels of extractable copper in the surrounding farmland soils. In overall, the concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)in Nakuru town soils did have a significant ($P \leq 0.05$) effect on the concentration levels of extractable copper in the surrounding farmland soils and contributed to 78.6 % in the variation levels of extractable copper in the surrounding farmland soils.

The concentration levels of extractable copper (Cu) and lead (Pb)in Nakuru town soils showed a significantly ($P \leq 0.05$) positive effect on extractable levels of nickel in the surrounding farmland soils. The extractable levels of zinc (Zn) in Nakuru town soils had an insignificant ($P \leq 0.05$) positive effect on the concentration levels of extractable nickel (Ni)in the surrounding farmland soils. The concentrations levels of extractable cadmium (Cd) and nickel (Ni) in Nakuru town soils had a negative significant($P \leq 0.05$) effect while extractable levels of chromium (Cr) had an insignificant ($P \leq 0.05$) negative effect on the concentration levels of extractable nickel in the surrounding farmland soils. The concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town soils contributed to 99.9 % in the variation of extractable nickel levels in the surrounding farmland soils.

The concentrations levels of extractable chromium (Cr), nickel (Ni) and zinc (Zn) in Nakuru town soils showed an insignificant ($P \leq 0.05$) positive effect on the concentration levels of extractable lead (Pb) in the surrounding farmland soils. The concentration levels of extractable cadmium (Cd), copper (Cu) and lead (Pb) in Nakuru town soils had an insignificant ($P \leq 0.05$) negative effect on the concentration levels of extractable lead in the surrounding farmland soils. The concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town had an insignificant ($P \leq 0.05$) effect on the concentration of lead (Pb)in the surrounding farmland soils and contributed to 81.3 % in the variation of extractable lead (Pb)levels in the surrounding farmland soils.

The concentrations levels of extractable chromium (Cr), nickel (Ni) and zinc (Zn) in Nakuru town soils showed an insignificant ($P \leq 0.05$) negative effect on the concentration levels of extractable zinc (Zn) in the surrounding farmland soils. The concentration levels of extractable cadmium (Cd), copper (Cu) and lead (Pb) in Nakuru town soils had no significant effect on the concentration levels of extractable zinc in the surrounding farmland soils. The concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in Nakuru town soils had an insignificant($P \leq 0.05$)effect on the concentration levels of zinc (Zn) in the surrounding farmland soils and contributed to 98 % in the variation of extractable Zn levels in the surrounding farmland soils.

In summary, from the observations above, extractable levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) of Nakuru town soils except chromium (Cr) and nickel (Ni) had a positive or negative effect on the concentration levels of extractable cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) of the surrounding farmland soils. Therefore it suggests that the factors such as water runoffs from town, wastewater from the municipal and industrial activities, sewage sludge as soil fertilizers and atmospheric depositions on farmland could be the reason for the observed results (Binggan & Linsheng, 2010; Chen *et al*., 2007; Nguta & Guma, 2004).The interaction of metals with macronutrients such as nitrogen and phosphorus in the soil induces metal deficiency resulting in low solubility of metal ion and this can cause the variation in extractable heavy metals as observed in this study (Alkorta *et al*., 2004).The characterization by a strong spatial heterogeneity resulting from the various inputs of exogenous materials and the mixing of original soil materials can also affect the levels of extractable heavy metals in soils (Giuffr'e *et al*., 2012).

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

In conclusion of this study the heavy metals (cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn))under investigation were present in Nakuru town and the surrounding farmlands soils. The findings indicated that the concentration levels were low compared to the stipulated maximum permissible levels and therefore they were insignificant. It can be concluded based on these findings that Nakuru town and the surrounding farmland soils are not at risk of contamination and heavy metal toxicity is minimal.

The chemical properties as observed showed that Nakuru town soils ranged from slightly acidic to neutral while in the surrounding farmland, the soils were moderately acidic. The soils of Nakuru town were higher in soil pH due to human modification of soils whereby the soils become more compacted and less acidic due to the liming effect of concrete. The amount of organic carbon and the status of cation exchange capacity as observed in Nakuru town and the surrounding farmland soils were moderate. The observation indicated that the chemical properties of the soil could facilitate the accumulation of heavy metals over time which can lead to soil pollution which is a potential health risk. Although a relationship (positive to negative) between the chemical properties and the levels of heavy metals in Nakuru town and the surrounding farmland soils was observed, the influence was insignificant and therefore the environment was not threaten.

In general, Nakuru town soils showed a higher heavy metal loading level than the farmland surrounding it and the total heavy metal content in Nakuru town soils was significant. The difference in concentration levels was possibly the traffic emissions (vehicle exhaust particles, tire wear particles, weathered street surface particles, brake lining wear particles), industrial emissions (power plants, coal combustion, metallurgical industry, auto repair shop, chemical plant, etc.), domestic emissions, weathering of buildings and pavement surfaces and atmospheric deposition in Nakuru town soils. This was an indication that monitoring and assessment of heavy metal input into the environment was required.

The observations from relationships of extractable heavy metals of Nakuru town soils and those of the surrounding farmland was generally significant due to runoffs, wastewaters from industrial processes and atmospheric or aerial deposition that contain heavy metals into the farmlands. Although the levels of heavy metals observed from the study were low, there is a potential danger of heavy metal accumulation and toxicity in the farmlands.

5.2 Recommendations

The following recommendations were made from this study

i. Studies to establish a comprehensive geochemical database for Nakuru town and its surrounding farmland is needed which will help in assessing and monitoring the status of the area in terms of heavy metal pollution or contamination.
ii. Studies on the sources of heavy metal pollution within Nakuru town and the surrounding farmlands are needed in order to mitigate any further heavy metal input into the soil
iii. There is need to expand studies on the relationships between all physicochemical properties of the soil and heavy metals to help understand distribution, retention, solubility and mobility of heavy metals in this area of study.

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Appendix 1: Key Data Analysis Outputs

Output1

Out The CORR Procedure

15 Variables: pH OC CEC Cdx Cdy Crx Cry Cux Cuy Nix Niy Pbx Pby Znx Zny

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
pH	48	6.13792	0.53729	294.62000	5.29000	6.96000
OC	48	1.65146	0.55480	79.27000	0.80000	2.34000
CEC	48	12.49208	5.62257	599.62000	3.90000	26.04000
Cdx	48	0.72021	0.27015	34.57000	0.23000	1.43000
Cdy	48	0.31104	0.16928	14.93000	0.05000	0.77000
Crx	48	1.19604	0.44932	57.41000	0.54000	2.29000
Cry	48	0.54021	0.21804	25.93000	0.05000	1.20000
Cux	48	2.13646	0.80010	102.55000	0.91000	4.46000
Cuy	48	0.93229	0.30332	44.75000	0.51000	1.63000
Nix	48	0.96604	0.48731	46.37000	0.45000	2.15000
Niy	48	0.48000	0.23132	23.04000	0.18000	1.21000
Pbx	48	0.74729	0.24934	35.87000	0.43000	1.45000
Pby	48	0.31333	0.14144	15.04000	0.13000	0.67000
Znx	48	0.22917	0.09308	11.00000	0.10000	0.47000
Zny	48	0.12917	0.20457	6.20000	0.04000	1.30000

Output 2

Pearson Correlation Coefficients, N = 48
Prob > |r| under H0: Rho=0

	pH	OC	CEC	Cdx	Cdy	Crx	Cry	Cux
pH	1.00000	-0.32071	0.52459	-0.12886	-0.01560	0.58026	0.34385	0.28250
		0.0263	0.0001	0.3827	0.9162	<.0001	0.0167	0.0517
OC	-0.32071	1.00000	0.09506	-0.14146	-0.20475	-0.28875	-0.04221	-0.35166
	0.0263		0.5204	0.3375	0.1627	0.0465	0.7757	0.0142
CEC	0.52459	0.09506	1.00000	0.02684	0.09949	0.39770	0.25409	-0.11425
	0.0001	0.5204		0.8563	0.5011	0.0051	0.0814	0.4394
Cdx	-0.12886	-0.14146	0.02684	1.00000	0.85201	-0.26360	0.11410	-0.31174
	0.3827	0.3375	0.8563		<.0001	0.0702	0.4400	0.0310
Cdy	-0.01560	-0.20475	0.09949	0.85201	1.00000	-0.40091	0.04974	-0.41026

	0.9162	0.1627	0.5011	<.0001		0.0047	0.7371	0.0038
Crx	0.58026	-0.28875	0.39770	-0.26360	-0.40091	1.00000	0.44033	0.23828
	<.0001	0.0465	0.0051	0.0702	0.0047		0.0017	0.1029

Output 3

The CORR Procedure

Pearson Correlation Coefficients, N = 48
Prob > |r| under H0: Rho=0

	pH	OC	CEC	Cdx	Cdy	Crx	Cry	Cux
Cry	0.34385	-0.04221	0.25409	0.11410	0.04974	0.44033	1.00000	0.07492
	0.0167	0.7757	0.0814	0.4400	0.7371	0.0017		0.6128
Cux	0.28250	-0.35166	-0.11425	-0.31174	-0.41026	0.23828	0.07492	1.00000
	0.0517	0.0142	0.4394	0.0310	0.0038	0.1029	0.6128	
Cuy	0.27454	-0.20743	0.23135	0.04658	0.06638	0.11061	0.23255	0.52504
	0.0590	0.1572	0.1136	0.7533	0.6540	0.4542	0.1117	0.0001
Nix	0.69340	-0.05977	0.63609	0.11102	0.05878	0.58237	0.57030	0.01379
	<.0001	0.6866	<.0001	0.4525	0.6915	<.0001	<.0001	0.9259
Niy	0.45026	-0.16118	0.33616	0.30169	0.44407	-0.05242	-0.00759	0.19432
	0.0013	0.2738	0.0195	0.0372	0.0016	0.7234	0.9592	0.1857
Pbx	0.57825	0.13781	0.09122	-0.25449	-0.29477	0.44991	0.36609	0.05436
	<.0001	0.3503	0.5375	0.0809	0.0420	0.0013	0.0105	0.7136
Pby	0.29115	0.22208	0.04416	0.01518	-0.13477	0.24588	0.17549	-0.11575
	0.0447	0.1292	0.7657	0.9184	0.3611	0.0921	0.2329	0.4334
Znx	0.52966	0.03748	0.46388	-0.30885	-0.17090	0.34140	-0.16784	0.03876
	0.0001	0.8003	0.0009	0.0327	0.2455	0.0176	0.2542	0.7937
Zny	0.25182	0.09269	0.17088	0.04740	0.10834	-0.04061	0.01856	-0.01716
	0.0842	0.5309	0.2456	0.7491	0.4636	0.7840	0.9004	0.9078

Output 4

Pearson Correlation Coefficients, N = 48
Prob > |r| under H0: Rho=0

	Cuy	Nix	Niy	Pbx	Pby	Znx	Zny
pH	0.27454	0.69340	0.45026	0.57825	0.29115	0.52966	0.25182

	0.0590	<.0001	0.0013	<.0001	0.0447	0.0001	0.0842
OC	-0.20743	-0.05977	-0.16118	0.13781	0.22208	0.03748	0.09269
	0.1572	0.6866	0.2738	0.3503	0.1292	0.8003	0.5309
CEC	0.23135	0.63609	0.33616	0.09122	0.04416	0.46388	0.17088
	0.1136	<.0001	0.0195	0.5375	0.7657	0.0009	0.2456
Cdx	0.04658	0.11102	0.30169	-0.25449	0.01518	-0.30885	0.04740
	0.7533	0.4525	0.0372	0.0809	0.9184	0.0327	0.7491

Output 5

The GLM Procedure

Class Level Information

Class	Levels	Values
Location	2	Farm Town
Site	8	1 2 3 4 5 6 7 8
Rep	3	1 2 3

Number of observations 48

Nakuru

The GLM Procedure

Dependent Variable: pH

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	13.55485417	0.79734436	1793.46	<.0001
Error	30	0.01333750	0.00044458		
Corrected Total	47	13.56819167			

R-Square	Coeff Var	Root MSE	pH Mean
0.999017	0.343523	0.021085	6.137917

Source	DF	Type I SS	Mean Square	F Value	Pr > F

Rep	2	0.01152917	0.00576458	12.97	<.0001
Location(Site)	15	13.54332500	0.90288833	2030.86	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Rep	2	0.01152917	0.00576458	12.97	<.0001
Location(Site)	15	13.54332500	0.90288833	2030.86	<.0001

Output 6

The GLM Procedure

Dependent Variable: OC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	14.45454375	0.85026728	2116.12	<.0001
Error	30	0.01205417	0.00040181		
Corrected Total	47	14.46659792			

R-Square	Coeff Var	Root MSE	OC Mean
0.999167	1.213781	0.020045	1.651458

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Rep	2	0.00007917	0.00003958	0.10	0.9065
Location(Site)	15	14.45446458	0.96363097	2398.25	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Rep	2	0.00007917	0.00003958	0.10	0.9065
Location(Site)	15	14.45446458	0.96363097	2398.25	<.0001

Nakuru

Output 7

The GLM Procedure

Dependent Variable: CEC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	1485.757171	87.397481	39355.9	<.0001
Error	30	0.066621	0.002221		
Corrected Total	47	1485.823792			

R-Square	Coeff Var	Root MSE	CEC Mean
0.999955	0.377233	0.047124	12.49208

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Rep	2	0.001179	0.000590	0.27	0.7686
Location (Site)	15	1485.755992	99.050399	44603.3	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Rep	2	0.001179	0.000590	0.27	0.7686
Location (Site)	15	1485.755992	99.050399	44603.3	<.0001

Appendix 2: Publication Abstract

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LEVELS OF HEAVY METALS IN NAKURU TOWN, KENYA AND THE SURROUNDING FARMLAND SOILS

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Abstract

Purpose: The purpose of the study was to investigate the concentration levels of total and extractable selected heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), and Zinc (Zn) in soils of Nakuru town and the surrounding farmlands. In addition, soil chemical properties such as pH, % organic carbon and cation exchange capacity were also determined.

Methodology: The study area was divided into two sampling sections, the town area being within 2 Km from the town center and the surrounding farmlands being those beyond 2 Km from the town center. From each section eight (8) sampling sites were established based on their activities and the samples collected in triplicate. The samples were air-dried, crushed, sieved, and stored at ambient temperature before analysis. The soil suspension was used to measure pH (potentiometric method) and the cation exchange capacity (ammonium acetate method), and the organic carbon was determined using oxidation-titration method. The potentially extractable heavy metals were extracted using EDTA method and total heavy metals extracted using digestion method and the concentration estimated using an atomic absorption spectrophotometer. The data obtained from the experimental analysis were subjected to descriptive statistics to get the mean concentration levels.

Results: The results obtained for total content in town soils were, 0.44-1.03 mg/Kg Cd, 0.88-2.24 mg/Kg Cr, 1.61-2.73 mg/Kg Cu, 0.92-2.00 mg/Kg Ni, 0.61-1.49 mg/Kg Pb and 0.21-0.46 mg/Kg Zn while the total content in the surrounding farmland were, 0.26-1.39 mg/kg Cd, 0.59-1.65 mg/Kg Cr, 0.91-4.39 mg/Kg Cu, 0.58-0.83 mg/Kg Ni, 0.50-0.83mg/Kg Pb and 0.11-0.31 mg/Kg Zn indicating higher content in town soils. Extractable heavy metal content levels in town soils were 0.12-0.74 mg/Kg Cd, 0.06-1.10 mg/Kg Cr, 0.76-1.55 mg/Kg Cu, 0.25-0.83 mg/Kg Ni, 0.17-0.11 mg/Kg Pb and 0.07-0.18 mg/Kg Zn, and those from the surrounding farmland soils were, 0.07-0.59 mg/Kg Cd, 0.30-0.59 mg/Kg Cr, 0.61-1.55 mg/Kg Cu, 0.25-0.42 mg/Kg Ni, 0.17-0.33 mg/Kg Pb and 0.04-0.12 mg/Kg Zn indicating the same trend as for the total content. The chemical properties such as pH, % organic carbon and cation exchange capacity in town soils were 6.02-6.92, 0.84-2.3 and 8.13-26 respectively while in surrounding farmland, 5.3-6.65, 0.81-2.3 and 3.9-14 respectively.

Unique contribution to theory, practice and policy: There is need for environmental quality assessment of heavy metal-contaminated soils to disclose the effects of human activities on the environment which will provide the critical information for sustainable development of the limited

Appendix 3: Research Permit

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OFFICE OF THE DIRECTOR GRADUATE SCHOOL

Ref:.............SM11/2293/08....   Date:......8th June, 2011

Mr. Simion Kipruto Misoi,
Department of Chemistry,
Egerton University,
P. O. Box 536,
EGERTON.

Dear Mr. Misoi,

RE: CORRECTED PROPOSAL

This is to acknowledge receipt of two copies of your corrected proposal, entitled **"Determination of Heavy Metal Levels in Nakuru Town and the Surro Farmland Soils".**

You are now at liberty to commence your fieldwork.

Thank you.

Yours sincerely,

Prof. M.A. Okiror,
DIRECTOR, BOARD OF POSTGRADUATE STUDIES

c.c. Supervisors

MAO/qma