VARIATION OF LEVELS OF SELECTED METAL POLLUTANTS WITH DEPTH IN PETROLEUM CONTAMINATED SOILS AND THEIR IMPLICATIONS

BY

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DECLARATION

Declaration by the candidate

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This thesis has been submitted for examination with our approval as the university supervisors

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DEDICATION

To my parents Jacob and Anne, to my wife Edith and daughter Shirley for their support.

ABSTRACT

Human activities have led to increased metal contamination in the environment, among these is petroleum spillage. Effect of petroleum spillage on the Fe, Pb, Ni, Zn, Cd and Cu levels extracted from petroleum-contaminated soils was investigated at different seasons and soil depth. Forty soil samples were collected from four sites (S_1- S_4) in both wet and dry seasons at 15 cm depth intervals from 0 - 75 cm and kept in clean polythene bags. Stones and plant fragments were immediately removed by passing the samples through a < 0.2 mm sieve and then crushed to fine powder using mortar and pestle. The concentration of metals were analyzed using atomic absorption spectrophotometer. For S_1 at shallower depth (0-30 cm), the levels were 3.95 ppm, 0.51 ppm, 0.05 ppm, 0.20 ppm and 0.08 ppm for Fe, Zn, Ni, Pb and Cu, respectively. At deeper depth (45-75 cm), the corresponding values were 3.31 ppm, 0.55 ppm, 0.55 ppm, 0.27 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu. As for S_2 at shallower depth, the values were 4.83 ppm, 0.72 ppm, 1.00 ppm, 0.47 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu, respectively. At deeper depth, the respective values were 3.20 ppm, 0.82 ppm, 0.42 ppm, 0.42 ppm, and 0.00 ppm for Fe, Zn, Ni, Pb and Cu. Site 3 at shallower depth had respective values 4.67 ppm, 0.69 ppm, 0.57 ppm, 0.44 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu, whereas at deeper depth, the corresponding values were 3.48 ppm, 0.67 ppm, 0.70 ppm, 0.11 ppm and 0.13 ppm. For S_4 at shallower depth, the levels were 4.72 ppm, 0.68 ppm, 0.54 ppm, 0.47 ppm and 0.11 ppm for Fe, Zn, Ni, Pb and Cu, respectively. At deeper depth, the levels were 4.00 ppm, 0.78 ppm, 0.64 ppm, 0.45 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu, sequentially using one way ANOVA. There were insignificant statistical differences between the four sites with $p > 0.05$. Levels of Fe and Pb decreased with depth, whereas Zn and Ni levels increased with depth. Copper and Cd had little vertical movements. Variation of Ni with depth was statistically significant ($p = 0.01098$, $F = 3.83$) unlike Zn, Pb, Cu, Fe and Cd and this could threaten ground water. Wet season (April 2013) had higher mean metal levels than the dry season (Dec 2012) and this was significant for Ni, Zn and Cu ($p < 0.05$, $t > 1$, $r > 0.1$). A significant correlation ($p <0.05$, $r > 0.5$) existed between mean metal levels and petroleum spillage signifying spillage of petroleum elevates metal levels in soil. Mean Pb levels were above the crude oil quality group (COQG) permissible limits at sites S_2, S_3 and S_4. Regular assessment of elements from petroleum should provide a framework for control. Heavy metal permissible limits should be included in assessment of petroleum quality by the Kenya Bureau of Standards.

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ANOVA: Analysis of Variance.
ATSDR: Agency for toxic substances and drug registry.
CDC: Centers for Disease Control and prevention.
COQG: Crude Oil Quality Group.
DES: New Hampshire Department of Environmental Services.
DTIE: Division of Technology, Industry and Economics.
EHC: Environmental Health Criteria
FAAS: Flame atomic absorption spectroscopy.
FDA: Food and Drug Administration.
ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometer.
KPC: Kenya Pipeline Company.
RPC (K) ltd: Raiply Company Kenya limited.
SEP: Sequential extraction Procedure
TPHCWG:Total petroleum hydrocarbon Criteria working group
UNEP: United Nations Environmental Programme.
WHO: World Health Organization.
ZDTPs: Zinc dialkyl dithiophosphates.
ZDTPPs: Zinc dithiophosphates.

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CHAPTER ONE

INTRODUCTION

1.1 Background information

Soils receive potentially toxic elements from both natural and a wide range of anthropogenic sources, including the weathering of primary minerals, mining, fossil fuel combustion, the metallurgical, car batteries and chemical industries and waste disposal. The application of domestic and industrial sludge to soils for agricultural and disposal purposes is often the most environmentally acceptable and economical method (Tokalioglu *et al*., 2001).

There is concern that heavy metals and other contaminants in sludge accumulate in the soil, reducing its quality for agriculture *inter alia*. Indeed, many potential contaminants are necessary for agricultural production but become hazardous when they occur in excess in the soil. The ash contained in heavy fuel oil contains the (inorganic) metallic content, other non-combustibles and solid contaminants. The inorganic ash content consists of metals such as V, Ni, Fe, Na, K or Ca (American Bureau of Shipping, 2001).

Heavy fuel oils with high trace metal (oil soluble) concentrations of V, Ni and Pb can cause accelerated fouling and tenacious deposits, performance reductions and corrosion. To compensate for the effects of these trace metals on exhaust valves and turbo charger blading, a chemical inhibitor can be mixed with the heavy fuel oil to modify the chemical and physical properties of the resulting ash, which is the source of previously mentioned deposits and fouling (American Bureau of Shipping, 2001).

The Crude Oil Quality Group (COQG) is dedicated to the belief that maintaining the integrity and consistency of the refining characteristics of petroleum products is critical to petroleum quality and environmental safety. According to COQG, the commonly used industry standards of gravity and sulphur do not adequately define petroleum quality and should be expanded to include other characteristics like the allowable metal levels. It is opposed to concealed modification of petroleum properties through alteration and blending of different petroleum streams that have different properties, which traditionally has been done by pipeline companies without informing shippers. Among these, blending petroleum oil with gasoline, butanes and chlorinated hydrocarbons has led to contamination of petroleum. Chlorinated hydrocarbons are capable of decomposing into HCl which causes corrosion, forming pits in the heat exchangers. Pipeline companies can control contamination of their oil by minimizing blending and alterations. Alteration is normally done through addition of salt water and augmentation of production chemicals which contain heavy metals like Pb, Zn, Fe, Ni, Mn and Cu (COQG, 2004).

A comprehensive knowledge of the interactions between the trace elements and the soil matrix is required in order to judge their environmental impact. The depth profile studies of heavy metal concentration in soils provide information on mobility and sorption of the selected cations in soil. Since the behaviour of the elements in a soil-water-plant system depends on their forms, the determination of trace metals in soils is often performed by single or sequential extraction (Tokalioglu *et al*., 2001).

1.2 Historical cause leading to the problem

Petroleum products have continuously been released to the environment through accidents, as managed releases, or as unintended by-products of industrial, commercial or private actions. Indiscriminate disposal of industrial, petrochemical, agrochemical and mining wastes along road highways has led to accumulation of toxic elements. Agbogidi and Eruotor (2012) investigated morphological changes of *Jatropha curcas* seedlings due to petroleum spillage and found that heavy metals accumulated with time in oil contaminated sites. Levels of Fe, Zn, Cd, Cu, Mn, Pb, Cr and Ni were found to be significantly higher in seedlings growing in areas of petroleum spillage relative to the uncontaminated subplots. Similar findings were reported by Essiett *et al.,* (2010) who compared metal levels in plants grown in areas of oil spillage *vis a vis* those grown in uncontaminated soils. Through weathering processes and water run-offs, these elements have found their way into arable lands leading to extensive contamination of lands (TPHCWG, 1997). In a related investigation, Onojake and Okonkwo (2011) found that oil polluted soils had higher metal levels than the soils unpolluted with petroleum.

In water, oil forms an insoluble layer that *anoxiates* aquatic organisms. Although microbial degradation breaks down petrochemicals into simple inert products, the presence of toxic heavy metals in soils appears to hinder organic biodegradation through impacting both the physiology and ecology of organic degrading microorganisms. This passivates microbial degradation processes (Sandrin and Maier, 2003). There are reported cases of plants wilting in areas of oil spillage, death of animals and even events of rapid fires. Thus petrochemicals need to be broken down into simple environmentally innocuous products by these microorganisms. Metal transport in soil can result into pollution of ground water. Levels of pH and organic matter plays a role towards enhancing metal mobility and retention. In a study by Shirdast *et al.,* (2010), it was found that Fe and Mn levels decreased with depth but Pb, Cd and Ni fluctuated with depth, and these differences were attributed to fluctuation in organic matter content. Similar findings were made by Behbahaninia *et al.,* (2008), Carroll *et al.,* (2002), Chunhacherdchai *et al.,* (2011), Aniket (2011) and Ogboi (2012) affirming that metal levels vary with depth.

1.3 Problem statement

Persons in the vicinity of hazardous waste sites are likely to be exposed to used heavy petroleum through the skin, surface run – offs and ingestion of foods containing bioaccumulated heavy metals (Hestone, 1990).

Regulations and restrictions on use of heavy metals are less comprehensive or less well enforced in Kenya. This has resulted in some of the health and environmental risks, local and regional, which accompany the use, management (including collection, storage, recycling and treatment) and disposal of products containing metals. These hazardous disposal practices include open burning and indiscriminate dumping in sensitive ecosystems such as rivers and wetlands (UNEP DTIE, 2008).

Developing countries are daunted with the challenge of demands for new and used products containing toxic metals, including petroleum oils and car batteries. Unfortunately these countries lack the capacity to manage and dispose of hazardous metals in these products in an environmentally sound manner at the end of their life. Besides, developing societies are oblivious to the contributions of petroleum oil to the total heavy metal content that finds its way to the sewers and arable soils (UNEP DTIE, 2008).

Maintenance of good soil quality is of prime importance for sustainable agriculture. Soil biology is a significant component of soil quality and microorganisms play vital roles in soil fertility and primary production through organic matter decomposition and nutrient cycling. When some stress factors such as temperature, extreme pH or chemical pollution is imposed on a natural environment, soil biota can be affected as well as the ecological processes that these microorganisms regulate (Oliveira and Pampulha, 2006). Metal toxicity is most commonly ascribed to the tight binding of metal ions to sulphydryl (–SH) groups of enzymes essential for microbial metabolism (Sandrin and Maier, 2003).

It is on this premise that sources, distribution and bioavailability of these heavy metals has increasingly become areas of research interest especially in the developing world where the use of heavy metals has not been strictly checked. There is a need to develop and improve exposure assessments and use and release inventories, especially for developing countries (UNEP DTIE, 2008).

1.4 Justification of the study

Despite the potential dangers of heavy metals on soil, water and biota, more emphasis has been put on metal levels in water, soil, sediments and speciation. Findings have established that petroleum spillage elevates metal levels in soils and plants grown in oil polluted sites relative to unpolluted sites. Majority of the Kenyan public overlook the fact that continuous spillage of petroleum products on soil can contribute to accumulation of heavy metals in soils as well as the elevation of metal pollutants in soil due to seasonal variations. Metal transport in soil can lead to ground water contamination or lead to increased bioavailability of toxic metals to roots of plants. The selected study area near the KPC depot experiences regular petroleum spillage. From the study, both the public and industry will benefit from accurate and timely environmental toxicological data generated. Ultimately, the findings can be incorporated into health risk assessments of petroleum contaminated soils.

1.5 Objectives

1.5.1 General objective

The main objective of this study was to collect soil samples; contaminated with oil spills and uncontaminated as well as to determine the relative metal pollutant levels.

1.5.2 Specific Objectives

1. To determine the levels of Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} in both petroleum - contaminated and uncontaminated sites.
2. To determine the variation of metals Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} with depth.
3. To compare the mean levels of Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} to the Crude Oil Quality Group (COQG) acceptable levels.
4. To compare variation of Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} levels with seasonal changes.

1.6 Hypotheses

1. Petroleum spillage does not increase metal levels in soils.
2. There is no variation of metal levels with depth of soil.
3. Mean levels do not exceed the COQG permissible standards.
4. Seasonal change has no impact on metal levels.

1.7 Study area

This study was done near the Kenya Pipeline Company, Eldoret. Eldoret town is located in Uasin Gishu county in the Western region of Kenya and borders Kakamega and Trans Nzoia counties to the west, Nandi county to the south and Elgeyo Marakwet and Nakuru counties to the east. It experiences two rainy seasons, namely long and short rains. Long rains start from March to May. The short rains start in August and end in October. The dry spell starts from December to February. Figure 1.1 below presents the location of the four (4) study sites. The control point, site one (S_1) was 50 metres from experimental sites S_2, S_3 and S_4. The experimental sites S_2, S_3 and S_4 were 20 metres apart.

Fig 1.1: A map of the study area showing sites one to four (S_1 - S_4)

(Google Maps, 2014)

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, the state of knowledge about the elements under study is explored. Their occurrence, mobility in soil, effects of petroleum spillage and seasonal changes on metal levels is discussed. The chapter also reviews some of the methods used to extract metals from soils. These include wet digestion method applied, sequential extraction procedures and ion exchange extraction methods.

2.2 Sequential extraction procedures, ion exchange methods and the wet digestion method

Determination of metals in soil can be accomplished via wet digestion, ion exchange resins and sequential extraction procedures (SEP), the latter is still controversial. Sequential extraction procedure and cation exchangers are generally accepted but are plagued by limitations discussed below (Amanda and Weindorf, 2009).

2.2.1 Cation exchange method

Vogel (1988), explain that a cation exchanger consists of a polymeric anion resin with active anions. The most widely used cation resin consists of sulphonated styrene-divinylbenzene co - polymer. The sulphonate group associates to the exchangeable cations say B^+. Cation exchange occurs when the resin is brought into contact with a solution containing cations C^+, the latter exchanges with the former. Size of ions, magnitude of charges on ions, degree of cross linkage in the resin determines selectivity of the exchanger. The main limitation of ion exchangers is their decreasing efficiency with time, poor resolving efficiency under low pH and the need to remove suspended solids before separation. The wet digestion method is a relatively simpler metal extraction method.

2.2.2 SEP

The theory behind SEP is that the most mobile metals are removed in the first fraction and continue in order of decreasing mobility. All SEPs facilitate fractionation. The fractions are: exchangeable carbonate bound, Fe and Mn oxide bound, organic matter bound and residual. The main limitations of SEPs include: non-selectivity of the reagents and the tendency for metals to redistribute among the remaining fractions during the extraction process by sorbing to the freshly exposed surfaces (Amanda and Weindorf, 2009).

2.2.3 Laboratory method of Soil and Plant analysis (The wet digestion method)

The total available metal is measured in a digest obtained by treating soil samples with H_2O_2 + H_2SO_4 + Se + salicylic acid digestion mixture (Okalebo *et al*., 2002). Sulphuric acid destroys the organic matter to release chemisorbed metals. Selenium catalyzes oxidation of soil samples using H_2O_2 as the oxidant in acidic media. The main advantages of this method are: only single digestion is applied to solvate all metal ions, there are no metal losses via volatilization and the method is also quicker.

2.3 Elements and their health effects

2.3.1 Iron

Iron is the second most abundant metal in the earth's crust after Al, hence Fe accounts for about 5%. Elemental Fe is rarely found in nature, as the Fe^{2+} and Fe^{3+} readily combine with oxygen - and sulphur - containing compounds to form oxides, hydroxides, carbonates and sulphides. Iron is most commonly found in nature in the form of its oxides (Sheffer, 2005).

Possible sources of Fe in crude oil samples could also stem from drilling equipments and machineries which are predominantly made of Fe. Relatively high levels of Ni and V have been reported to be associated with most crude oil samples obtained from marine environment. This is expected for marine source rocks where there is an abundant input of Fe porphyrin – precursor chlorophylls to the organic matter derived from algae and bacteria (Udeme and Udoessien, 2012).

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for Iron depend on age, sex, physiological status, and Fe bioavailability and range from about 10 to 50 mg/day. The average lethal dose of Fe is 200–250 mg/kg of body weight, but death has occurred following the ingestion of doses as low as 40 mg/kg of body weight. Autopsies have shown hemorrhagic necrosis (death of cells) and sloughing of areas of mucosa in the stomach with extension into the sub mucosa. Chronic Fe overload results primarily from a genetic disorder (haemochromatosis) characterized by increased Fe absorption and from diseases that require frequent blood transfusions. Adults have often taken Fe supplements for extended periods without deleterious effects and an intake of 0.4–1.0 mg/kg of body weight per day is unlikely to cause adverse effects in healthy persons (Sheffer, 2005).

The metals present in the crude oils are mostly Ni(II) porphyrins, V(II) porphyrins and non-porphyrins. Other metal ions reported from crude oils; include Fe, Pb, Cu, Mg, Na, Mo, Zn, Cd, Ti, Cr, Co, Sb, U, Al, Sn, Ba, Ga, Ag and As (Khuhawar and Lanjwani, 1996).

2.3.2 Lead

Because the demand for high octane gasoline (petrol) is increasing, countries face the added challenge of controlling the quality of their gasoline because Pb is often added to gasoline after it has left the refinery to increase the octane rating (Von Storch *et al*., 2003). The major sources of Pb in the environment, of significance to living organisms, arise from Pb mining and the refining and smelting of Pb and other metals.

In terrestrial soils, Pb accumulates mostly in the humus layer, compounded in metallo-organic complexes. Particles found in fluvial and marine systems with high Pb concentrations are mostly not as a result of atmospheric deposition but of fluvial discharge sources instead. The major dispersive, non-recoverable use of Pb is in the manufacture and application of alkyl Pb fuel additives (Von Storch *et al.*, 2003).

From a mass balance point of view, the transport and distribution of Pb from stationary or mobile sources is mainly via air. Although large amounts are probably also discharged into soil and water, Pb tends to localize near the points of such discharge. Lead discharged into the air over areas of high traffic density falls out mainly within the immediate metropolitan zone. The fraction that remains in air (about 20%, based on very limited data) is widely dispersed (Von Storch *et al.*, 2003).

The German Human Biomonitoring Commission offered in 1995 categories for the risk associated with different Pb concentrations in human blood. Levels above 250 mg Pb/L were considered dangerous for adults, requiring medical analysis. For children and embryos, levels of 150 mg Pb/L were classified as critical (Von Storch *et al.*, 2003).

In the United States some researchers are convinced that the intellectual development of children is disturbed already at a blood Pb level of 100 mg Pb/L (CDC, 1991). Lead is causing concern in particular due to the possible impacts on children. Lead influences the nervous system, slowing down nerval response. This influences learning abilities and behaviour. Children are exposed to Pb right from their birth, as children in the embryonic stage receive Pb from their mothers through the blood. Children are furthermore exposed to Pb via dust and soil contaminated by deposition from air and other sources (Holm *et al*., 2002).

In Germany, despite the implementation of unleaded gasoline in the autumn of 1985, Pb emissions decreased only slowly in the following years because unleaded gasoline was only slowly accepted by the consumer. The media alleged that unleaded gasoline contained a high percentage of carcinogenic benzene and consequently the use of leaded gasoline consumption rose. The negative attitude was shared by many of the automobile garages and petrol stations, who kept using leaded gasoline (Westheide, 1987).

Measurements of oxygen consumption revealed increased microbial activity after the addition of oil to soils, but the presence of Pb markedly reduced this activity with a prolonged lag phase in the biodegradation of oil sludge. Other elements of concern include Zn, Cu, Cr, Ni and Cd. With repeated applications of oily sludge to a land farm operation, heavy metals may accumulate at levels where microbial biodegradation could be reduced (TPHCWG, 1997).

2.3.3 Nickel

Nickel occurs in both coal and crude oil in minor quantities, originating from vegetation and from percolating waters containing Ni leached from rocks. The major natural sources include the aerosols constantly produced by the oceanic surface, windblown soil dusts, and volcanic ash. Nickel is released from plants during growth, at different levels depending on soil composition. Forest fires produce Ni -containing smoke particles. A part of atmospheric Ni originates from meteoric dusts. Atmospheric Ni concentrations for remote areas that are considered to be relatively free from man-made Ni emissions are in the range of < 0.1-1 ng/m^3 (marine) and 1-3 ng/m^3 (continental) (Schmidt and Andren, 1980).

The wide variation in ambient Ni concentrations reflects the influence of Ni emissions from distant sources being transported by means of meteorological processes. Vanadium and Nickel metalloporphyrins are present in large quantity in heavy crude oils. Their presence causes many problems because such metals have a deleterious effect on the hydrogenation catalysts used in upgrading processes. In addition to, a heavy metal when present in fuel fractions decreases the quality and performance of fuel (Khuhawar and Lanjwani, 1996).

Zare - Maivan (2010) in a study to examine the distribution of heavy metals associated with petroleum in the Northern Persian Gulf found that the sediments were contaminated with Ni, V and S.

According to Udeme and Udoessien (2012), trace metals have been found in different proportions in different crudes and consequently in their derivatives. Frequently Ni and V are found in largest concentrations contributing to environmental pollution. Because of their mutagenic and carcinogenic potential, Ni and V emissions have been strictly controlled in several countries. Other metals such as Fe, Cu and Zn, may also be present in significant amounts.

Heavy metals are often found to be part of crude oil samples. Possible sources of trace metals in crude oil are: through incorporation and *diagenesis* of metal complexes of the original biological materials; through incorporation into the organic matrix during *diagenesis* of the biological materials in the source rocks either from clay minerals or interstitial aqueous solution; through an aqueous phase during primary and secondary migration and from formation waters or reservoirs' rock minerals (Udeme and Udoessien, 2012).

Furthermore, most soils associated with the areas where crude oil is found in Nigeria are also associated with appreciable deposits of metal ores such as Fe, V and Ni (Udeme and Udoessien, 2012).

According to Madu *et al*., (2011), small amounts of Ni in the feed stock introduced to the catalyst in desulphurization of fuel oil or catalytic cracking may be poisonous. The purpose of desulphurization is to reduce SO_2 emissions from automobiles. The ashes of these metal-containing fuels have strong corrosive effect on gas turbine generators. Nickel complexes apparently affect the soil - water interfacial tension and stability of emulsion. Nickel may also poison the catalysts used in the refineries.

Nickel can be released into the atmosphere by oil-burning power plants, coal-burning power plants, and trash incinerators. In the air, it attaches to small particles of dust that settle to the ground or are taken out of the air by rain or snow and this usually takes many days. Nickel released in industrial waste-water ends up in soil or sediment where it strongly attaches to particles containing Fe or Mn. Both the Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC) concur that Ni compounds are human carcinogens. The EPA has determined that Ni refinery dust and NiS are human carcinogens. Workers who drank water containing high amounts of Ni had stomachache and suffered adverse effects to their blood and kidneys. The EPA recommends that drinking water should contain no more than 0.1 mg/L (ASTDR, 2004).

2.3.4 Copper

In a study of automobile exhaust emitted from light duty vehicles conducted in Denver, USA, it was shown that this source of Cu emission makes a small local contribution to copper in air. The amount of Cu emitted in the exhaust from automobiles powered by regular gasoline has been measured to be between 0.001–0.003 mg/mile (ATSDR, 2004).

Copper ores are mined, smelted and refined to produce many industrial and commercial products. Copper is widely used in making bronze which is a major component of turbines in petroleum industries, cooking utensils and water distribution systems, as well as fertilizers, bactericides, fungicides, algicides and antifouling paints. It is also used in animal feed additives and growth promoters, as well as for disease control in livestock and poultry. Copper is used in industry as an activator in froth floatation of sulfide ores, production of wood preservatives, electroplating, azo-dye manufacture, as a mordant (combines with dye to fix the dye on a garment) for textile dyes, in petroleum refining and the manufacture of Cu compounds (ATSDR, 2004).

Copper is released to water as a result of natural weathering of soil and discharges from industries and sewage treatment plants. Much of the Cu discharged to water is in particulate form and tends to settle out, precipitate out or be adsorbed by organic matter, hydrous Iron, Manganese Oxides and clay in the sediment or water column. In the aquatic environment the concentration of Cu and its bioavailability depend on factors such as water hardness and alkalinity, ionic strength, pH and redox potential, complexing ligands, suspended particulate matter and carbon, and the interaction between sediments and water (Dameron and Howe, 1998).

The largest release of Cu is to land; the major sources of release are mining operations, agriculture, solid waste and sludge from treatment works. Most Copper deposited in soil is strongly adsorbed and remains in the upper few centimetres of soil. Copper adsorbs to organic matter, carbonate minerals, clay minerals, hydrous Iron and Manganese oxides. Soil acidity favours leaching and hence transport of Cu in soil. A number of important factors influence the fate of copper in soil. These include the nature of the soil *per se*, pH, presence of oxides, redox potential, charged surfaces, organic matter and cation exchange (Dameron and Howe, 1998).

ATSDR (2004) affirms that everyone must absorb small amounts of Cu every day because Cu is essential for good health approximately 0.9 mg per day. High levels of Cu can be harmful. Breathing high levels of Cu can cause irritation of nose and throat. Ingestion of high levels of Cu can cause nausea, vomiting and diarrhoea. Very high doses of Cu can cause damage to the liver and kidneys, and even death. Wilson's disease is an inherited (genetic) disorder in which Cu builds up in the liver. Symptoms of liver toxicity (jaundice, swelling, pain) usually do not appear until adolescence (DES, 2013). The Environmental Protection Agency (EPA) has determined that drinking water should not contain more than 1.3 mg/L of Cu.

2.3.5 Zinc

Additives are introduced to lubricating oils to improve its physical and chemical properties. Consequently, lubricating oils have high additive contents (up to 20%), especially detergents and dispersants which constitute 2-15% of oil weight (Vasquez-Duhalt, 1989). These dispersants consists of a mixture of surfactants and solvents used to emulsify oil spills. However, several of the Zinc compounds are oil additives but toxic environmental contaminants, for example ZDTPPs and ZDTPs; calcium alkyl phenates; Mg, Na and Ca sulphonates; tricresyl phosphates; molybdenum disulphide; heavy metal soaps and other organometallic compounds that contain heavy metals like Cd. Hence, very high levels of Zn and Cd are found in new motor oil Hewstone (1994) and Vasquez-Duhalt (1989).

Zinc is required for proper growth and development in children. The recommended dietary allowance (RDA) of Zn is 11 mg per day. Very little amounts of Zn leads to loss of appetite, decreased sense of taste and slow healing of wounds, whereas very high concentrations of Zn could result into stomach cramps, nausea, skin irritation, impaired pancreas and inhibition of protein metabolism (ATSDR, 2004).

2.3.6 Cadmium

Automotive oil has negligible levels of Cd (< 4 μg/L of oil), Cd therefore accumulates in motor oil during use. Improper disposal practices of used motor oil, such as dumping in the sanitary sewer or storm drain system or simply pouring used oil on the ground, can result in Cd making its way into sanitary and combined sewers (TPHCWG, 1997).

Cadmium’s mobility in soil depends on several factors including the pH of the soil and the availability of organic matter. Generally, Cd will bind strongly to organic matter leading to immobilization of Cd (ATSDR, 2004).

However, immobilized Cd is bioavailable to plants and can easily enter the food supply. Cadmium in soil tends to be more available when the soil pH is acidic but adsorbs strongly to soils with higher pH. The average Cd emission factors for combustion of coal and oil are about 0.1 and 0.05 g/ton in the USA (ATSDR, 2004).

According to Xiong and Lu (1991), Cd is a probable human carcinogen. Like Pb, Cd also accumulates in the lysosomes of the renal proximal tubular cells as Cd - metallothionein complex, where the Cadmium complex degrades and releases Cd^{2+}. Cadmium (II) inhibits the proteolytic enzymes in the lysosomes and damages the cell (Xiong and Lu, 1991).

Cadmium accumulates especially in the kidneys leading to dysfunction of the kidney with increased secretion of proteins in urine (proteinuria) and other effects. The accumulation of Cd in the kidney (in the renal cortex) leads to dysfunction of the kidney with impaired re-absorption of, for instance, proteins, glucose and amino acids. It is estimated that 1% of all smoking women in Sweden with low body Fe stores may today experience adverse kidney effects due to the Cd load (Holm *et al*., 2002).

Cadmium interacts with the Calcium metabolism of animals. In fish it causes lack of Ca (hypocalcaemia), probably by inhibiting Ca uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth (AMAP, 1998).

According to the ATSDR (2004), Cd binds strongly to soil particles and breathing high levels of Cd can severely damage the lungs. Eating food or drinking water with very high levels severely irritates the stomach, leading to vomiting and diarrhoea. Long-term exposure to lower levels of Cd in air, food, or water leads to a buildup of Cd in the kidneys and possible kidney disease. Other long-term effects are lung damage and fragile bones.

The Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC) in USA have determined that Cd and its compounds are human carcinogens. The Environmental Protection Agency (EPA) established that Cd is a human carcinogen. Animal studies also indicate that young people are more susceptible than adults to a loss of bone and decreased bone strength from exposure to Cd. The Food and Drug Administration (FDA) has determined that the Cd concentration in bottled drinking water should not exceed 0.005 mg/L (ATSDR, 2004).

2.4 Petroleum oil and metals

In a study done to evaluate the morphological changes due to spent engine oil contamination and its heavy metal components of J. curcas seedlings in Delta State, Nigeria; it was noted that heavy metals accumulated with time in areas of oil impact. The levels of heavy metals Fe, Zn, Cd, Cu, Mn, Pb, Cr and Ni were significantly higher ($P \leq 0.05$) in contaminated areas relative to the uncontaminated subplots (Agbogidi and Eruotor, 2012).

From a study conducted on heavy metal levels in used and unused oil, Adesodun and Mbagwu (2007) explain that the type of metals present in certain wastes depends on processes which generated this waste. In their findings, metals present in spent oil were not necessarily the same as those present in the unused lubricants; they observed that most metals like V, Pb, Al, Ni and Fe that were below detection in unused lubricant oil gave high concentration values in used oil.

In another study by Warmate *et al*., (2010), levels of heavy metals (Cu, Ni, Pb and Zn) in soils and water receiving used engine oil were investigated. Soil and water samples were collected at discharge and control points at each study site. The heavy metals were analyzed using FAAS. The results showed that about 80% of used engine oil was disposed of directly into the environment and 20% was recycled via use in civil works. The levels of metals in test soil and water samples exceeded permissible limits to cause environmental and health concern.

Ash deposits of heavy petroleum can cause localized overheating of metal surfaces to which they adhere and lead to the corrosion of the exhaust valves. Excessive ash may also result in abrasive wear of cylinder liners, piston rings, valve seats and injection pumps and deposits which can clog fuel nozzles and injectors. In heavy fuel oil, soluble and dispersed metal compounds cannot be removed by centrifuging. They can form hard deposits on piston crowns, cylinder heads around exhaust valves, valve faces and valve seats and in turbo charger gas sides (American Bureau of Shipping, 2001).

From the Vasquez-Duhalt (1989) heavy oil report, most of the toxicity of used mineral-based crankcase oil has been attributed to additives present in the oil or contaminants that have accumulated in the oil with use. Elements commonly found as additives or contaminants in used mineral-based crankcase oil include Pb, Zn, Ca, Ba, Mg, Fe, Na, Cd, Cu, Al, Cr, Mn, K, Ni, Sn, Si, B and Mo. In some cases, observed toxicity has been correlated with individual constituents of the used oil, but this aspect of toxicity with used mineral-based crankcase oil has not been extensively studied.

Essiett *et al*., (2010) conducted a field study to assess heavy metal concentrations in plants grown on crude oil contaminated soil in Akwa Ibom State in Nigeria. Plant samples obtained from polluted and unpolluted (control) sites were digested and analyzed for Mn, Fe, Li, Zn, Cu, Cd, Cr, Pb, Co, V, Mo, Hg and Se. Considerable amount of Mn and Fe were found to accumulate in all the plants grown on contaminated soil, while other elements assessed were obtained in trace amounts with statistically insignificant differences. The order of bioacculation of trace metals were Mn > Fe > Zn > Li > Co > Pb > Mo > Cd > V = Hg > Cu = Se > Cr.

Radulescu *et al*., (2012) studied the contribution of crude oil on soil pollution and found that crude oil extraction activity brings serious heavy metal contamination of soil. The risk associated with the presence of metals in soil depends on their ability to transfer to water or plants. The higher concentrations of Pb, Cd, Cu, Cr and Zn were found in all contaminated soil samples exceeding the values specified in Romanian legislation. Each metal can cause pollution of soil with dangerous implication concerning the environment and health.

In a study conducted by Onojake and Okonkwo (2011) on metal pollution through oil spillage, soil samples were collected from crude oil polluted sites in Bodo city in Niger Delta. An uncontaminated sample collected 50 metres away from the spill site but within the same geographical area was used as control sample. Trace elements such as, As, Cu, Cr, Cd, Fe, Pb, Ba, Ni, V, Hg and cation exchange capacity constituents of the oil contaminated and non-contaminated soils were determined with AAS. The values of these trace elements were relatively higher at the epicenter of the spill and enhanced more at the surface soils signifying input from oil pollution. Differences in metal levels between contaminated and uncontaminated sites were not statistically significant because soils were sampled from the same geographical area.

2.5 Metal variation with depth

A study was conducted to evaluate soil pollution in the downstream area of a landfill, North of Iran, in relation to changes in soil chemical characteristics and heavy metals concentrations. Soil samples were analyzed for Cd, Ni, Pb, Fe and Mn using AAS. It was observed that the selected metal levels in soil varied with depth. Iron and Manganese levels in shallower depths were higher than in deeper depth. Lead, Cadmium and Nickel showed fluctuations in all the three sites. The main factor for these variations was due to the kind of organic compounds whose composition varied with depth. These compounds had the ability to stabilize these elements in soil (Shirdast *et al.*, 2010).

Heavy metal transfer in soil profiles is a major environmental concern because even slow transport through the soil may eventually lead to deterioration of groundwater quality. In a study to determine variation of levels of Cd and Cu with depth, soil samples in sludge and wastewater irrigation were collected in the soil profiles from the surface to 100 cm. The results indicated movement of metals, but the levels were different. Cadmium accumulated in soil surface layers and had low vertical movement. Most of Cd was found in topsoil that is 0-20 cm depth with a concentration of 4.5 mg/kg. Concentration of Cd, however, decreased after 20 cm. Most Cu was obtained in top soil 27.76 mg/kg and similarly decreased with depth. Heavy metals remained in topsoil layer which is a result of chemical reaction between heavy metals and organic matter and firm bounds with these components (Behbahaninia *et al*., 2008).

From a study done by Bada and Olarinre (2012) to characterize soils and determine metal content in oil - spilled sites in Nigeria; it was reported that soil pH increased with distance from the epicenter of spillage, higher heavy metal levels were obtained in the soil very close to the source of pollution and this decreased with soil depth. The higher metal content was likely to be due to proximity to the source of pollution and reduced leaching due to increased alkalinity. Nigerian crude oil contained heavy metals which were not completely removed during refining processes.

In a study to evaluate in situ geochemistry of metals Cd, Cr, Fe, Pb, Mn and Zn as a function of sediment depth (0 to 100 cm) from a 60 year record of contamination at the Alameda Naval Air Station, California, it was observed that dominant reactions that removed dissolved metals occured in the oxic and suboxic sediments. Any Zn and Cd bound to Fe (oxy) hydroxides and sulphate sediments dissolved and re- precipitated as sulphides in the suboxic sediment layer which were at shallower depth. Any Pb bound to carbonates and phosphates did neither dissolved nor re-precipitated. There were minimum dissolution and re-precipitation at deeper depth implying that levels of Zn, Cd and Pb decreased with depth and time (Carroll *et al*., 2002). When exchangeable sites in soils become saturated, metals compete for adsorption. Presence of Ca^{2+} is known to reduce adsorption of Cd^{2+} on soil, hence increasing the mobility of Cd to deeper depths (McLean and Bledsoe, 1992).

Another study was done to investigate heavy metals in soil tailings from Akara Gold mine, Thailand, by using a three-step SEP method. The maximum depth for the study was four metres and heavy metals studied were: Ag, As, Cd, Co, Cu, Mn, Ni, Pb and Zn. Data from ICP - OES indicated that samples between 0-2 metre depth had higher levels of Cd, Co, Cu, Mn, Pb and Zn than at 2-4 metre depth. Nonetheless, the opposite was true for metals As, Ag and Ni (Chunhacherdchai *et al*., 2011).

Aniket (2011) conducted studies on metal variations with depth in groundwater samples taken from the project area in the Hortobágy region in east of Hungary between years 2001 to 2006. Samples were analyzed for Cr, Zn, Co, Ni, Ba, Al, Cu, Mo, B, Pb, Cd, Sr and Li at the MÁFI Lab using ICP–OES. Generally the levels of the metals were found to decrease with the depth except for Al, Ba and Li which increased with depth.

Another study was carried out in the Niger Delta region of Nigeria to determine the movement and concentration of heavy metals (Cd, Cr and Pb) in soil profiles of crude oil polluted soil (Ogboi, 2012). It was found that heavy metals were more concentrated in the upper sections of the soil profile (0-40 cm) probably due to the complexation effect of organic matter on the heavy metals. However, these metals were also found in the sub soil sections of the profile even down to the depth of between 164 and 200 cm. The movement of these metals down to the depth (160-200 cm) may be a threat to the underground water bodies within this area since the depth of the underground water was between 300 and 400 cm deep from the soil surface. Hence application of organic matter to the soil is very important in order to slow down the rate of movement of these heavy metals down the soil (Ogboi, 2012).

2.6 Effects of seasonal variations on metal levels

From a study done to examine seasonal variations in heavy metal status of the Calabar River in Nigeria, Ewa *et al.*, (2013) reported that the wet season had higher metal levels than the dry season, attributing the increase to mineral weathering and runoff from oil industries, agricultural inputs and residential land-uses. The sequence of metal levels was Mn > Pb > Cu > Zn > Fe during both seasons probably because Mn was more soluble in the river water. Furthermore, Bouka *et al*., (2013) in a study to investigate the impact of phosphate mining on pollution, during both wet and dry seasons in Togo reported that the wet season had higher levels than the dry season. The increase was attributed to erosion of metals from the nearby phosphate plant to the farm lands. The decreasing order of metal levels was Pb > Zn > Cd signaling that Pb was more soluble in the runoff hence transported more effectively by water.

A study was conducted to investigate the impact of mining and agriculture on heavy metal levels in environmental samples in Nigeria, soil samples from the dry and rainy seasons were analyzed for Cd, Cu, Pb and Zn (Omono and Kakulu, 2012). The levels of these metals were higher during the rainy season compared to the dry season. A number of factors affect the metal sorption by soils like rainfall distribution, erosion, soil drainage, redox potential, texture and organic matter and clay content. The dominant process at any specific time determines the heavy metal retention capacity. The rainy season having higher metal levels could be due to topography of the farm, differences in the individual metal solubility, non-equilibrium distribution of water and microbial mediated processes (Omono and Kakulu, 2012).

Delbari and Kulkarni (2011) conducted studies on the effects of seasonal variations on concentrations of heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in agricultural soil in Iran during the rainy and dry seasons. From their study, Zn, Cr, Pb, Cu and Ni had higher levels during the rainy season while Mn and Fe had higher levels during the dry season. The differences in levels of Fe between the two seasons was insignificant. The levels of Cd remained unchanged during both seasons. Metals bind differently to various soil types and the binding ability could be enhanced or depressed or be unaffected during the wet season. This explains why the levels of some metals were higher during the rainy season, some were higher during the dry season while some remained constant. Olubunmi and Olanipekun (2010) evaluated the status of heavy metal pollution of soil and plants around the Bitumen deposit area in Nigeria during the rainy and dry seasons. They reported that the wet season had higher metal levels than the dry season. Runoff water is capable of removing and mobilizing metals from soil hence the higher metal levels during the rainy season than the dry season. The decreasing order of metal levels was Fe > Zn > Ni > Cu > Cd. Iron binds less firmly to soil compared to Zn, Ni, Cu and Cd justifying why run-off water mobilized Fe more than other elements from the Bitumen deposit area.

Achudume and Olawale (2009) studied the variations in Fe, Pb, Cd, Cr and Cu concentrations in plants and soil from a waste dumping site in Nigeria during the dry and wet seasons. Generally higher values were noted in the wet season than in dry season. There were significant variations in the concentrations of various metals at different sites, perhaps due to differences in land gradient. The order of metal levels was Fe > Cd > Cr > Pb > Cu during both seasons. The slope of land could enhance faster erosion of metals down from the waste dumping site.

A study was done to assess the effect of seasonal variations on the concentration of heavy metals Pb, Cd, Zn, Ni, Cr, Cu, Co, V and Hg along two main roads in Saudi Arabia. From their findings, the wet season had higher metal levels than the dry season. This could be due to increase in pH and organic matter content in the rainy season compared to the dry season. The pH value of soil samples was alkaline and the organic matter content was higher in the rainy relative to the dry season. The elevated pH values were probably due to hydrolysis reaction between water and calcium carbonate derived from the upper cretaceous rocks. Hydrolysis yields hydroxyl ions (OH^-) leading to pH increase hence increasing the ability of soil to adsorb and fix these elements. The order of concentration was Zn > Cr > Ni > V > Pb > Cd > Co > Cu > Hg (Odat and Alshammari, 2011).

In a related study by Yahaya *et al.*, (2009), assessment of seasonal variation in concentration of the heavy metals - Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Abattoir dump site soil at Nigeria, was undertaken during the dry and rainy seasons. Soil samples (0 – 15cm) were collected during the rainy and dry seasons. In the dry season, the sequence of metal concentrations in the dump site soil was Fe > Mn > Ni > Cr > Cu > Zn > Pb > Co while for the wet season, the order was Fe > Mn > Ni > Cr > Zn > Cu > Pb > Co. Generally higher mean heavy metal concentrations were recorded in soil during the dry season than in the wet season (Yahaya *et al.*, 2009). In a study to investigate the effects of seasonal variation on heavy metal distribution in the sediments in Nigeria, findings showed that the average concentration of the metals were higher during the dry season than the wet season (Adefemi *et al*., 2007). In a related study on seasonal variations in heavy metal concentrations in soil and some selected crops at a landfill in Nigeria, it was found that the concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the dry season were higher than those in the wet season. This might be due to the runoff effect that is capable of removing heavy metals from the farmland and the effect of rainfall which may facilitate the leaching of the soil and contributes to the dilution of soil solution during the wet season (Oluyemi *et al*., 2008). From a study to assess heavy metal contamination of agricultural soil as a function of seasonal variations in Bangladesh, the average concentration of metals during the dry season in the surface layer of the soil was found to be higher than the wet season (Syed *et al*., 2012).

CHAPTER THREE

EXPERIMENTAL

3.1 Chemical reagents and equipment

3.1.1 Apparatus and glassware

Centrifuge/shaker, refrigerator, 40 sample vials, drying oven, FAAS, digestion bomb and polypropylene tubes.

3.1.2 Analytical grade reagents

Reagents used in the preparation of standards included: concentrated HNO_3, Concentrated HCl, pure metals Pb, Ni, Cu, Zn and Fe, Cd. Reagents used for wet digestion were: concentrated Sulphuric acid, Selenium powder, Hydrogen peroxide and Salicylic acid. These reagents had percentage purities above 99% and were manufactured by Sigma - Aldrich (UK), Merck (Germany) and Loba Chimie (India).

3.2 Heavy metal concentrations in petroleum-contaminated soils

3.2.1 Sample collection and pre-treatment

Figure 1.1, in chapter one and section 1.7 shows the sampling area around the KPC-Eldoret terminus. The study area was a uniform field (in terms of slope, drainage and soil texture). The control site was 100 m from the KPC depot but 50 m from the experimental sites S_2, S_3 and S_4. Each site had an area of 10 m by 10 m. The experimental sites were 20 m from each other. Soils were collected from the four sites. From each site, samples were collected from three different points at different depths. The three soil samples per depth (measuring one pint) were thoroughly mixed to obtain a composite sample. Soils from all the four sites were sampled at 15 cm depth intervals 0-15, 15-30, 30-45, 45-60 and finally 60 - 75 cm using a stainless steel soil auger. Each site had five depth intervals making a total of five (5) composite samples per site, thus all the four sites had twenty (20) composite samples per season. Sampling was carried out during the dry season (December 2012) and wet season (April 2013). A total of forty composite samples were collected for both seasons in labeled polyethylene bags and taken for laboratory analysis.

3.2.2 The wet digestion procedure

The Okalebo *et al*., (2002) digestion procedure was used for total metal determination in soils. Stones and plant fragments in the soil samples were removed by passing the samples through a < 0.2 mm sieve. Soils were crushed to fine powder using mortar and pestle. Afterwards, the soil samples were then oven dried at 70 °C overnight. A 0.3 g of dried samples was transferred into a clean, dry digestion tubes. A 2.5±0.01 mL of fresh digestion mixture (3.2g salicylic acid in 100 ml of Se powder/ H_2SO_4 mixture) was added to each tube and also reagent blanks for each sample. Digestion was then done at 110 °C for 1 hour. The digest was then removed, cooled and three successive portions of 1 ±0.01 mL H_2O_2 added. The temperature was raised to 330 °C with continued heating. The contents were allowed to cool and 25±0.01 mL distilled water added. The contents were thoroughly mixed and finally made to 50 mL with de- ionized water. Determination of Cd, Zn, Fe, Cu, Ni and Pb in the extracts was performed by FAAS at the Kenya Government Chemist in Nairobi.

The FAAS used for analysis was AA 6300 SHIMADZU GFA-EX71, its instrumental specifications are presented in tables 3.1 and 3.2.

3.3 Preparation of standards (stock solution) corresponding to 1000 ppm

On the day of analysis, 1000±0.01 ppm stock solutions for the metals to be analyzed were prepared as follows. Using an electronic digital weighing balance, 1.0000±0.0001g of the Pb metal was weighed into a 250 mL volumetric flask and then reacted with 10 mL of analytical grade 5.3 mol L^{-1} HNO_3 followed by addition of 100 mL of de ionized water. The solution was boiled to expel nitrous oxide fumes, cooled, then transferred to a 1 litre volumetric flask and filled to the mark with de ionized water. The same procedure was repeated for Cu and Fe using similar amounts of fresh reagents. Stock solutions of Cd and Zn were prepared in the same way as Pb, Cu and Fe solutions except that 40 mL of 5.3M HNO_3 was used instead of 10 mL. For Ni, 1.0000 g of Ni metal was reacted with 10 mL of 5.1 M HCl and 10 mL of 5.3 M HNO_3 in a 250 mL volumetric flask. This was followed by the addition of 100 mL of de ionized water. The solution was boiled, cooled and then transferred to a one litre volumetric flask and the volume made to the mark. Calibration solutions were obtained from the stock solutions above through dilution Haavard (2003).

3.4 Preparation of blank and calibration solutions

3.4.1 Blank solution

A 210 mL of 5.1M HCl and 70 mL of 5.3M HNO_3 was mixed in a 1 litre flask and de ionized water added to the mark. The concentration values of the blank were subtracted from the measured concentration of the metals.

3.4.2 Calibration solutions

From 50±0.01 ppm of Cd standard solution, volumes 2 mL, 4 mL, 6 mL, 8 mL and 10 mL were, respectively, pipetted into 100 mL volumetric flasks. To each aliquot, 20±0.01 mL of blank solution was added and filled to the mark with de ionized water and then mixed thoroughly. The above respective volumes corresponded to concentrations 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm. The same procedure was repeated for stock solutions of Pb, Zn, Ni, Cu and Fe. Within this concentration range, the standards had absorbance values within the Beer’s linear range of less than 0.3 absorbance units hence increasing accuracy and precision of calibration of the samples Haavard (2003) and Perkin Elmer (1996).

3.5 Analysis of treated samples by AAS

Tables 3.1 and 3.2 presents analytical data for elements analyzed as well as the instrumental specifications for the FAAS used during analysis.

Table 3.1: Analytical data on elements analyzed

Element	Detection limit	Flame	Resonance line	Slit band width
Pb	0.010ppm	Fuel lean acetylene-air	217nm	0.2nm
Ni	0.010ppm	Fuel lean acetylene-air	232nm	0.7nm
Cu	0.003ppm	Fuel rich nitrous oxide-air	324.8nm	0.7nm
Cd	0.002ppm	Fuel lean acetylene-air	228.8nm	0.7nm
Fe	0.006ppm	Fuel lean acetylene-air	248.3nm	0.7nm
Zn	0.001ppm	Fuel lean acetylene-air	213.9 nm	0.7nm

(Haavard, 2003)

Table 3.2: Instrumental specifications for the AAS used in analysis

Attributes	
Graphite furnace	Yes
Lamps	6 lamps, 2 user-selected lamps can be illuminated at the same time (1 for measurement,1 warming up for next measurement)
Optical system	double beam
Wavelength range	185 to 900 nm
Power requirements	AC100V, 120V, 230V ±10% 50/60Hz (no sudden voltage fluctuations)
Peak power	230 Volt Ampere (VA)
Additional specifications	**Mounting:** Aberration-corrected Czerny-Turner mounting, Number of grating grooves: 1800lines/mm, Focal length: 298mm **Bandwidth:** 0.2 - 0.7 nm (4 step automatic switching) **Photometric method:** Flame: Optical double beam. Furnace: Electrical double beam **Background correction:** High-speed self-reversal method(BGC-SR), high-speed deuterium lamp method(BGC-D2) **Lamp mode:** Emission, NON-BGC, BGC-SR, BGC-D2,

(Haavard, 2003)

3.6 Estimation of linear relationship between absorbance and metal concentration

3.6.1 Lead absorbance against concentration

The linear relationship between Pb levels and absorbance had R^2 = 0.645 at confidence level 100%. This shows that levels of Pb linearly predicted absorbance by 64.5% thus obeying the Beer's law.

3.6.2 Nickel absorbance against concentration

The linear relationship between Ni concentration and absorbance had R^2 = 1.000 at confidence limits of 100% implying that the levels of Ni linearly predicted absorbance by 100%.

3.6.3 Zinc absorbance against concentration

The linear relationship between Zn levels and absorbance had R^2 = 0.946 at significance level of 100%. Thus the concentration of Zn linearly predicted absorbance by 94.6%.

3.6.4 Copper absorbance against concentration

The linear relationship between Cu levels and absorbance had R^2 = 0.995 at confidence level of 100%. This shows that levels of Cu linearly predicted absorbance by 99.5 %.

3.6.5 Cadmium absorbance against concentration

The linear relationship between Cd levels and absorbance had R^2 = 0.172 at significance level of 0.008. This shows that concentration of Cd linearly predicted absorbance by 17.2%. The low R - squared value of Cd could be due to negligible Cd values obtained as observed in appendix Ia.

3.6.6 Iron absorbance against concentration

The linear relationship between Fe levels and absorbance had $R^2 = 0.972$ at confidence level of 100% demonstrating that Fe levels linearly predicted absorbance by 97.2%.

From R - squared values, it is evident that there was a positive linear relationship between absorbance values of metals and their concentrations, showing conformity to the Beer's law. This is discernible from appendices VIa to VIf on pages 91 - 97.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Metal pollutant levels

4.1.1 Variation of metal levels with depth and seasons

Metal levels varied with seasons and depths for all the sites. Figures 4.1 to 4.8 presents illustrations for metal level variations with depths and seasons for all the sites.

Fig.4.1 depicts the metal levels in site S_1 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Fe while Cd was the least abundant.

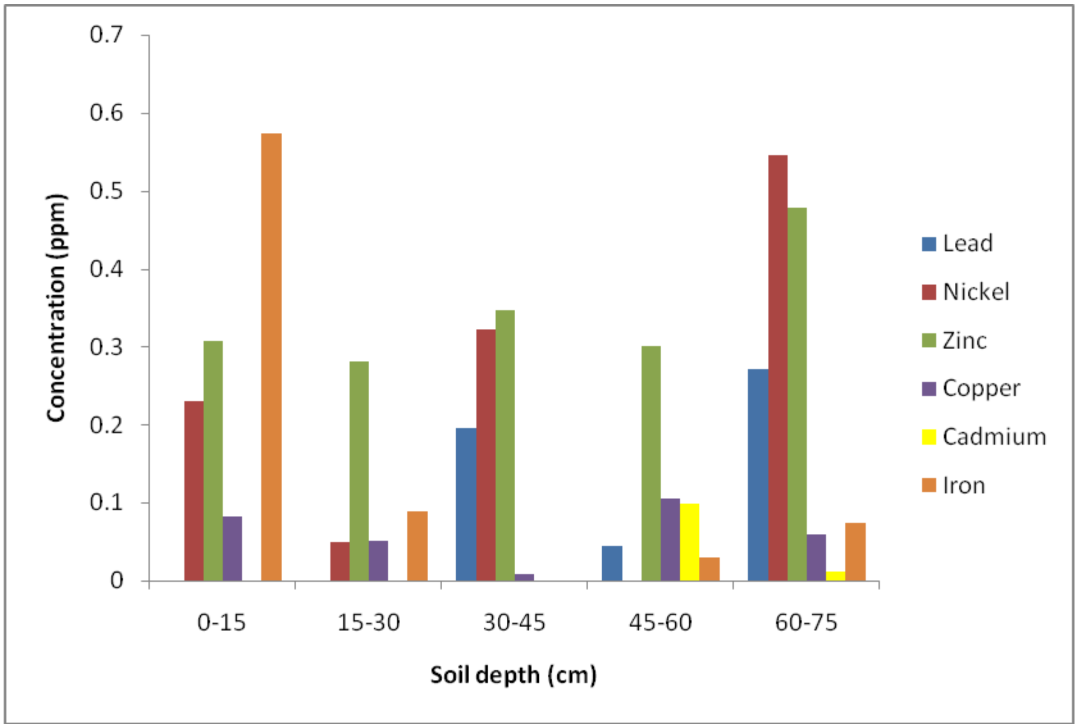


Fig 4.1: Metal levels in site S_1 during dry season (Dec 2012)

Fig 4.2 presents metal levels in site S_1 during the wet season in the range of 0 - 75 cm depth. From the Figure, Fe had highest levels whereas Cd had the least levels. There was

Cd at depth 45 - 60 cm probably because Cd was more mobile towards the bottom soil and that could be due to presence of high levels of Ca^{2+} in exchangeable sites capable of reducing Cd^{2+} adsorption, enabling Cadmium be mobile (McLean and Bledsoe, 1992).

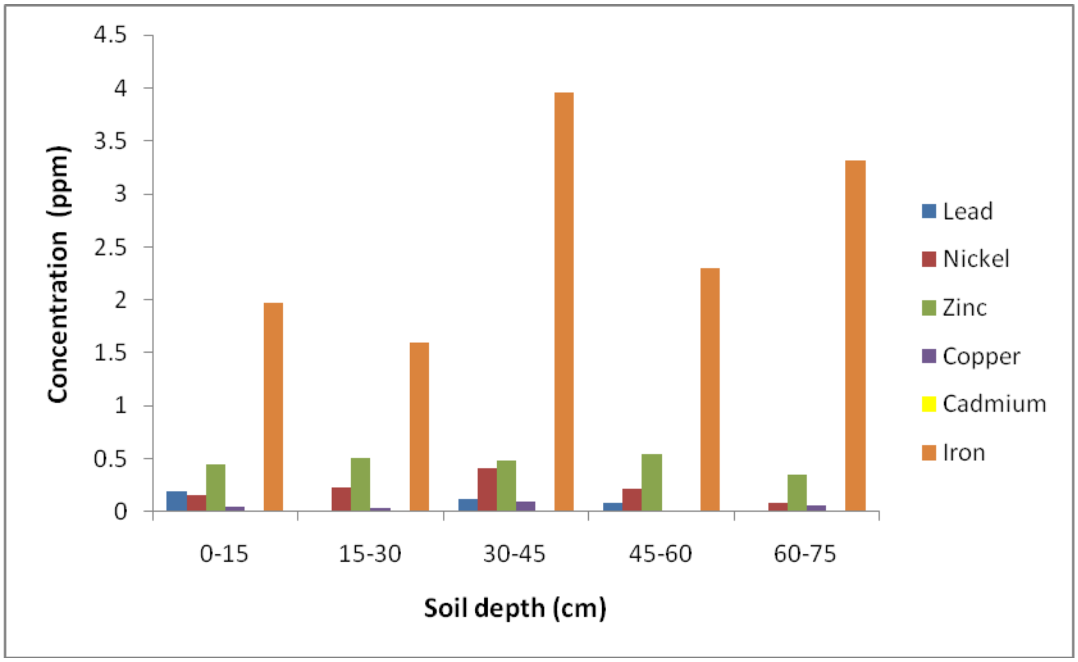


Fig 4.2: Metal levels in site S_1 during the wet season (April 2013)

As can be observed from Figures 4.1 and 4.2 above, the wet season had higher metal levels than the dry season. During the wet season, Fe had the highest levels relative to other selected metals. Also depth 45 - 60 cm (wet season) had the least metal levels compared to the top soil except for Fe and Zn. As per Fig. 4.1, Zn was highest at depth 45-60 probably because of stronger chelation with the type of organic matter at this depth Shirdast *et al.*, (2010). Metals complexed more effectively with the top soil more than depth 45 - 60 cm probably as a consequence of the top soil being richer in organic matter content than soil at 45 - 60 cm depth which acceded to Behbahaninia *et al.*, (2008) work on metal transport in soil.

Fig 4.3 depicts metal levels in site S_2 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Zn while Cd was the least abundant. Also shallower soil had higher composition of Pb relative to the deeper soil.

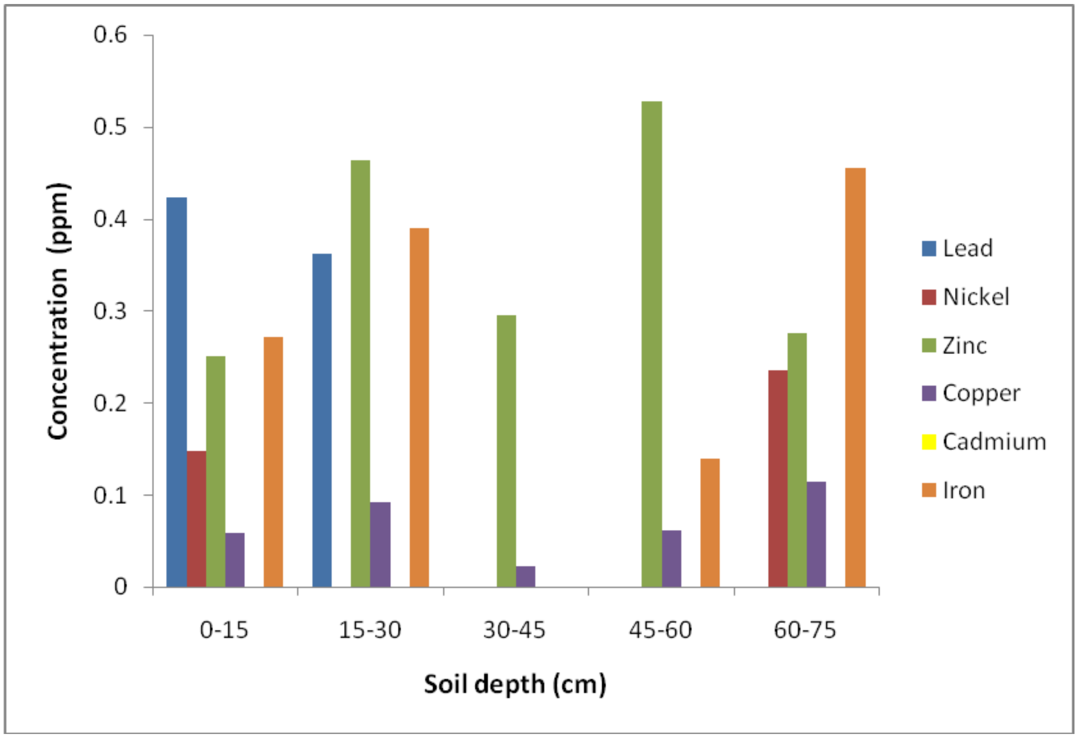


Fig 4.3: Metal levels for site S_2 during the dry season

Metal levels at site S_2 during the wet season are presented in Fig.4.4. As can be observed in Fig. 4.3 levels of Zn decreased relative to the dry season probably due to Zn being washed away by run - off water in the wet season.

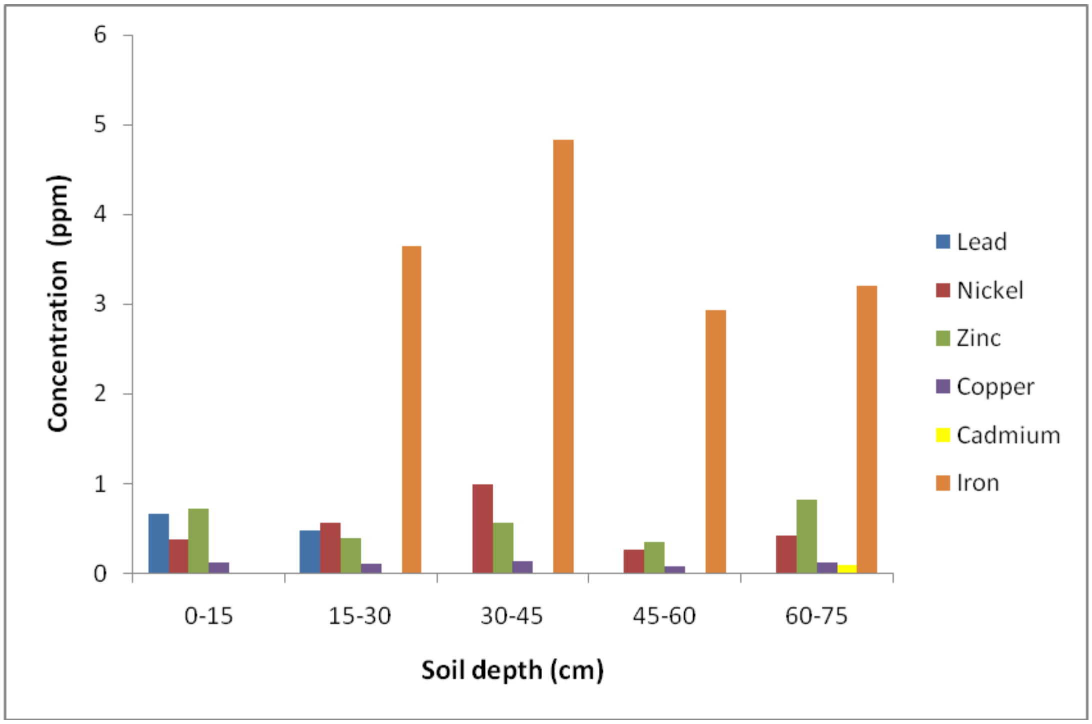


Fig 4.4: The metal levels for site S_2 during the wet season

As from Fig. 4.4 above, there was no Fe reported at depth 0-15 cm probably due to leaching during the rainy season. Iron has been known to be readily mobilized by runoff water (Olubunmi and Olanipekun, 2010).

Fig.4.5 below depicts the actual metal levels in site S_3 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Zn while Cd was the least abundant. Nickel levels were also higher in site S_3 relative to the other sites.

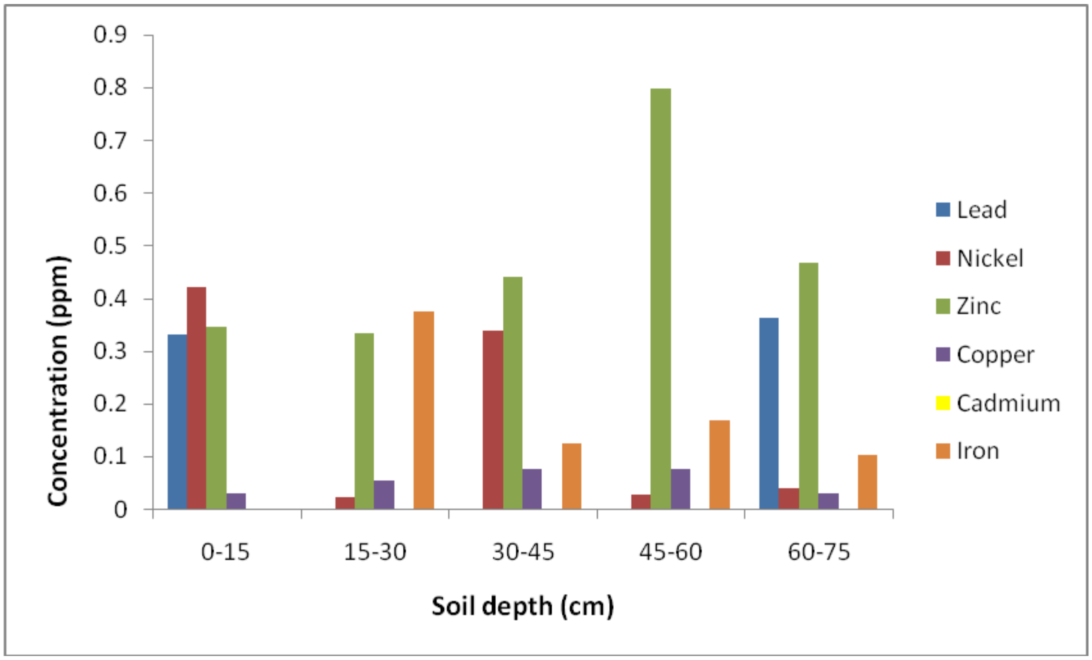


Fig 4.5: The metal levels in site S_3 during the dry season

Metal levels at site S_3 during the wet season are presented in Fig.4.6. As can be observed, levels of Fe in the wet season increased tremendously relative to the dry season, whereas, Zn levels remained fairly constant. Rainfall could have increased the rates of formation of organic matter and also led to hydrolysis of carbonates resulting in elevation of pH. Increased pH favoured Fe retention capacity of soil hence concurred with Odat and Alshammari (2011) findings, they found that rainfall increased hydrolysis of soils hence elevating the soil pH.

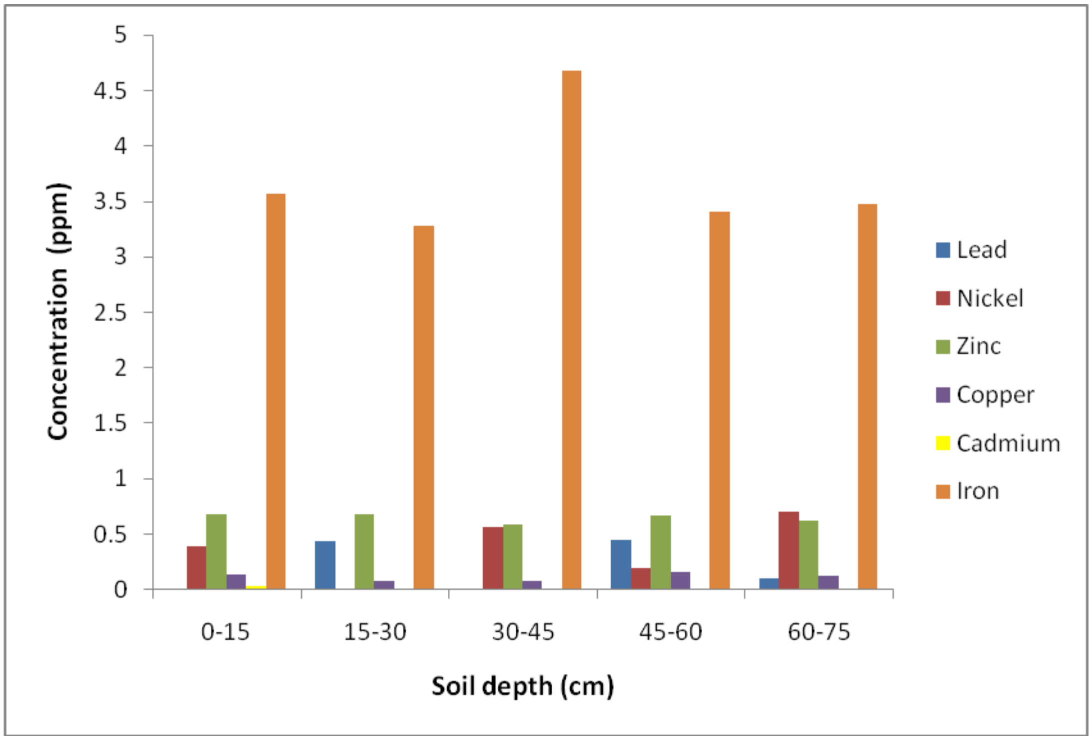


Fig 4.6: Metal levels for site S_3 (50 metres from KPC) during the wet season

Fig.4.7 depicts the metal levels in site S_4 during the dry season ranging from 0 - 75 cm depth. The levels of Pb were highest at this site relative to the other three sites, probably due to more petroleum spillage. At lower depths, Ni had highest levels relative to the other five selected metals probably due to the small ionic size of Ni^{2+} leading to a firmer complexation with the organic constituents of the top soil.

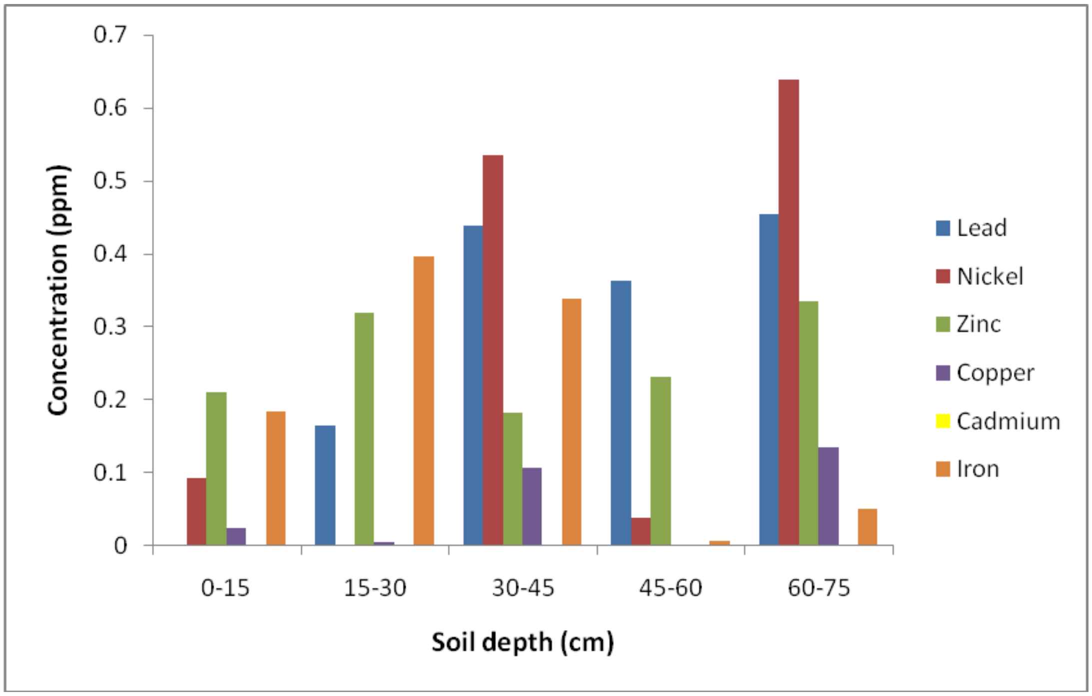


Fig 4.7: The metal levels for site S_4 during the dry season

As for Fig.4.8, the metal levels in site S_4 during the wet season ranging from 0 - 75 cm depth are presented. The levels of Fe were higher relative to its dry season at this depth. Zinc levels decreased when compared to the dry season. At deeper depth, Ni had higher levels relative to the shallower depth.

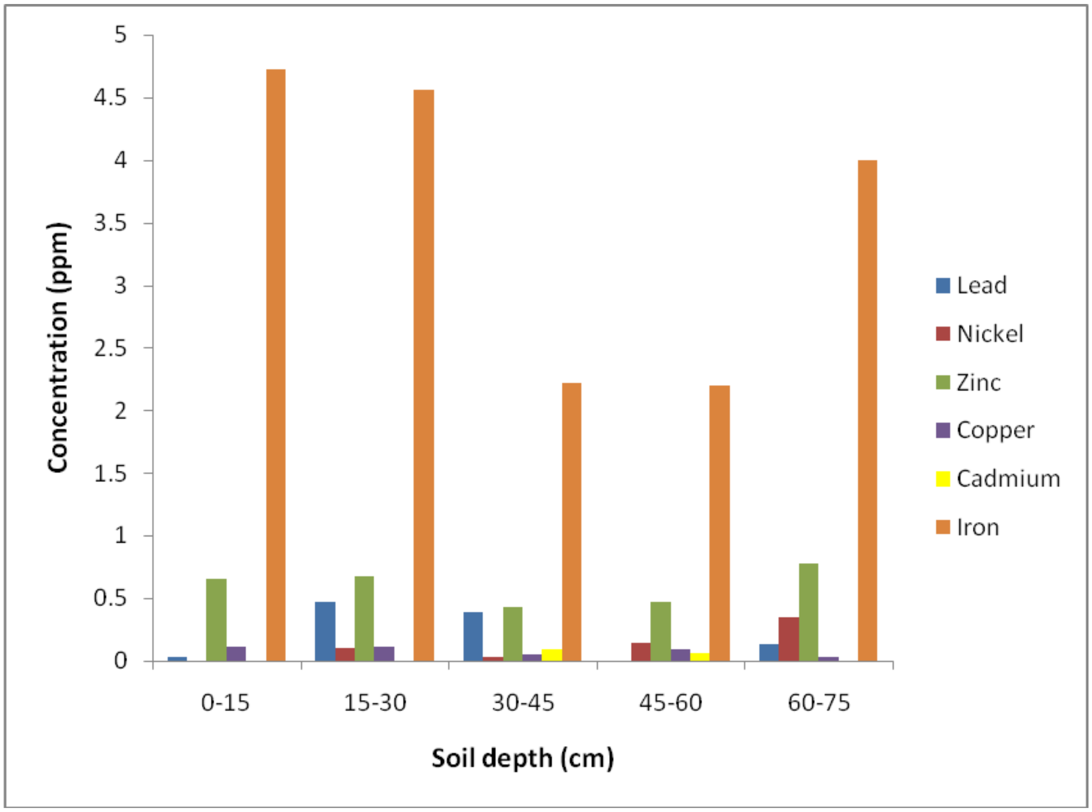


Fig 4.8: The metal levels for site S_4 during the wet season

4.1.2 Variation of metal levels with depth

As observed in Figures 4.1 to 4.8, metal levels varied with depth, the levels of Fe and Pb decreased with depth for all the sites. The type of organic matter found in the top soil complexed with Fe and Pb more effectively than the type of organic content in the deeper soil Behbahaninia *et al*., (2008) and Shirdast *et al*., (2010).

Contrary findings were noted for Ni and Zn where their actual levels increased with depth. At deeper depth, there could be different types of organic matter capable of stabilizing Ni and Zn. This is supported by Shirdast *et al*., (2010) who reported higher values than in this study.

Copper and Cadmium levels had limited vertical fluctuations. These elements bind firmly to soil hence run-off water did not mobilize the two elements. This observation was in agreement with Delbari and Kulkarni findings (2011) in Iran.

Appendix Ij is a tabulated summary of metal levels at different depths. For site S_1 at shallower depth (0 - 30 cm), the observed metal levels were 3.95 ppm, 0.51 ppm, 0.05 ppm, 0.20 ppm and 0.08 ppm for Fe, Zn, Ni, Pb and Cu, respectively while at deeper depth (45 - 75 cm), the observed values were 3.31 ppm, 0.55ppm, 0.55 ppm, 0.27 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu. Site S_2 at shallower depth reported metal levels to be 4.83 ppm, 0.72 ppm, 1.00 ppm, 0.47 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu with corresponding values at deeper depth of 3.20 ppm, 0.82 ppm, 0.42 ppm, 0.42 ppm and 0.00 ppm for Fe, Zn, Ni, Pb and Cu. Corresponding metallic levels at site S_3 at 0 - 30 cm, depth were 4.67 ppm, 0.69 ppm, 0.57 ppm, 0.44 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu, whereas at deeper depth were 3.48 ppm, 0.67 ppm, 0.70 ppm, 0.11 ppm and 0.13 ppm for Fe, Zn, Ni, Pb and Cu. At site S_4 the shallower depth recorded metal levels of 4.72 ppm, 0.68 ppm, 0.54 ppm, 0.47 ppm and 0.11 ppm for Fe, Zn, Ni, Pb and Cu with corresponding values of 4.00 ppm, 0.78 ppm, 0.64 ppm, 0.45 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu for deeper depth. At all the sites Fe levels decreased with depth, whereas Pb levels decreased with depth for sites S_2, S_3 and S_4. Similarly Cu levels decreased with depth for only sites S_2 and S_3. These trends were in concordance with the previous studies done by Aniket (2011), Behbahaninia *et al.*, (2008) and Shirdast *et al.*, (2010) who found that levels of Fe, Cu and Pb decreased with depth although their values were fairly higher than these findings, they explained that shallower soil when richer in organic matter chelated effectively with metals at top soil than in the deeper soils.

For sites S_1, S_3 and S_4, the levels of Ni generally increased with depth while levels of Zn increased with depth for sites S_1, S_2 and S_4. This agreed with the findings of Chunhacherdchai *et al*., (2011) on variation of Ni with depth in Thailand.

Soil contents determine the levels of metals that can be chemisorbed. Some types of organic compounds (pectins, lignins, purines and pyrimidines) found in the top most soil have the ability to stabilize metals Pb, Cu and Fe which explains why these metals were in higher proportions in the shallower depths (Shirdast *et al*., 2010) and (Behbahaninia *et al*., 2008). Further to that, top soil that was in contact with spilled petroleum oil had higher metal levels and these levels decreased with distance from the point of contact and this conceded with Bada and Olarinre (2012) findings in Nigeria. Besides that, petroleum spillage increases microbial activities resulting into increased rates of organic matter formation and hence increased adsorption capacities of metals by the shallower soils (Omono and Kakulu, 2012).

The increase in Ni and Zn level with depth could be due to variation of different types of organic matter with depth. Probably Zn and Ni preferred to chelate with the kinds of organic matter present at deeper depths (Shirdast *et al*., 2010). Besides that, the increasing values of Ni and Zn with depth could be attributed to their higher rank of hydration. Due to their smaller sizes, Zn and Ni cations emit a large electrical field hence are readily hydrated. During run- offs, these ions are readily transported to deeper depth because they bind less tightly to the soil particles (Dobrzanski and Zawadzki, 1993).

4.1.3 Metal variation with seasons

The wet season generally recorded higher metal levels than the dry season for virtually all the sites as evidenced by Figures 4.1 to 4.8. For instance Fe at site S_3, depth 30-45 cm had a value of 4.67 ppm during the wet season while at this depth recorded a value of 0.13 ppm during the dry season. The soils sampled could have consisted of a higher clay content. Soils with higher clay content adsorb metals more effectively during wet season than the dry season (Delbari and Kulkarni, 2011).

An equally significant aspect of metal variation with seasons is the effect of rainfall on microbial activities. Odat and Alshammari (2011) affirmed that rainfall increases microbial degradation leading to increased soil organic matter content. The increased organic matter could enhance adsorption of some metals depending on the type of organic content.

At depth 60-75 cm in site S_2, Zn concentration was 0.82 ppm during the wet season but at the same depth and location during the dry season, Zn level was 0.28 ppm. At site 4, depth 15-30 cm, the value of Pb was 0.47 ppm during the wet season but 0.17 ppm in the dry season for the same location and depth. These findings conformed with previous studies done by Omono and Kakulu (2012) and Delbari and Kulkarni (2011) who reported relatively lower metal values for the two seasons. From their studies, wet season had higher metal levels compared to the dry season due to elevated soil pH during rainy season and run off effect that washed away soils from waste deposit areas. During the wet season, runoff water could wash and mobilize metals from the nearby pipeline company to the sampling sites.

4.2 Descriptive statistics

A total of forty samples were collected for the study from four different locations with each site having ten samples. This was split evenly into five samples collected during the wet season and five during dry season. Samples were drawn from depths ranging between 0 and 75 centimetres.

It is evident from appendix Ib that the mean level of Zn was the highest with a value of 0.34 ppm. For the other metals, their mean levels were as follows: Ni 0.23 ppm, Fe 0.15 ppm, Pb 0.10 ppm, Cu 0.06 ppm and Cd 0.02 ppm. Their order of decreasing mean values was Zn > Ni > Fe > Pb > Cu > Cd which agreed with results reported by Radulescu *et al*., (2012) on crude oil contaminated soils in Hungary and this could be due to similarities in the chemical composition of soils in these two areas.

As can be inferred from appendix Ic, the order of mean concentrations was Fe > Zn > Ni > Pb > Cu > Cd. The mean values were 2.62 ppm, 0.47 ppm, 0.22 ppm, 0.08 ppm, 0.05 ppm and 0.00 ppm, respectively which acceded with Omono and Kakulu (2012) findings on the impact of mining and agriculture on heavy metal levels in environmental samples in Nigeria.

From appendix Id it is evident that Zn had the highest mean level of 0.36 ppm. The mean values for the other metals were Fe 0.25 ppm; Pb, 0.16 ppm; Ni, 0.08 ppm; Cu, 0.07 and Cd, 0.00 ppm. The order of accumulation in soil was Zn > Fe > Pb > Ni > Cu > Cd and is supported by previous studies conducted by Adesodun and Mbagwu (2007) on the distribution of heavy metals and hydrocarbon contents in *alfisol* contaminated with waste - lubricating oil in Nigeria.

The highest mean value for Fe plausible from appendix Ie was 2.92 ppm. The corresponding mean values for Zn, Ni, Pb, Cu and Cd were 0.56 ppm, 0.52 ppm, 0.22 ppm, 0.11 ppm and 0.02 ppm. The order of mean values followed the trend Fe > Zn > Ni > Pb > Cu > Cd which was similar to that reported by Omono and Kakulu (2012).

As can be deduced from appendix If, Zn had the highest mean level of 0.48 ppm. The corresponding levels for Ni, Fe, Pb and Cu were 0.17 ppm, 0.15 ppm, 0.14 ppm and 0.05 ppm. The order of mean levels in soil was Zn > Ni > Fe > Pb > Cu > Cd which was in agreement with Adefemi *et al.*, (2007) work on seasonal variation in heavy metal distribution who obtained higher metal levels in Nigerian sediments.

As evidenced from appendix Ig, the mean Fe level of 3.68 ppm was highest in site 3 during the wet season. Mean levels for Zn, Ni, Pb Cu and Cd were 0.65 ppm, 0.37 ppm, 0.20 ppm, 0.12 ppm and 0.01 ppm, respectively. The sequence of mean levels was Fe > Zn > Ni > Pb > Cu > Cd and this trend was in concordance with the findings by Omono and Kakulu (2012) although higher than the levels they reported.

As can be deduced from appendix Ih, Pb had the highest level with a mean value of 0.28 ppm followed by Ni with mean value of 0.26 ppm then Zn with a mean level of 0.26 ppm during the dry season. This was followed by Fe with a mean value of 0.20 ppm and Cu with a mean level of 0.05 ppm. Cadmium was not detected at this site during the dry season. Thus the trend of mean levels was Pb > Ni > Zn > Fe > Cu > Cd which agreed with the findings of Bouka *et al*., (2013) who recorded higher levels than in this study.

Discernible from appendix Ii is that Fe had the highest mean level of 3.54 ppm at site 4 during the wet season. This was followed by Zn with a value of 0.60 ppm, Pb (0.21 ppm), Ni (0.13 ppm), Cu (0.08 ppm) while the lowest mean in the sample was Cd with mean level of 0.03 ppm. The order of decreasing mean values was Fe > Zn > Pb > Ni > Cu > Cd which concurred with the findings of Olubunmi and Olanipekun (2010) although they reported higher metal levels than in this study. Virtually deducible from appendices Ib to Ii is that the mean levels of Zn, Ni, Fe, Pb, Cu and Cd were relatively higher at experimental sites S_2, S_3 and S_4 compared to the control site S_1. This implies that petroleum spillage increased metal pollutant levels although less significantly and hence agreed with the works of Radulescu *et al*., (2012), Onojake and Okonkwo (2011) and Essiett *et al*., (2010) on the effect of petroleum spillage on metal levels in soil and plants. As evidenced from one- way ANOVA for the four sites, pp 81-89, variation of metal pollutant levels with sites was statistically less significant ($p>0.05$) for Zn, Ni, Fe, Pb, Cu and Cd.

4.2.1: Two-sample t-tests for impact of seasonal variations

Two sample t - test statistical analysis is presented in the appendices from pages 72 - 77. As evidenced from the two sample t- tests, the mean of Pb samples from the wet season had higher levels in ppm (mean = 0.18, standard error of mean = 0.04797), relative to the dry season (mean = 0.17, standard error of mean = 0.04107). Statistically the difference in mean Pb levels between the seasons was insignificant with $t(38) = 0.12$, $p=0.451$, $r = 0.0195$. This observation agreed with Omono and Kakulu (2012) and Ewa *et al.*, (2013) who reported that Pb in the wet season was higher than the Pb levels in the dry season and equally the seasonal difference was less significant in their findings.

On average, Ni samples from the wet season had higher concentration (mean = 0.31, standard error = 0.05644), than those of dry season (mean = 0.18, standard error = 0.04745) as evidenced from the two sample t -test appendices and the seasonal difference was statistically significant t (38) = 1.69, p = 0.049, r = 0.264. This concurred with the results of Delbari and Kulkarni (2011) and Odat and Alshammari (2011) findings that reported Ni levels during rainy season exceeded those in the dry season, nonetheless, the mean differences were significant from their observations.

On average, Zn samples from the wet season had higher levels (mean = 0.57, standard error = 0.03157), than those of dry season (mean= 0.36, standard error = 0.03132). The difference between the wet and dry season was significant t (38) = 4.74, p = 0.001, r = 0.372. These findings concurred with Odat and Alshammari (2011) and Delbari and Kulkarni (2011) who reported significantly higher mean levels of Zn in the wet season relative to the dry season.

Copper samples from the wet season had higher concentration (mean = 0.09, standard error = 0.008798), than those of dry season (mean = 0.06, standard error = 0.008655). The difference was significant t (38) = 2.44, p=0.01, r = 0.136. These results are supported by those reported by Odat and Alshammari (2011) and Delbari and Kulkarni (2011) that Cu in the rainy season was higher than in the dry season.

Cadmium samples from the wet season had higher concentration (mean = 0.02, standard error = 0.007112), than those of dry season (mean = 0.01, standard error = 0.004961). The relative mean level differences between dry and wet season was statistically less significant t (38) = 1.11, p= 0.136, r = 0.032. These findings agreed with those reported by Omono and Kakulu (2012) and Achudume and Olawale (2009) who asserted that Cd in the rainy season was insignificantly higher than the dry season. They reported higher values of Cd than the findings in this study.

As for Fe, samples from the wet season had higher concentration (mean = 3.19, standard error = 3.318), than those of dry season (mean = 0.19, standard error = 0.039). The difference was significant t(38) = 1.90, p = 0.033, r = 0.087. These conformed with Odat and Alshammari (2011) and Delbari and Kulkarni (2011) who established that Fe in the rainy season was significantly higher than in the dry season.

From the two - sample t - test, all the selected metals from the wet season had higher mean levels than the dry season. This is attributable to rainfall that could have increased the organic matter content and the soil pH during the wet season. Odat and Alshammari (2011) deciphered that increased alkalinity and organic matter content improves metal retention ability of soils.

At the same time, metals bind differently to various soil types and the binding ability could be enhanced in presence of water if the soil is rich in clay content. This justifies why the levels of metals were higher during the rainy season (Delbari and Kulkarni ,2011). Further to the above explanations, a number of factors generally affect the metal sorption abilities on soils. Among these are: rainfall distribution, erosion, soil drainage, redox potential, texture and organic matter and clay content. Increased rainfall could enhance microbial - mediated processes like decomposition of biological matter leading to increased organic content which is a good adsorbent for metals in soil (Omono and Kakulu, 2012).

4.2.2: One way ANOVA for depth

ANOVA statistical treatment of data is presented in the appendices from pages 78 - 84.

From one way ANOVA [F(4, 35) = 0.43, *p* = 0.7827] for Pb, that is, variation along different depths decreased though the effect of decreasing Pb levels was less significant. This was in agreement with Aniket (2011) findings that levels of Cr, Zn, Co, Ni, Ba, Al, Cu, Mo, B, Pb, Cd, Sr decreased with depth and similarly the decrease was less significant.

When subjected to the same statistical treatment, Zn levels increased with depth albeit the increase with depth was not statistically significant [*F*(4,35) = 0.51, *p* = 0.7263]. These results did not agree with Carroll *et al*., (2002) and Chunhacherdchai *et al*., (2011) findings, who established that the levels Zn decreased with depth of soil. The difference could be due to the nature of organic matter present at deeper soil that complexed more effectively with Zn than at the shallower soil (Shirdast *et al*., 2010).

Unlike Pb and Zn, one way ANOVA statistic infers a significant effect of variation of Ni levels with depth [*F*(4,35) = 3.83, *p* = 0.0109]. Nickel levels significantly increased with depth implying that Ni was less firmly bound to soil and thus ground water could be at great risk of Ni contamination in the study area. These results acceded with Chunhacherdchai *et al*., (2011) findings that at deeper depth, levels of As, Ag and Ni were higher than at shallower depths. Evidenced by one way ANOVA [F*(*4, 35) = 0.14, *p* = 0.9641], the levels of Cu did not significantly vary with depth because Cu binds firmly to soil, nonetheless, these findings disagreed with those reported by Behbahaninia *et al*., (2008). Olubunmi and Olanipekun (2010) affirmed that Copper binds firmly to soil and has little vertical movements in soil.

There was no statistically significant differences between the Cd levels at different depths ANOVA [*F*(4,35) = 0.68, *p* = 0.6076]. Cadmium prefers to bind to top most soils with insignificant vertical movements to deeper soil. This concurred with Ogboi (2012) who obtained higher Cd levels than the findings in this study. From one way ANOVA [F*(*4, 35) = 0.36, *p* = 0.8330], decrease in Fe levels with depth was statistically insignificant. This was in agreement with Shirdast *et al*., (2010) findings that levels of Fe and Mn levels in shallower depth were higher than in deeper depth.

4.2.3: One way ANOVA for sites

One-way analysis of variance for metals at different sites

Although differences in levels existed for Pb at different sites, these differences were not statistically significant as evidenced from one-way ANOVA [*F*(3,36) = 0.71, *p* = 0.5509]. This could be due to sites having similar chemical composition and thus same abilities of stabilizing metals in soil as explained by Onojake and Okonkwo (2011) in Nigeria.

There was statistically insignificant differences between the Zn levels in the samples collected from the different sites (*F*(3,36) = 1.45, *p* = 0.2442). The levels of Zn in the control site was relatively lower than the other experimental sites. When subjected to the same statistical method, differences between Ni levels from sites 1 to 4 were insignificant (*F*(3,36) = 0.38, *p* = 0.7656) since the sites were in the same locality thus their soils could be similar. The levels of Cu in the control site were relatively lower than the experimental sites. Differences between the levels from sites 1 to 4 were not statistically significant (*F*(3,36) = 0.94, *p* = 0.4309). As a consequence of the sites being in the same geographical area, their soils could be similar at metal retention. These results are backed up by the findings of Essiett *et al*., (2010) in Nigeria.

Cadmium was below detection for most sites. There was no statistically significant difference between the Cd samples collected from the different sites as determined by one-way ANOVA ($F(3,36) = 0.47$, $p = 0.7056$). The sites could be having identical soil composition which permitted almost equal movement of Cd. The levels of Fe at the control site were relatively lower than the experimental sites. Differences between Fe levels from site to site were, however, statistically insignificant ($F(3,36) = 0.92$, $p = 0.4415$). Soils are usually rich in Fe which is the second most abundant element on earth. Oil spillage didn’t significantly increase the Fe levels in soil (Sheffer, 2005).

4.2.4: Comparison of metal levels with COQG permissible limits

In this section, the actual metal levels are compared relative to the Crude Oil Quality Group (2004) allowable limits. The essence of comparison is to assess whether the quality of petroleum products is threatened by the presence of higher metal levels. Table 4.1 below presents a comparison between the actual metal levels relative to the COQG permissible levels. As observed in Table 4.1, the mean metal levels for sites 1 to 4 are closer to the acceptable metal standards by the COQG (2004) in ppm.

Table 4.1: The metal in petroleum standards by the COQG in ppm

	Pb	Zn	Ni	Cu	Cd	Fe
COQG acceptable mean levels	0.13	2 .00	5.70	None	0.10	7.00
Site 1 mean levels - Dry	0.10	0.34	0.23	0.06	0.02	0.15
Site 1 mean levels - Wet	0.08	0.47	0.22	0.05	0.00	2.26
Site 1 Mean levels	0.09	0.40	0.23	0.06	0.01	1.21
Site 2 mean levels - Dry	0.16	0.36	0.08	0.07	0.00	0.25
Site 2 mean levels - Wet	0.22	0.56	0.52	0.11	0.02	2.92
Site 2 Mean levels	0.19	0.46	0.30	0.09	0.01	1.59
Site 3 mean levels - Dry	0.14	0.48	0.17	0.05	0.00	0.15
Site 3 mean levels - Wet	0.20	0.65	0.37	0.12	0.01	3.68
Site 3 Mean levels	0.17	0.56	0.27	0.09	0.00	1.92
Site 4 mean levels - Dry	0.28	0.26	0.26	0.05	0.00	0.20
Site 4 mean levels - Wet	0.21	0.60	0.13	0.08	0.03	3.54
Site 4 Mean levels	0.24	0.43	0.19	0.07	0.02	1.87

COQG (2004)

From Table 4.1 Pb (0.13 ppm), Zn (2.00 ppm), Ni (5.70 ppm), Cu (none), Cd (0.10 ppm) and Fe (7.00 ppm) are the acceptable mean levels. Lead exceeded COQG permissible mean level of 0.13 ppm at sites 2, 3 and 4 while other elements were within the acceptable range.

It is evident that site 4 had the highest mean level of Pb ranging from 0.21 ppm (dry season) to 0.24 ppm (wet season). The mean concentration levels were higher in comparison with the acceptable level of 0.13 ppm. On average the mean Pb levels increased at site 1 from mean levels of 0.08 ppm in wet season to mean levels of 0.28 ppm in site 4 during the dry season. Large amounts of oil spillage, the type of soil and soil pH in site 4 could have led to higher levels of Pb relative to site 1.

For Zn, the mean levels were below the acceptable limit of 2.00 ppm. The mean levels ranged from 0.26 ppm (site 4 dry) to 0.65 ppm (site 3 wet). It can therefore be inferred that the mean Zinc values increased from the dry season to the wet season since oil spillage slows down the transport of metals by run offs (Bada and Olanrire, 2012). The mean values for Ni were, however, below the acceptable limit of 5.70 ppm with site 2 having the lowest level of 0.08 ppm during the dry season whereas the wet season had the highest value of 0.52 ppm. This could be because Ni is readily hydrated and binds less firmly to soil (Delbari and Kulkarni, 2011).

For Pb, there was a correlation between the mean levels for the four sites. Sites 1 and 4, respectively, had mean levels decreasing from highest of 0.23 ppm and 0.26 ppm in the dry season to lowest of 0.22 ppm and 0.13 ppm, respectively, in the wet season. On the other hand, the mean levels tended to increase from the dry season to wet season in sites 2 and 3. Proximity of sites 1 and 4 to each other could have resulted in the two sites experiencing similar anthropogenic activities. Alternatively, the two sites could be having the same soil composition. The same scenario could be true for soils in sites 2 and 3.

The lowest mean value of Cu was 0.05 ppm in site 1 during wet season with the highest mean level being 0.12 ppm in site 3 during the wet season. In general, the mean levels had a small variance as can be seen from the difference between the lowest and highest value which was less than 0.07 ppm. For Cd, the highest mean level was in site 4 during the wet season of 0.03 ppm. The Cd levels were, however, much below the maximum acceptable level of 0.10 ppm. Cadmium binds firmly to soil more than the other selected metals and this explains why Cd levels were comparatively lower for all the sites and this was supported by ATSDR (2004). All the sites showed that the mean levels for Fe were higher during the wet season than dry season. The highest mean level was found in site 1 with a value of 2.26 ppm while the lowest being in site 3 of 0.15 ppm. The metal levels were, however, below the acceptable value of 7.00 ppm.

4.3 Correlation coefficient

There existed a significantly positive correlation between mean metal levels and petroleum spillage. In terms of metals, Pb mean levels impacted on Ni with $r = 0.67$, $p = 0.012$. This shows that the levels of Pb and Ni were co-determined implying that petroleum spillage which could have contributed to increased levels of Pb in soils and hence could have led to increased Ni levels in soil. The Zn mean levels impacted on the Cu mean levels, $r = 0.73$, $p = 0.006$. To the same extent, Ni and Cu mean levels were co-determined with $r = 0.69$, $p = 0.009$. The same scenario applies to Ni and Cu or Cu and Zn. This therefore implies that the mean levels of Ni and Pb, Zn and Cu, Ni and Cu were linearly interdependent and petroleum spillage could have contributed to their increased levels in soil. This was in consonance with Agbogidi and Eruotor (2012), Radulescu *et al.*, (2012), Onojake and Okonkwo (2011), Essiett *et al.*, (2010) and Vasquez-Duhalt (1989) who reported that petroleum spillage increased metal levels in soils. Agbogidi and Eruotor (2012) affirmed that metal pollutants accumulate with time in areas of petroleum spillage leading to higher mean levels at petroleum contaminated plots relative to uncontaminated sites. Vasquez-Duhalt (1989) averred that Pb, Zn, Cu, Cd and Ni are among the elements added to petroleum to modify its properties. Elements like Fe and Cu are constituents of motor vehicles equipments and petroleum machinery and are significantly present in used petroleum but may be absent in unused petroleum Warmate *et al.*, (2010) hence when petroleum containing these elements is spilled, then such spillage elevates metal levels in soils.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results of the study showed that there was contamination of soil by the metal pollutants in the four sites. There was strong positive correlation between metal levels and petroleum spillage ($p<0.05$, $r>0.5$) implying that petroleum spillage elevated levels of metal pollutants in soil. Virtually the mean levels for experimental sites S_2, S_3 and S_4 were higher than the control site (S_1). This is discernible from Table 4.1; site S_1 had Pb level 0.09 ppm, however, experimental sites S_2, S_3 and S_4, had respectively, 0.19 ppm, 0.17 ppm and 0.24 ppm. There were differences in metal levels from site to site, the differences were, nonetheless, statistically insignificant. Cadmium was not detected in most of the sites.

The study showed that the levels of Pb and Fe decreased with depth while levels of Ni and Zn increased with depth. The downward movement of Ni was statistically significant ($p = 0.01098$, $F = 3.83$) and could contaminate ground water in the area. Copper was less mobile with limited variation of Cu levels with depth signifying firm binding on soil.

The mean levels of Pb at S_2, S_3 and S_4 exceeded the standards set by the crude oil quality group of 0.13 ppm, whereas levels of Fe, Zn, Cd and Ni were within the acceptable thresholds. Metal pollution surged up during seasonal change from dry to wet season ($p < 0.05$, $t > 1$, $r > 0.1$) and that was significant for Ni, Cu and Zn. The increased levels of metals during the wet season could be as a result of increased soil pH and rates of formation of organic matter due to rainfall and petroleum spillage.

5.2 Recommendations

Even though from the study Zn, Cd, Ni and Fe were within the acceptable levels, continuous discharge of contaminated petroleum oil to soil may lead to accumulation of these metal pollutants.

Since Ni levels increased significantly with depth in the study area, more studies should be done on what soil aspects aid mobility of Ni towards deeper depth. The effects of parameters like the types of organic matter, pH, cation exchange capacity (CEC), soil type and leachability on metal mobility in soils should also be done.

Comparisons should also be made between metal levels in used oil and unused oil in order to compare the elements present in both. These comparisons should aid in understanding the significance of automobile wear and tear on soil pollution.

Further studies should be done on seasonal variations of soil metal levels over a longer duration than a year, moreover, such investigations should also include variation of nutrient levels over seasons.

REFERENCES

Achudume, A.C. and Olawale, J.T. (2009). Seasonal variations in heavy metals concentrations in Chromolaena odorata (L.) King & Robinson foliage and soil at a solid waste dump site in Osun State. *Journal of Tropical Agriculture,* Vol 47, (1-2), pp 58-61.

Adefemi, O.S., Olaofe, O. and Asaolu, S.S. (2007). Seasonal Variation in Heavy Metal Distribution in the Sediment of Major Dams in Ekiti-State. *Pakistan Journal of Nutrition*, Vol 6 (6), pp 705-707.

Adesodun, J.K. and Mbagwu, J.S.C. (2007). Distribution of heavy metals and hydrocarbon contents in an alfisol contaminated with waste-lubricating oil amended with organic wastes. *Journal of Bioresour. Technol.*Vol.05. pp 1 - 10.

Agbogidi, O. M. and Eruotor, P.G. (2012). Morphological Changes Due to Spent Engine Oil Contamination and Its Heavy Metal Components of Jatropha curcas Linn Seedlings. International Conference on Bioscience, Biotechnology and Healthcare Sciences, pp 1 - 6.

Amanda, Z. J. and Weindorf, D. C. (2009). Heavy Metal and Trace Metal Analysis in Soil by Sequential extraction: A Review of Procedures. pp 13-15, Louisiana State University Geology and Geophysics, USA.

AMAP (1998). Assessment of heavy metals report*:* Arctic pollution issues. pp 447 - 472. Norway.

American Bureau of Shipping (2001). Heavy fuel oil. pp 27-34.

Aniket, J. (2011). Microanalysis of groundwater elements with respect to time and depth in the Hortobagy region. *Journal of earth and environmental sciences*, Vol 3, pp 39-47.

ATSDR (2004). Toxicology profile for used mineral base crankcase oil. pp 1-14, Dept of Health and Human Services, Public Health Services Press, Atlanta,USA.

Bada, B.S. and Olarinre, T.A. (2012*).* Characteristics of soils and heavy metal content of Vegetation in Oil Spill Impacted Land in Nigeria. Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy: Vol. 17, Article 2, pp 1 - 8.

Behbahaninia, A., Mirbagheri, S. A. and Javid, A. H. (2008). Heavy Metals Transport in the Soil Profiles under the Application of Sludge and Wastewater. World Academy of science and Technology, Vol 48, pp 1-3.

Bouka, E., Povi, L., Kwashie, E., Kodjo, A. and Messanvi, G. (2013). Heavy metal concentration in soil, water and tubers around phosphate exploitation area in Togo. *Research journal of environmental toxicology*, Vol 7(1), pp 18 - 28.

Carroll, S., O'Day, A.P., Esser, B. and Randall, S. (2002). Speciation and fate of trace metals in estuarine sediments under reduced and oxidized conditions, Seaplane Lagoon, Alameda Naval Air Station (USA). pp 12-28, Lawrence Livermore National Laboratory, CA 94550, USA.

CDC (1991). Strategic plan for the elimination of childhood lead poisoning.US Department of Health and Human Services. pp17- 48, Washington, DC.

Chunhacherdchai, L., Chotpantarat, S. and Chantra, T. (2011). Investigating heavy metals in different depths of soil tailings from Akara gold mine in Thailand using three-step BCR sequential extraction. pp 1-17, Chulalongkorn University, Thailand.

COQG (2004). Crude Oil Quality. pp 7 - 234. New Orleans, USA.

Dameron, C. and Howe, P. D. (1998). Environmental health criteria for Copper. pp 1 - 29. Geneva, Switzerland.

Delbari, A.S. and Kulkarni, D.K. (2011). Seasonal variations in heavy concentrations in agriculture soils in Tehran-Iran. *Journal of Bioscience Discovery*, Vol 2 (3), pp 333-340.

DES (2013). Environmental Fact Sheet on Copper. pp 1-17, USA.

Dobrzanski, B., and Zawadzki, S. (1993). Studies on Ni variation with soil depth. *Journal of plant and soil environment*, Vol 76, pp 3 - 15.

Essiett, U.A., Effiong, G.S., Ogbemudial, F.O. and Bruno, E.J. (2010). Heavy metal concentrations in plants growing in crude oil contaminated soil in Akwa Ibom State, *Afr. J. Pharm. Pharmacol*. Vol. 4(7), pp 465-470.

Ewa, E.E., Njar, G.N., Essoka, P.A., Iwara, A.I. and Offiong, V.E. (2013). Seasonal Variations in Heavy Metal Status of the Calabar River, Cross River State, Nigeria. *Journal of Natural Sciences Research,* Vol.3, No.11, pp 1 - 7.

Google Maps (2014) represents the location of the sampling sites near the Kenya pipeline Company, Eldoret depot in Kenya.

Haavard, H. (2003). Trace elements determination by AAS. pp 3 - 40, Norwegian Institute for Water Research.

Hestone, K. P. (1990). Peat as a sorbent for removal of heavy metals from waste waters. Seattle, USA. *Journal of Agricultural sciences*, pp 323 - 341.

Hewstone, R.K. (1994). Environmental health aspect of lubricant additives, Oxford university press, pp 1 - 37.

Holm, O., Hansen, E., Lassen, C., Stuer-Lauridsen, F., Kjølholt, J. and COWI Consulting Engineers and Planners (2002). Heavy metals in waste final report. 5th ed, pp 347 – 417, European commission in Denmark.

Khuhawar, M.Y. and Lanjwani, S.N. (1996*).* Simultaneous high performance liquid chromatographic determination of Vanadium, Nickel, Iron and Copper in crude petroleum oils using bis(acetylpivalmethane) ethylenediimine as complexing reagent, Talanta, Vol 43, pp 767-770.

Madu, A., Njoku, P.C. and Iwuoha, G.A. (2011). Extent of heavy metals in oil samples in Escravous, Abiteye and Malu platforms in Delta State Nigeria. *Journal of Agriculture and Environmental Studies*, Vol 2 (2), pp 41- 44.

McLean, J.E., and Bledsoe, B.E. (1992). Behaviour of metals in soils. Environmental protection agency, pp 1 - 25.

Odat, S. and Alshammari, A.M. (2011*).* Seasonal Variations of Soil Heavy Metal Contaminants along Urban Roads: A Case Study from the City of Hail, Saudi Arabia. *Jordan journal of Civil Engineering*, Volume 5, No. 4, pp 1 - 11.

Ogboi, E. (2012). *Heavy metal movement in Crude oil polluted soil in Niger Delta region.* Journal of Agriculture and Veterinary Sciences, Vol 4, pp 1-8.

Okalebo, J.R., Gathua, K.W. and Woomer, P.L. (2002). Laboratory methods of Soil and Plant analysis: A working manual. 2nd ed SACRED Africa.

Oliveira, A. and Pampulha, M. E. (2006). Effects of Long-Term Heavy Metal Contamination on Soil Microbial Characteristics. *Journal of bioscience and bioengineering*, vol. 102, no. 3, pp 157–161.

Olubunmi, E. F. and Olanipekun, E.O. (2010). Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (Chromolaena odorata) of Agbabu Bitumen Deposit Area in Nigeria. *American-Eurasian Journal of Scientific Research*, Vol 5 (4), pp 241-248.

Oluyemi, E.A., Feuyit, G., Oyekunle., J.A.O. and Ogunfowokan, A.O. (2008). Seasonal variations in heavy metal concentrations in soil and some selected crops at a landfill in Nigeria. *African Journal of Environmental Science and Technology*, Vol. 2 (5), pp. 89-96.

Omono, M. A. and Kakulu, S. (2012). Impact of Mining and Agriculture on Heavy Metal Levels in Environmental Samples in Okehi Local Government Area of Kogi State. *Int. J. Pure Appl. Sci. Technol.*, Vol 12(2) , pp. 66-77.

Onojake, M.C. and Okonkwo, V. (2011). Trace Metals Associated with Oil Spillage: A case study. *Journal of Chem. Pharm. Res*., Vol 3(6), pp 742-751.

Perkin Elmer manual (1996). Analytical methods for atomic absorption spectroscopy. Manual number 0303-0152, release D, pp 1 - 310, PerkinElmer corporation, USA.

Radulescu, C., Stihi, C., Popescu, I., Toma, G., Chelarescu, E.D. and Stirbescu, R. (2012). Assessment of heavy metals content of crude oil contaminated soil. *Journal of science and Arts, No. 4(21), pp. 459-468.*

Sandrin, R.T. and Maier, R.M. (2003). Impact of Metals on the Biodegradation of Organic Pollutants. Environ Health Perspect Vol 111, pp 1093–1101.

Schmidt, J. A., and Andren, A.W. (1980). The atmospheric chemistry of Nickel, in Nickel in the Environment, edited by J. O. Nriagu, pp. 93– 135, Wiley, New York.

Sheffer, M. (2005). Guidelines for drinking-water quality, 2nd ed. Vol. 2. pp 2 - 9, World Health Organization, Geneva, Switzerland.

Shirdast, M., Mirseyed, H., Hosseini, A. and Samardiyana, F. (2010). Variation in soil heavy metal concentrations around and downstream of a municipal waste landfill, University of Tehran, Karaj, Iran.

Syed, H. R., Dilara, K., Tanveer, M. A., Mohammad, S. I., Mohammad, A. A. and Mohammad, A. (2012). Assessment of Heavy Metal Contamination of Agricultural Soil around Dhaka Export Processing Zone (DEPZ): Implication of Seasonal Variation and Indices. *J. Appl. Sci.,* Vol 2, pp 584 - 601.

Tokalioglu, S., Kartal, S. and Birol, G. (2001). Application of a three stage sequential extraction procedure for the determination of extractable metal contents in highway soils. *Turkish J.Chem*, vol 27 , pp 333 – 346.

TPHCWG (1997). Selection of Representative TPH Fractions Based on Fate and Transport Considerations.Vol. 3. pp 1-35.

Udeme, J.D. and Udoessien, E.I. (2012). Physicochemical studies of Nigeria's crude oil blends. *Journal of Petroleum & Coal*, Vol 54 (3), pp 243-251.

UNEP DTIE (2008). Draft final review of scientific information on cadmium. An environmental report, pp 78-142.

Vasquez-Duhalt, R. (1989). Environmental impact of used motor oil. *Journal of total environ*.Vol.79, pp 1-23.

Vogel, A. (1988). Quantitative chemical analysis, 5th ed. Thomas polytechnic London.

Von Storch, H., Costa-Cabral, M., Hagner, C., Feser, F., Pacyna, J., Pacyna, E. and Kolb, S. (2003). Four decades of gasoline lead emissions and control policies in Europe: a retrospective assessment. The Science of the total Environment, Vol 311, pp 151–176.

Warmate, A.G., Ideriah, T.J.K., Tamunobereton, I.T., Udonam-Inyang, U.E. and Ibaraye, T. (2010*)*. Concentrations of heavy metals in soil and water receiving used engine oil in Port Harcourt. *Journal of Ecology and the Natural Environment,* Vol. 3(2), pp. 54-57.

Westheide, E. (1987). The introduction of Pb free, low benzenes and low pollution automobiles in the republic of Germany cum supporting economic stimuli, control of air pollution in research and practice, pp 67 -96, Berlin, Germany.

Xiong, L. M. and Lu, R. (1991*)*. Influence of phosphate on transformation and plant uptake of Cadmium in Cd-amended soils. Vol 1, pp 63-72.

Yahaya, M.I., Mohammad, S. and Abdullahi, B. K. (2009). Seasonal Variations of Heavy Metals Concentration in Abattoir Dumping Site Soil in Nigeria. *J. Appl. Sci. Environ. Manage*. Vol. 13(4), pp 9 - 13.

Zare- Maivan, H. (2010). Distribution of Heavy Metals Associated with Petroleum in the Northern Persian Gulf: Bushehr and Nayband Bay Area. *Journal of the Persian Gulf (Marine Science)*, Vol.1, pp 1-5.

APPENDICES

Appendix Ia: Metal levels for sites S_1 to S_4 during the dry and wet season

Site	Season	Depth (cm)	Pb (ppm)	Ni (ppm)	Zn (ppm)	Cu (ppm)	Cd (ppm)	Fe (ppm)
1	Dry	0-15	.0000	.2293	.3079	.0818	.0000	.5731
		15-30	.0000	.0491	.2808	.0514	.0000	.0882
		30-45	.1956	.3222	.3460	.0076	.0000	.0000
		45-60	.0450	.0000	.3007	.1046	.0992	.0294
		60-75	.2713	.5461	.4782	.0590	.0108	.0735
1	Wet	0-15	.1956	.1529	.4492	.0456	.0000	1.9693
		15-30	.0000	.2348	.5072	.0380	.0090	1.5945
		30-45	.1202	.4150	.4782	.0932	.0000	3.9532
		45-60	.0901	.2130	.5489	.0152	.0000	2.2926
		60-75	.0000	.0874	.3478	.0628	.0000	3.3140
2	Dry	0-15	.4234	.1474	.2500	.0590	.0000	.2719
		15-30	.3624	.0000	.4637	.0913	.0000	.3894
		30-45	.0000	.0000	.2953	.0228	.0000	.0000
		45-60	.0000	.0000	.5271	.0609	.0000	.1396
		60-75	.0000	.2348	.2753	.1141	.0000	.4556
2	Wet	0-15	.6533	.3659	.7191	.1176	.0000	.0000
		15-30	.4692	.5515	.3804	.1008	.0000	3.6373
		30-45	.0000	.9884	.5634	.1217	.0000	4.8277
		45-60	.0000	.2621	.3424	.0780	.0072	2.9319
		60-75	.0000	.4150	.8188	.1160	.0992	3.1970
3	Dry	0-15	.3320	.4205	.3442	.0285	.0000	.0000
		15-30	.0000	.0218	.3333	.0533	.0000	.3747
		30-45	.0000	.3386	.4402	.0742	.0000	.1249
		45-60	.0000	.0273	.7988	.0742	.0000	.1690
		60-75	.3624	.0382	.4673	.0304	.0000	.1029
3	Wet	0-15	.0000	.3877	.6757	.1408	.0307	3.5638

		15-30	.4386	.0000	.6865	.0856	.0000	3.2846
		30-45	.0150	.5679	.5833	.0856	.0000	4.6733
		45-60	.4539	.2020	.6738	.1617	.0000	3.4095
		60-75	.1051	.6990	.6213	.1293	.0000	3.4756
4	Dry	0-15	.0000	.0928	.2101	.0247	.0000	.1837
		15-30	.1654	.0000	.3188	.0057	.0000	.3968
		30-45	.4386	.5351	.1830	.1065	.0000	.3380
		45-60	.3624	.0382	.2319	.0000	.0000	.0073
		60-75	.4539	.6389	.3351	.1350	.0000	.0514
4	Wet	0-15	.0300	.0000	.6539	.1084	.0000	4.7248
		15-30	.4692	.1038	.6793	.1122	.0000	4.5580
		30-45	.3929	.0328	.4257	.0514	.0956	2.2191
		45-60	.0000	.1474	.4710	.0970	.0613	2.1971
		60-75	.1353	.3495	.7753	.0266	.0000	3.9973

Appendix Ib: The mean heavy metal levels for site 1 during the dry season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.1024	0.3427	0.2293	0.0608	0.0220	0.1528
Std. Error of Mean	0.0554	0.0355	0.0985	0.0163	0.0194	0.1062
Std. Deviation	0.0124	0.0793	0.2203	0.0363	0.0134	0.1375
Maximum	0.2713	0.4782	0.5461	0.1046	0.0992	0.5731
Minimum	0.0000	0.2808	0.0000	0.0076	0.0000	0.0000
Skewness	0.7200	1.780	0.5720	-0.5160	2.1740	2.1140

Source: (Research Data, 2013)

Appendix Ic: The mean heavy metal levels of site 1 during the wet season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.0812	0.4663	0.2206	0.0510	0.0018	2.6247
Std. Error of Mean	0.0373	0.0339	0.0549	0.0130	0.0018	0.9784
Std. Deviation	0.0735	0.0758	0.1229	0.0292	0.0004	1.9150
Maximum	0.1956	0.5489	0.4150	0.0932	0.0090	3.9532
Minimum	0.0000	0.3478	0.0874	0.0152	0.0000	1.5945
Skewness	0.3500	-0.989	1.0500	0.4870	2.2360	2.2300

Appendix Id: Statistics for site 2 during the dry season statistics (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.1572	0.3623	0.0764	0.0696	0.0000	0.2513
Std. Error of Mean	0.0967	0.0557	0.0488	0.0155	0E-7	0.0827
Std. Deviation	0.1263	0.1246	0.0191	0.0347	0E-7	0.1850
Maximum	0.4234	0.5271	0.2348	0.1141	0.0000	0.4556
Minimum	0.0000	0.2500	0.0000	0.0228	0.0000	0.0000
Skewness	0.6540	0.6780	0.9580	-0.0630	0.0	-0.4010

Appendix Ie: The statistics of site 2 during the wet season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.2245	0.5648	0.5166	0.1068	0.0213	2.9188
Std. Error of Mean	0.1405	0.0927	0.1268	0.0080	0.0195	0.7987
Std. Deviation	0.1142	0.2072	0.2836	0.0179	0.0037	1.7859
Maximum	0.6533	0.8188	0.9884	0.1217	0.0992	4.8277
Minimum	0.0000	0.3424	0.2621	0.0780	0.0000	0.0000
Skewness	0.8000	0.1300	1.5370	-1.3570	2.2080	-1.2820

Appendix If: Statistics from site three collected during the dry season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.1389	0.4768	0.1693	0.0521	0.0000	0.1543
Std. Error of Mean	0.0852	0.0846	0.0869	0.0100	0.0000	0.0617
Std. Deviation	0.1005	0.1893	0.1042	0.0224	0.0000	0.1380
Maximum	0.3624	0.7988	0.4205	0.0742	0.0000	0.3747
Minimum	0.0000	0.3333	0.0218	0.0285	0.0000	0.0000
Skewness	0.6230	1.7250	0.7050	-0.0700	0.0000	1.0910

Appendix Ig: Statistics of site three during the wet season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.2025	0.6481	0.3713	0.1206	0.0061	3.6814
Std. Error of Mean	0.1011	0.0198	0.1251	0.0152	0.0061	0.2521
Std. Deviation	0.1262	0.0442	0.2797	0.0340	0.0037	0.5638
Maximum	0.4539	0.6865	0.6990	0.1617	0.0307	4.6733
Minimum	0.0000	0.5833	0.0000	0.0856	0.0000	3.2846
Skewness	0.4760	-0.9520	-0.2530	-0.0790	2.2360	2.0530

Appendix Ih: The mean heavy metal levels of site four during the dry season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.2841	0.2558	0.2610	0.0544	0.0000	0.1954
Std. Error of Mean	0.0876	0.0302	0.1349	0.0278	0E-7	0.0765
Std. Deviation	0.1960	0.0675	0.3017	0.0521	0E-7	0.1711
Maximum	0.4539	0.3351	0.6389	0.1350	0.0000	0.3968
Minimum	0.0000	0.1830	0.0000	0.0000	0.0000	0.0073
Skewness	-0.8590	0.3460	0.6220	0.6320	0.0000	0.1170

Appendix Ii: The mean heavy metal levels for site four during the dry season (ppm)

	Pb	Zn	Ni	Cu	Cd	Fe
Samples	5	5	5	5	5	5
Mean	0.2055	0.6010	0.1267	0.0791	0.0314	3.5392
Std. Error of Mean	0.0956	0.0659	0.0614	0.0170	0.0199	0.5567
Std. Deviation	0.1237	0.1474	0.1174	0.0381	0.0446	1.2447
Maximum	0.4692	0.7753	0.3495	0.1122	0.0956	4.7248
Minimum	0.0000	0.4257	0.0000	0.0266	0.0000	2.1971
Skewness	0.4480	-0.2170	1.3180	-0.7490	0.9310	-0.4100

Appendix Ij: Levels of selected heavy metals at shallower and deeper soil depths (ppm)

SITES	**DEPTHS**	**Fe**	**Zn**	**Ni**	**Pb**	**Cu**
Site 1	Shallower depth(0-30 cm)	3.95	0.51	0.05	0.20	0.08
	Deeper depth (45-75 cm)	3.31	0.55	0.55	0.27	0.10
Site 2	Shallower depth(0-30 cm)	4.83	0.72	1.00	0.47	0.10
	Deeper depth (45-75 cm)	3.20	0.82	0.42	0.42	0.00
Site 3	Shallower depth(0-30 cm)	4.67	0.69	0.57	0.44	0.14
	Deeper depth (45-75 cm)	3.48	0.67	0.70	0.11	0.13
Site 4	Shallower depth(0-30 cm)	4.72	0.68	0.54	0.47	0.11
	Deeper depth (45-75 cm)	4.00	0.78	0.64	0.45	0.14

Two sample t - tests

a) Pb

Variate: Lead

Group factor: Season

Test for equality of sample variances

Test statistic F = 1.36 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) = 0.050

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
Dry	20	0.1706	0.03373	0.1837	0.04107
Wet	20	0.1784	0.04603	0.2145	0.04797

Difference of means: -0.0078

Standard error of difference: 0.0631

95% one-sided confidence interval for difference in means: (..., 0.09867).

Test of null hypothesis: There is no significant difference in the Pb levels between dry season and wet season.

Test statistic, t = 0.12 on 38 d.f. , Probability = 0.0451. The null hypothesis is therefore accepted since t <1.

$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

$$r = \sqrt{\frac{0.12^2}{0.12^2 + 38}} = 0.0195$$

b) Ni

Variate: Nickel

Group factor: Season

Test for equality of sample variances

Test statistic F = 1.41 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) = 0.046

Summary

				Standard	Standard error
Sample	Size	Mean	Variance	deviation	of mean
Dry	20	0.1840	0.04502	0.2122	0.04745
Wet	20	0.3088	0.06370	0.2524	0.05644

Difference of means: -0.1248

Standard error of difference: 0.0737

95% one-sided confidence interval for difference in means: (..., -0.0004831)

Test of null hypothesis: There is no significant difference in the Ni levels between dry season and wet season.

Test statistic t = 1.69 on 38 d.f., Probability = 0.049. The null hypothesis is therefore rejected because t >1.

$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

$$r = \sqrt{\frac{1.69^2}{1.69^2 + 38}} = 0.264$$

c) Zn

Variate: Zinc

Group factor: Season

Test for equality of sample variances

Test statistic F = 1.02 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) = 0.0497

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
Dry	20	0.3594	0.01962	0.1401	0.03132
Wet	20	0.5701	0.01994	0.1412	0.03157

Difference of means:	-0.2107
Standard error of difference:	0.0445

95% one-sided confidence interval for difference in means: (..., -0.1357)

Test of null hypothesis: mean of Zn with dry season is not significantly less than mean with wet season

Test statistic t = 4.74 on 38 d.f., Probability = 0.001. The null hypothesis is therefore rejected because t >1.

$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

$$r = \sqrt{\frac{4.74^2}{4.74^2 + 38}} = 0.372$$

d) Cu

Variate: Copper

Group factor: Season

Test for equality of sample variances

Test statistic F = 1.03 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) = 0.0494

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
Dry	20	0.05925	0.001498	0.03871	0.008655
Wet	20	0.08938	0.001548	0.03934	0.008798

Difference of means: -0.0301

Standard error of difference: 0.0123

95% one-sided confidence interval for difference in means: (..., -0.009318)

Test of null hypothesis: There is no significant difference in the Cu levels between dry season and wet season.

Test statistic t = 2.44 on 38 d.f., Probability = 0.010. The null hypothesis is rejected because t >1.

$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

$$r = \sqrt{\frac{2.44^2}{2.44^2 + 38}} = 0.136$$

e) Cd

Variate: Cadmium

Group factor: Season

Test for equality of sample variances

Test statistic F = 2.06 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) = 0.13

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
Dry	20	0.00550	0.0004922	0.02219	0.004961
Wet	20	0.01515	0.0010117	0.03181	0.007112

Difference of means: -0.00965

Standard error of difference: 0.00867

95% one-sided confidence interval for difference in means: (..., 0.004970)

Test of null hypothesis: There is no significant difference in the Cd levels between dry season and wet season. The null hypothesis is therefore rejected since t >1.

Test statistic t = 1.11 on 38 d.f., Probability = 0.0136

$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

$$r = \sqrt{\frac{1.11^2}{1.11^2 + 38}} = 0.032$$

f) Fe

Variate: Iron

Group factor: Season

Test for equality of sample variances

Test statistic F = 7113.00 on 19 and 19 d.f.

Probability (under null hypothesis of equal variances) < 0.001

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
Dry	20	0.1885	0.031	0.1760	0.039
Wet	20	3.1910	3.371	1.836	1.318

Difference of means: -3.3003

Standard error of difference: 1.279

95% one-sided confidence interval for difference in means: (..., -0.7090)

Test of null hypothesis: There is no significant difference in the Fe levels between dry season and wet season. The null hypothesis is rejected since t >1 implying that tabulated t-value is less than calculated t-value.

Test statistic t = 1.90 on 38 d.f., Probability = 0.033

$$r = \sqrt{\frac{t^2}{t^2 + \ d.f}}$$

$$r = \sqrt{\frac{1.90^2}{1.90^2 + \ 38}} = 0.087$$

One way Analysis of Variance for depth

a) Pb

Number of obs = 40 R-squared = 0.0473

Source	SS	df	MS	F	Prob >F
Between depth	.07	4	.02	0.43	0.7827
Within depth	1.52	35	.04		
Total	1.59	39	.06		

Intraclass Asy. correlation S.E. [95% Conf. Interval]. .

Estimated SD of depth effect .

Estimated SD within depth .2083503

Est. reliability of a depth mean 0.00000 (evaluated at n=20.00)

(*) Truncated at zero.

b) Zn

Number of obs = 40 R-squared = 0.0554

Source	SS	df	MS	F	Prob> F
Between depth	.09	4	.02	0.51	0.7263
Within depth	1.29	35	.03		
Total	1.38	39	.05		

Intraclass Asy. correlation S.E. [95% Conf. Interval]

Estimated SD of depth effect .

Estimated SD within depth .1919675

Est. reliability of a depth mean 0.00000*

(evaluated at n=20.00) (*) Truncated at zero.

c) Ni

Number of obs = 40 R-squared = 0.3047

Source	SS	df	MS	F	Prob < F
Between depth	.70	4	.18	3.83	0.0109
Within depth	1.61	35	.05		
Total	2.31	39	.23		

Intraclass Asy.

correlation S.E. [95% Conf. Interval]

0.11566 . . .

Estimated SD of depth effect .080658

Estimated SD within depth .2142342

Est. reliability of a depth mean 0.72344 (evaluated at n=20.00)

d) Cu

Number of obs = 40 R-squared = 0.0163

Source	SS	df	MS	F	Prob >F
Between depth	.001	4	.000	0.14	0.9641
Within depth	.074	35	.002		
Total	.075	39	.002		

Intraclass Asy.

correlation S.E. [95% Conf. Interval]

0.00000* . . .

Estimated SD of depth effect .

Estimated SD within depth .0459502

Est. reliability of a depth mean 0.00000*

(evaluated at n=20.00) (*) Truncated at zero.

e) Cd

Number of obs = 40 R-squared = 0.0725

Source	SS	df	MS	F	Prob < F
Between depth	.002	4	.0005	0.68	0.6076
Within depth	.027	35	.0008		
Total	.029	39	.0013		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.00000* . . .

Estimated SD of depth effect .

Estimated SD within depth .0278515

Est. reliability of a depth mean 0.00000*

(evaluated at n=20.00) (*) Truncated at zero.

f) Fe

Number of obs = 40 R-squared = 0.0399

Source	SS	df	MS	F	Prob > F
Between depth	77.086	4	19.271	0.36	0.8330
Within depth	1856.297	35	53.037		
Total	1933.383	39	72.308		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] Estimated SD of depth effect

Estimated SD within depth 7.282654

Est. reliability of a depth mean 0.00000*

(evaluated at n=20.00) (*) Truncated at zero.

One way ANOVA for sites

a) Pb

Number of obs = 40 R-squared = 0.0561

Source	SS	df	MS	F	Prob < F
Between location	.089	3	.030	0.71	0.5509
Within location	1.509	36	.042		
Total	1.589	39	.072		

Intraclass Asy. correlation S.E. [95% Conf. Interval]

0.00000* . . .

Estimated SD of location effect .

Estimated SD within location .2044919

Est. reliability of a location mean 0.00000*

(evaluated at n=23.33)

b) Zn

Number of obs = 40 R-squared = 0.1079

Source	SS	df	MS	F	Prob < F
Between location	.147	3	.049	1.45	0.2442
Within location	1.222	36	.034		
Total	1.369	39	.083		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.01562 . . .

Estimated SD of location effect .0255729

Estimated SD within location .1839515

Est. reliability of a location mean 0.27026

(evaluated at n=23.33)

c) Ni

Number of obs = 40 R-squared = 0.0310

Source	SS	df	MS	F	Prob > F
Between location	.072	3	.024	0.38	0.7656
Within location	2.239	36	.062		
Total	2.311	39	.086		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.00000* . . .

Estimated SD of location effect .

Estimated SD within location .2493813

Est. reliability of a location mean 0.00000*

(evaluated at n=23.33) (*) Truncated at zero.

d) Cu

Number of obs = 40 R-squared = 0.0727

Source	SS	df	MS	F	Prob < F
Between location	.005	3	.002	0.94	0.4309
Within location	.070	36	.00188		
Total	.075	39	.00388		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.00000* . . .

Estimated SD of location effect .

Estimated SD within location .0439886

Est. reliability of a location mean 0.00000*

(evaluated at n=23.33) (*) Truncated at zero.

e) Cd

Number of obs = 40 R-squared = 0.0376

Source	SS	df	MS	F	Prob >F
Between location	.001	3	.000367	0.47	0.7056
Within location	.028	36	.000782		
Total	.029	39	.001049		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.00000* . . .

Estimated SD of location effect .

Estimated SD within location .027974

Est. reliability of a location mean 0.00000*

(evaluated at n=23.33) (*) Truncated at zero.

f) Fe

Number of obs = 40 R-squared = 0.0711

Source	SS	df	MS	F	Prob < F
Between location	137.522	3	45.840	0.92	0.4415
Within location	1795.860	36	49.885		
Total	1933.382	39	95.725		

Intraclass Asy.

correlation S.E. [95% Conf. Interval] 0.00000* . . .

Estimated SD of location effect .

Estimated SD within location 7.062931

Est. reliability of a location mean 0.00000*

(evaluated at n=23.33)

Appendix II: depicts the correlation between different metals and sites

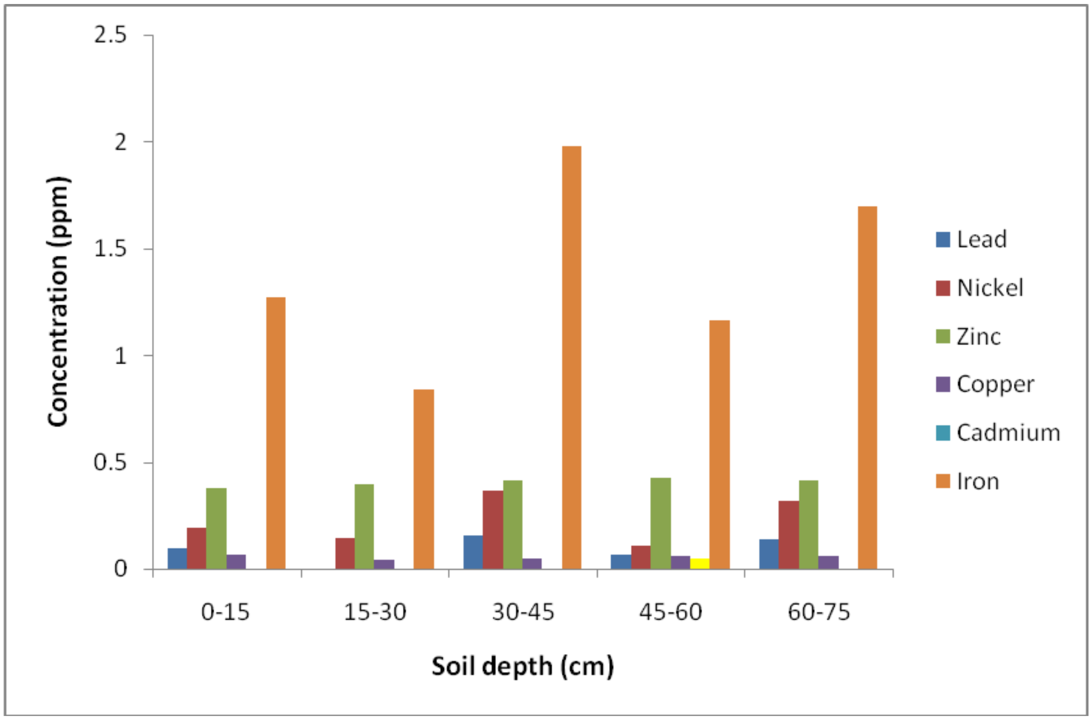
Correlations

Control Variables			Pb	Zn	Ni	Cu	Cd	Fe
Site	Pb	Correlation	1.000	-.168	.669	.450	.114	-.273
		Significance (1-tailed)	.	.310	.012	.082	.370	.208
		Df	0	9	9	9	9	9
	Zn	Correlation	-.168	1.000	.405	.725	.289	.298
		Significance (1-tailed)	.310	.	.108	.006	.194	.186
		Df	9	0	9	9	9	9
	Ni	Correlation	.669	.405	1.000	.693	.148	-.021
		Significance (1-tailed)	.012	.108	.	.009	.332	.476
		Df	9	9	0	9	9	9
	Cu	Correlation	.450	.725	.693	1.000	.242	-.133
		Significance (1-tailed)	.082	.006	.009	.	.237	.349
		Df	9	9	9	0	9	9
	Cd	Correlation	.114	.289	.148	.242	1.000	-.063
		Significance (1-tailed)	.370	.194	.332	.237	.	.427
		Df	9	9	9	9	0	9
	Fe	Correlation	-.273	.298	-.021	-.133	-.063	1.000
		Significance (1-tailed)	.208	.186	.476	.349	.427	.
		Df	9	9	9	9	9	0

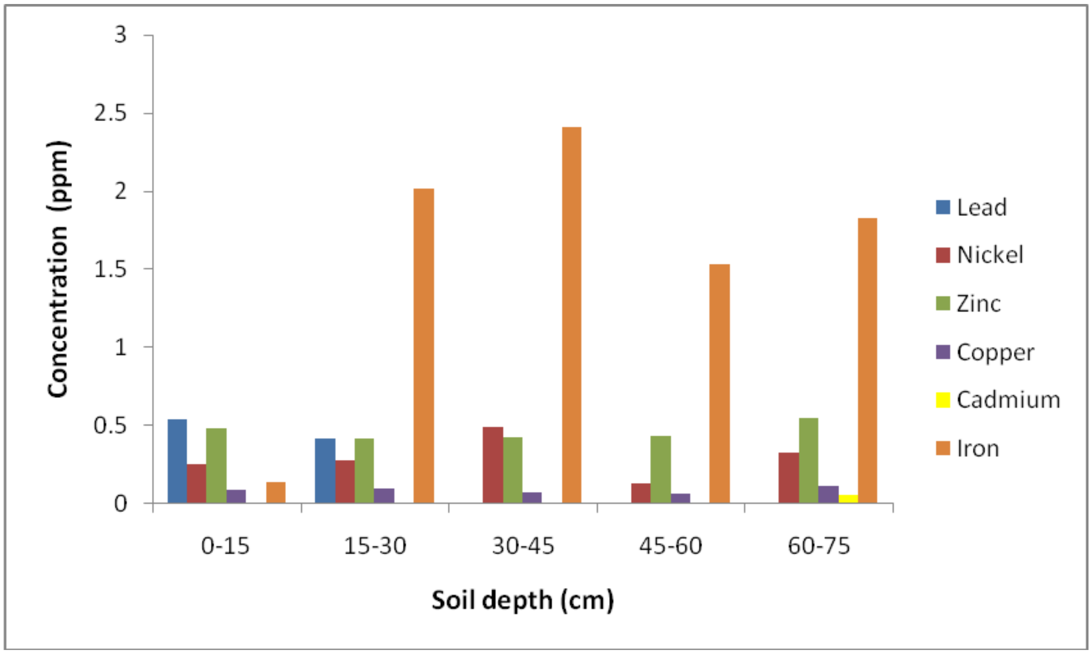
Source: Research data (2013)

Appendix III: Average metal concentration levels for all the sites

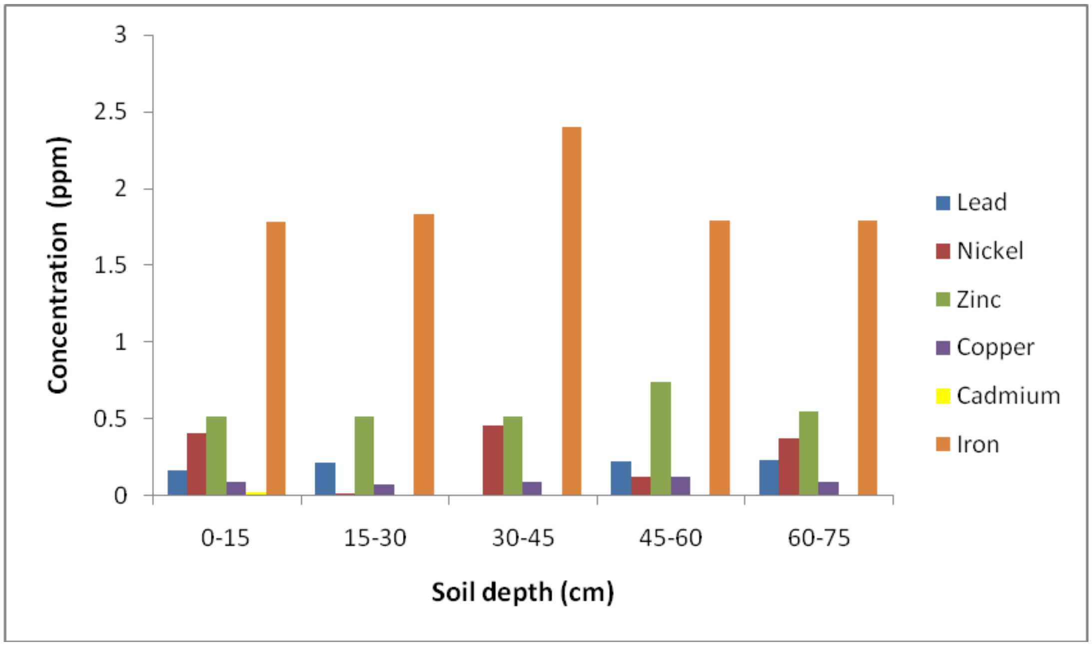
Appendix IIIa: Average metal concentration levels in site 1



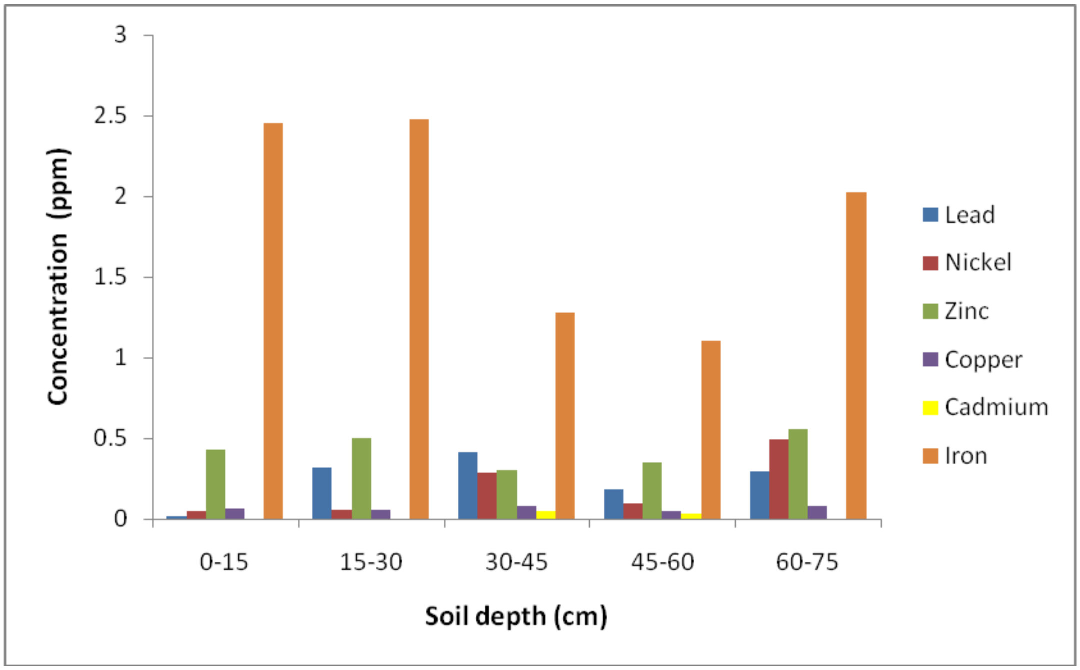
Appendix IIIb: Average metal concentration levels in site 2



Appendix IIIc: Average metal concentration levels in site 3

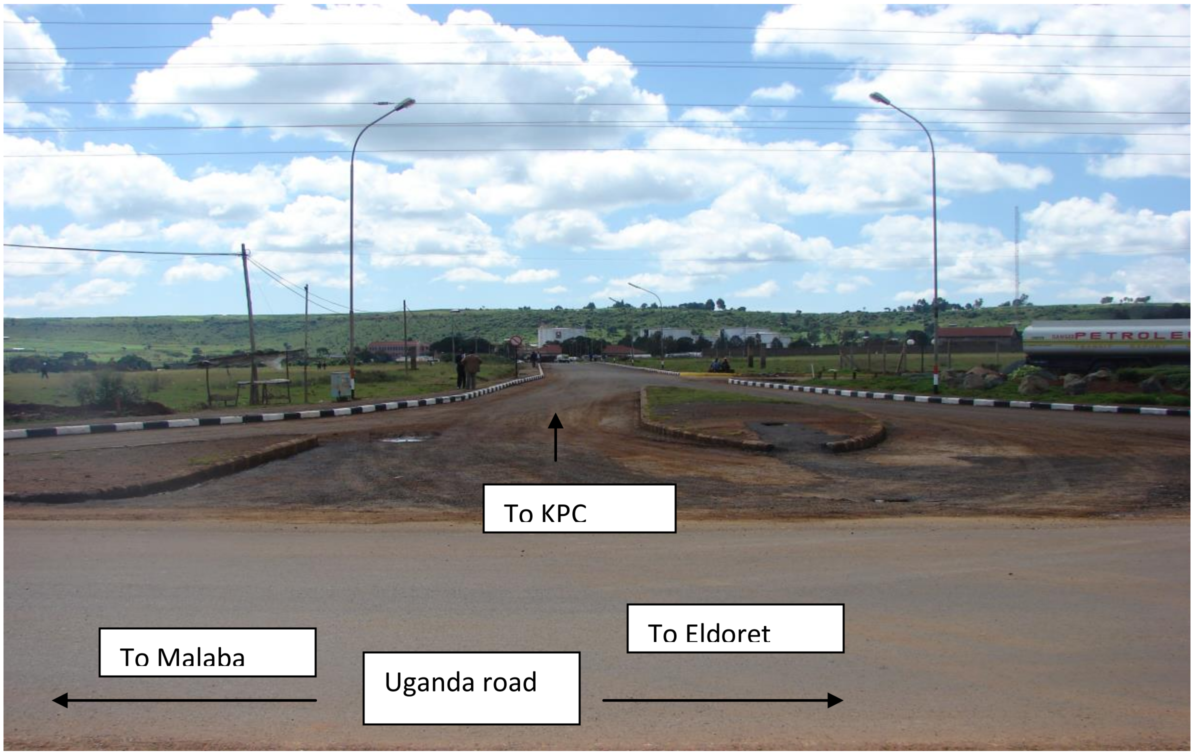


Appendix IIId: Average metal concentration levels in site 4



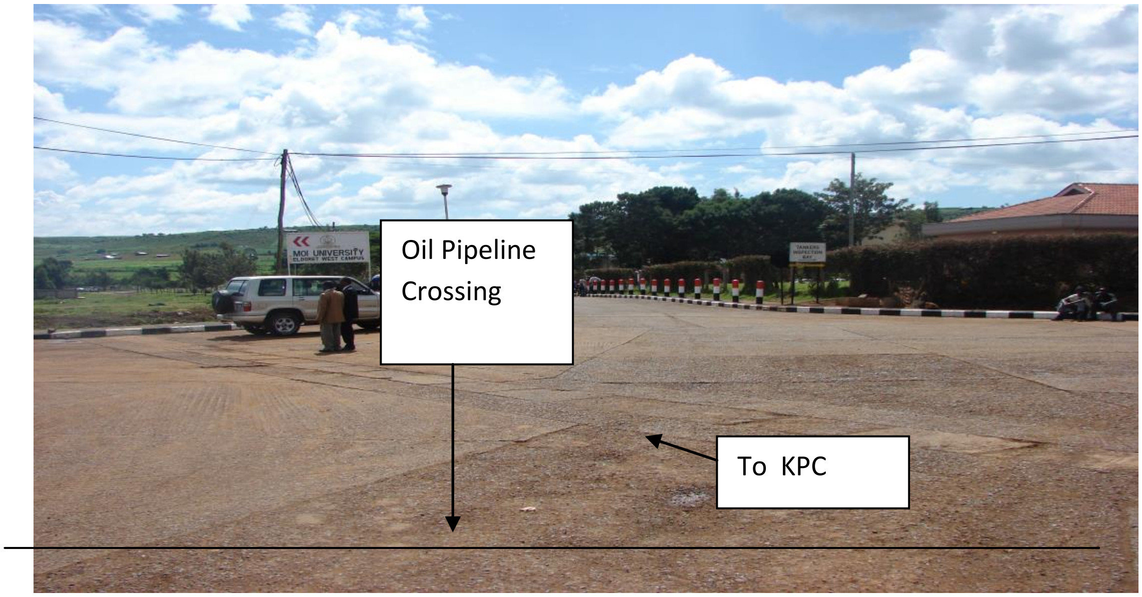
Appendix IV: Access roads and the sampling area near KPC Eldoret terminus

Appendix IVa: Access road from Uganda road, photo by KPC(2012)

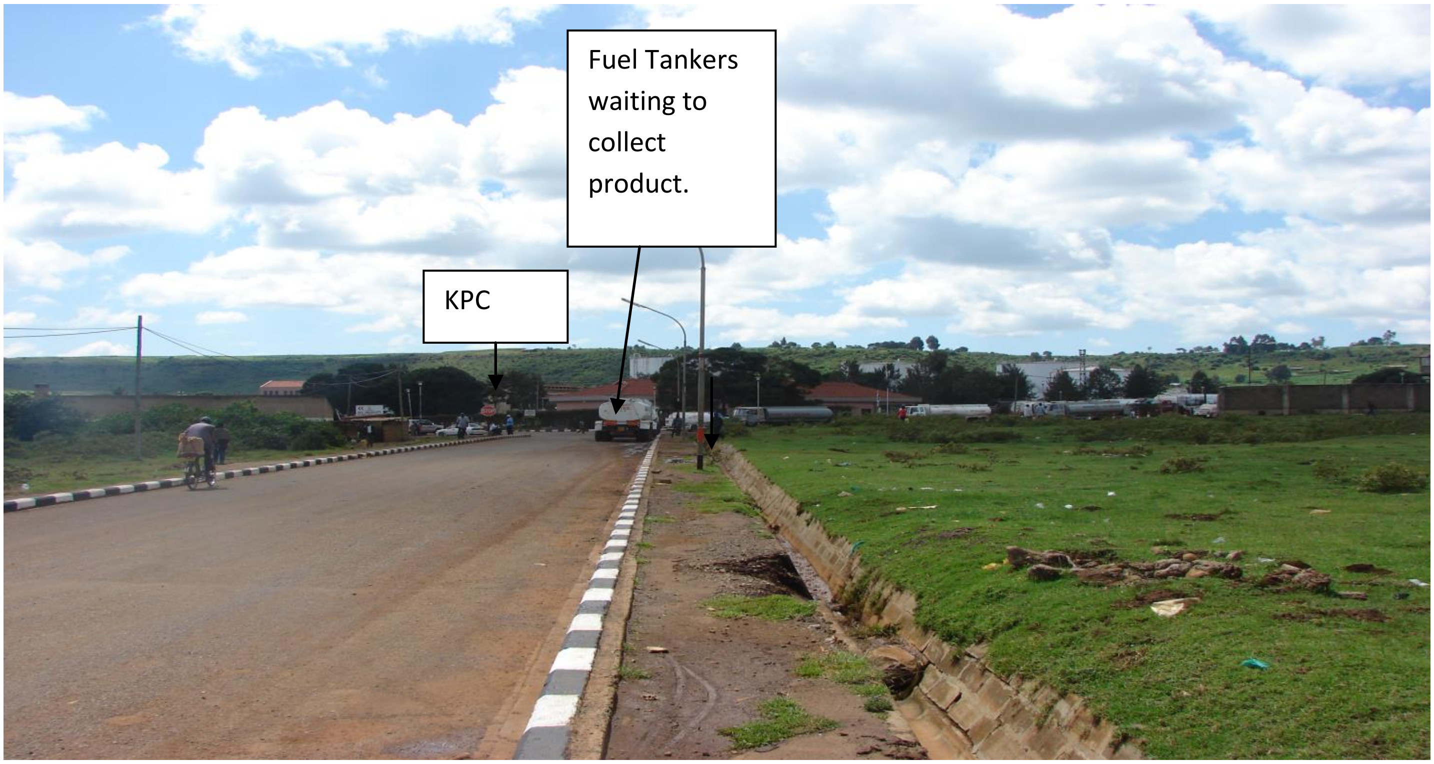


Appendix IVb: The Kenya Pipeline Company, Eldoret terminus photo by KPC (2012)

Appendix IVc: Oil pipeline crossing, Photo by KPC (2012)



Appendix IVd: Sampling area on the right, Photo by KPC (2012)



Appendix V: Equation for computation of t – statistic to an r - statistic

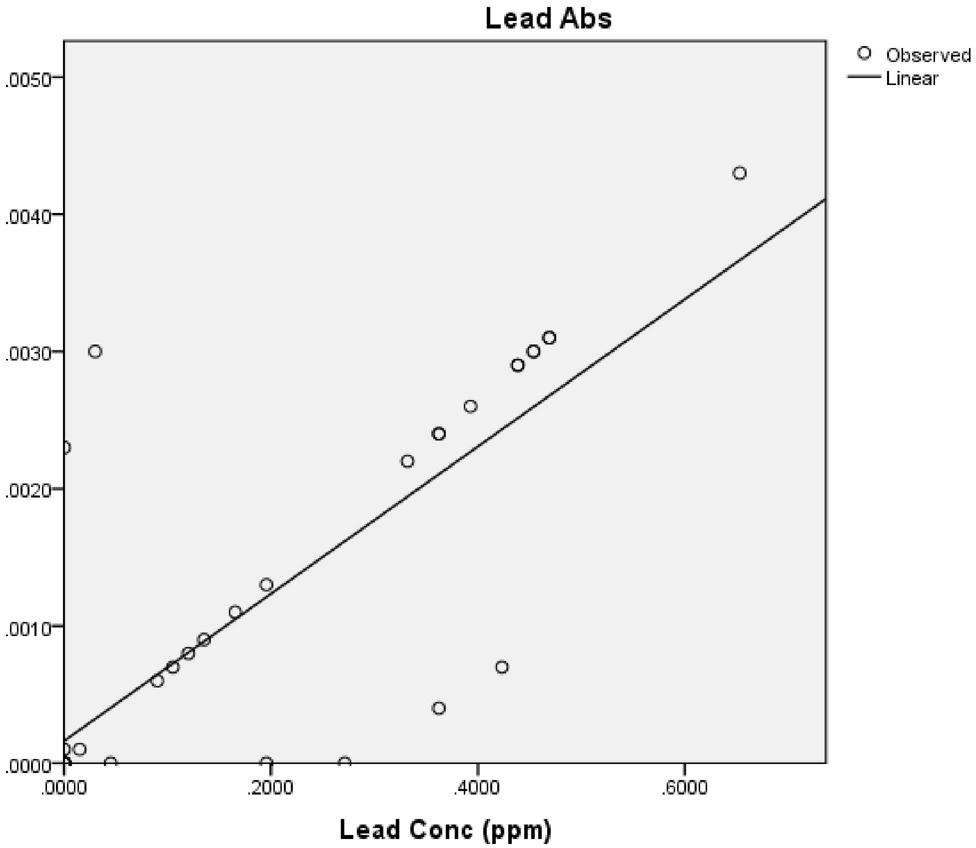
$$r = \sqrt{\frac{t^2}{t^2 + d.f}}$$

Appendix VI: Linear regression of concentration against absorbance

Appendix VIa: Absorbance against Lead concentration

Model Summary and Parameter Estimates							
Dependent Variable: Lead Absorbance							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	.645	68.952	1	38	.000	.000	.005

The independent variable is Lead Concentration (ppm).

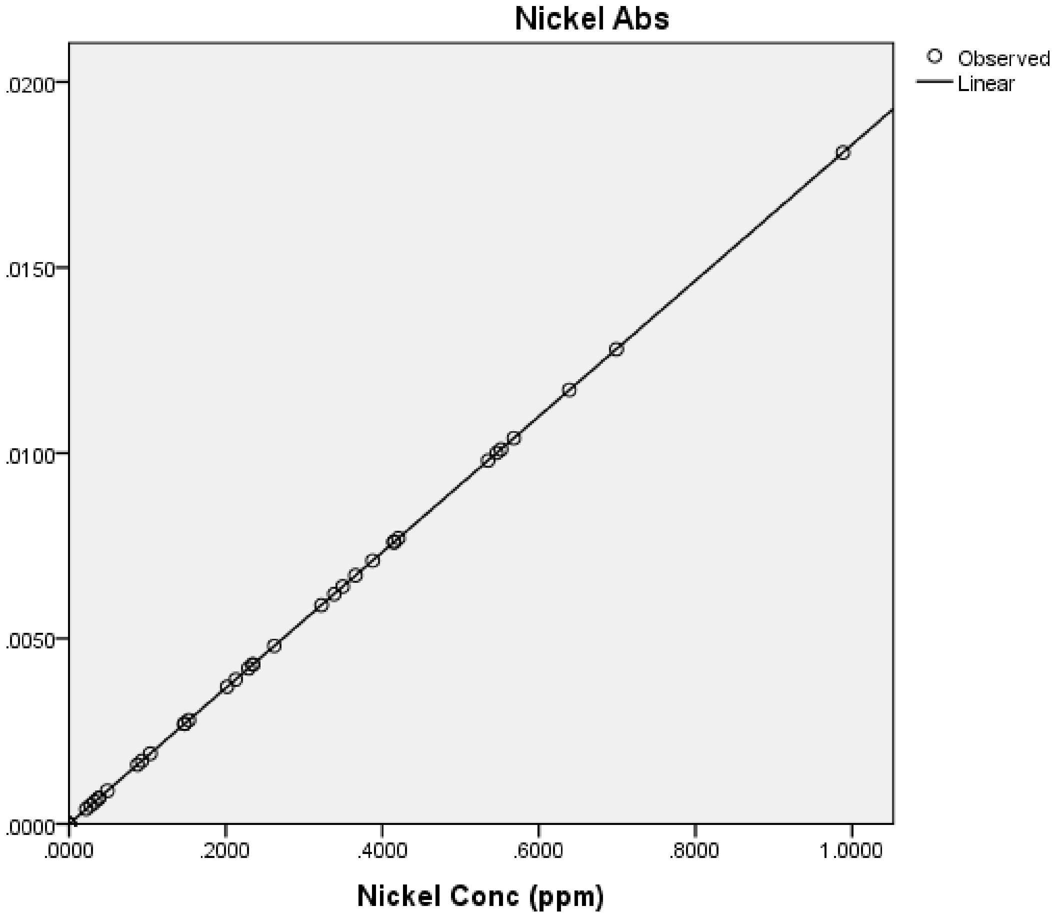


Abs = 0.000 + 0.005 Concentration

Appendix VIb: Absorbance against Nickel concentration

Model Summary and Parameter Estimates							
Dependent Variable: Nickel Abs							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	1.000	3032442879.78	1	38	.000	1.536E-007	.018

The independent variable is Nickel Concentration (ppm).

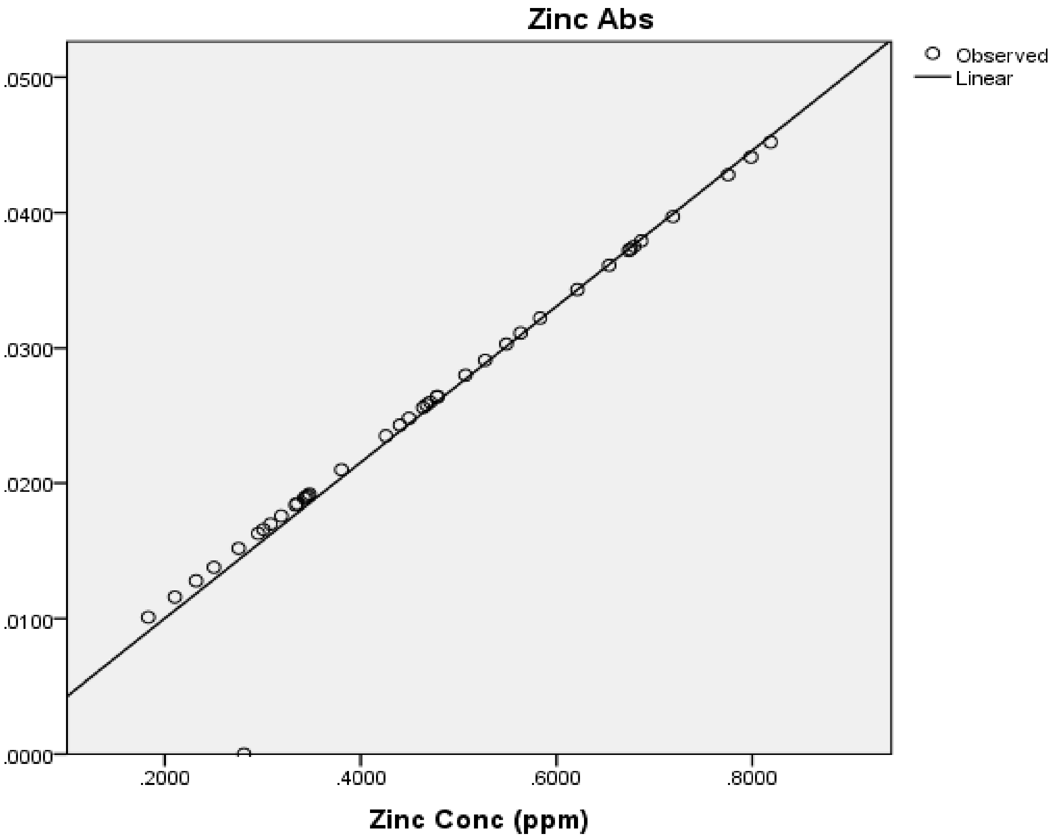


Absorbance = 1.536E-7 + 0.018 Concentration

Appendix VIc: Absorbance against Zinc concentration

Model Summary and Parameter Estimates							
Dependent Variable: Zinc Abs							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	.946	662.327	1	38	.000	-.001	.058

The independent variable is Zinc Concentration (ppm).

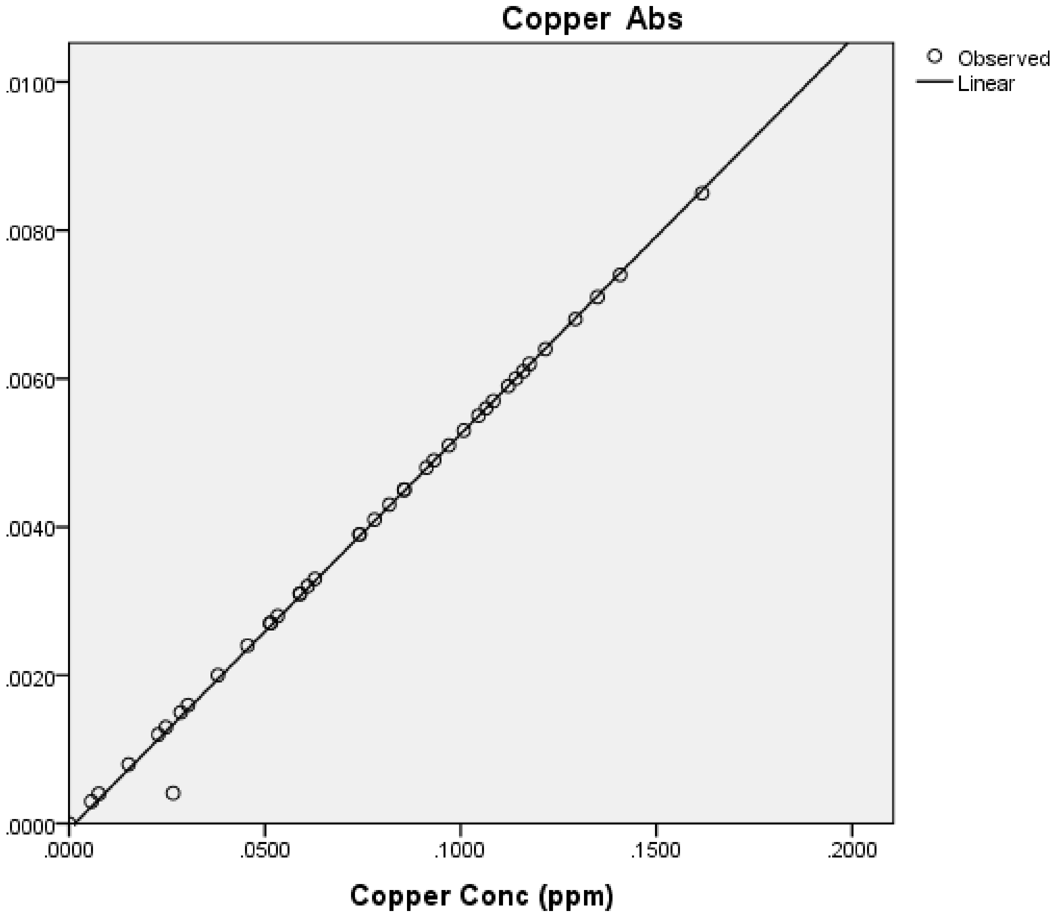


Absorbance = -0.001 + 0.058 Concentration

Appendix VId: Absorbance against Copper concentration

Model Summary and Parameter Estimates							
Dependent Variable: Copper Abs							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	.995	7855.110	1	38	.000	-7.738E-005	.053

The independent variable is Copper Concentration (ppm).

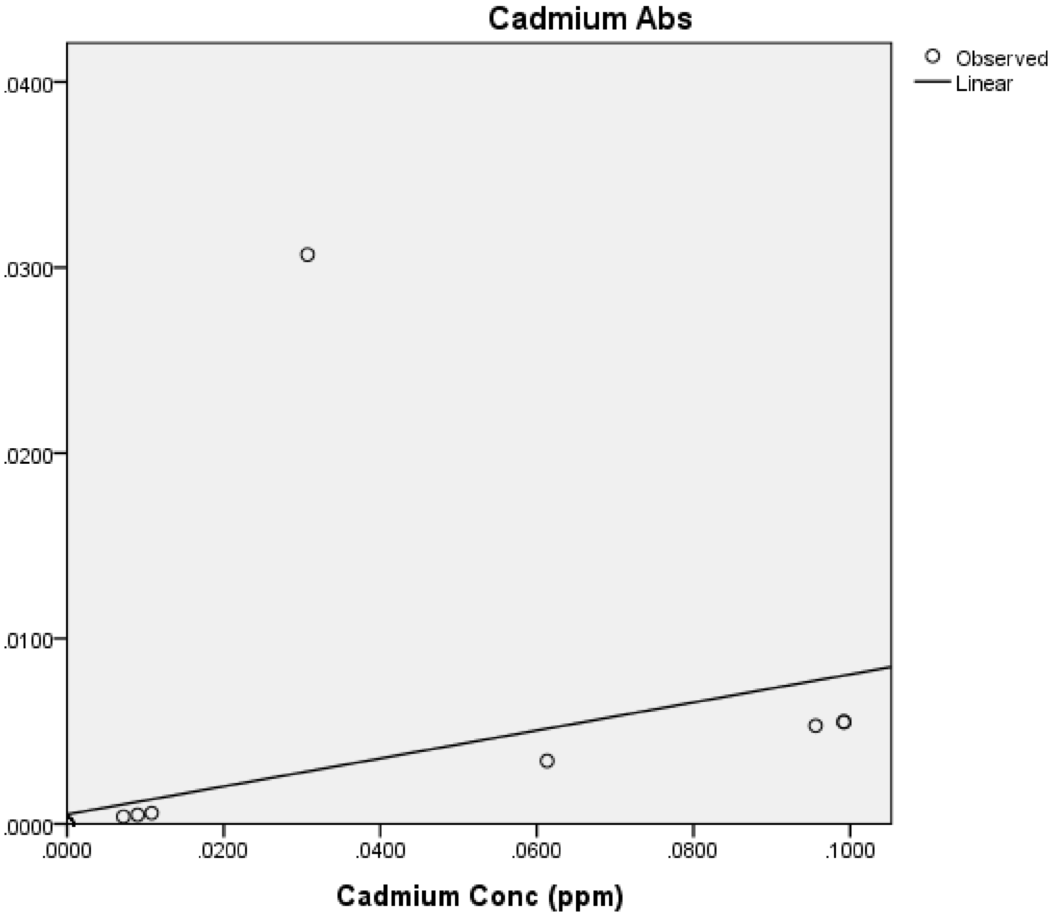


Abs = -7.738E-005 + 0.053 Concentration

Appendix VIe: Absorbance against Cadmium concentration

Model Summary and Parameter Estimates							
Dependent Variable: Cadmium Abs							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	.172	7.903	1	38	.008	.001	.075

The independent variable is Cadmium Concentration (ppm).

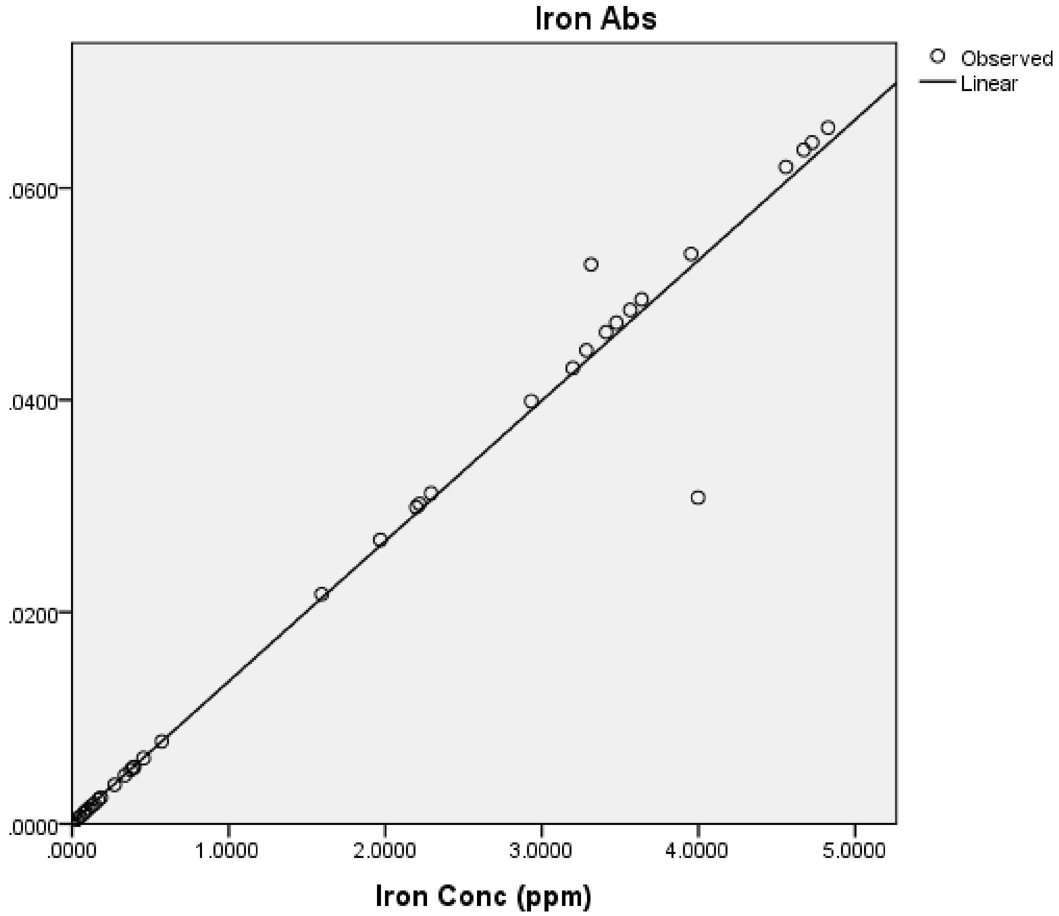


Abs = 0.001 + 0.075 Concentration

Appendix VIf: Absorbance against Iron concentration

Model Summary and Parameter Estimates							
Dependent Variable: Iron Abs							
Equation	Model Summary					Parameter Estimates	
	R Square	F	df1	df2	Sig.	Constant	Conc
Linear	.972	1330.937	1	38	.000	.000	.013

The independent variable is Iron Concentration (ppm).



Abs = 0.000 + 0.013 Concentration

Appendix VII: Table of absorbance values and concentration of standards

Appendix VIIa: Absorbance values and concentrations of Pb standards

Lead concentration (ppm)	Absorbance units
1.00000	0.0080
2.00000	0.0131
3.00000	0.0171
4.00000	0.0250
5.00000	0.0300

Appendix VIIb: Absorbance values and concentrations of Ni standards

Nickel concentration (ppm)	Absorbance units
1.00000	0.0118
2.00000	0.0412
3.00000	0.0510
4.00000	0.0730
5.00000	0.0936

Appendix VIIc: Absorbance values and concentrations of Zn standards

Zinc concentration (ppm)	Absorbance units
1.00000	0.0847
2.00000	0.1216
3.00000	0.1705
4.00000	0.2211
5.00000	0.2625

Appendix VIId: Absorbance values and concentrations of Cu standards

Copper concentration (ppm)	Absorbance units
1.00000	0.0525
2.00000	0.1176
3.00000	0.1636
4.00000	0.2184
5.00000	0.2479

Appendix VIIe: Absorbance values and concentrations of Cd standards

Cadmium concentration (ppm)	Absorbance units
1.00000	0.0000
2.00000	0.0737
3.00000	0.1501
4.00000	0.2378
5.00000	0.3013

Appendix VIIf: Absorbance values and concentrations of Fe standards

Iron concentration(ppm)	Absorbance units
1.00000	0.0102
2.00000	0.0250
3.00000	0.0408
4.00000	0.0531
5.00000	0.0707